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Studies on the suitability of oxidizing agents for discolouring lime and poplar wood in the first stage of transparent wood forming process

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Abstract: *Studies on the suitability of oxidizing agents for discolouring lime and poplar wood in the first stage of transparent wood forming process*. Series of lime and poplar wood samples were prepared and subjected to oxidising agent in order to decolourise wood in bulk. Sodium chlorite solution in the environment of diluted acetic acid and alkaline hydrogen peroxide solution were used as different treating agents, followed by intense rinsing in water and drying the samples. The effect of wood delignification conditions such as time of treatment and reagent used was investigated. Changes in mass and dimensions of the samples were measured, and thus density changes were calculated. Colour changes were measured with colorimeter in CIE Lab colour space. In the case of lime wood swelling of the samples was observed at the first stage, along with mass loss, leading to density decrease by 10 % after 20 h exposure. In the case of poplar wood, shrinking of the samples was observed, but due to severe mass loss, final density was similar to lime wood. Colour changes correlated mainly with lightness parameter of the samples. Significant colour differences were found even at the shortest time of treatment.

Keywords: transparent wood, delignification, lime, poplar, wood colour

INTRODUCTION

The properties of wood and its suitability for industrial purposes depend mainly on wood anatomical features, the chemical composition and the structure of cell wall (Krzysik 1974). Wood is one of the most abundant resources in the bio-based industry and yet it is also one of the most complex materials. Wood is essentially composed of cellulose, hemicelluloses, lignin, and extractives. The relative composition, however, varies greatly for various wood species (Stenius 2000). As technology advances, wood does not lose its significance. Development of new technologies allows modifying wood properties and thus the range of wood applications is still wider.

Natural wood is not transparent in the visible spectra range and this is due to strong absorption and scattering of light. To make wood transparent, both absorption and scattering effects need to be eliminated. Light absorption is strongly dependent on the chemical composition and wood brownish colour can be connected to the presence of light-absorbing components such as lignin, low-molecular weight phenols and tannins. Among these, lignin accounts for around 80-95% of light absorption in wood (Müller et al. 2003). Lignin has originally yellow-brownish colour due to its phenolic character – responsible for aromatic ring absorption in the visible spectrum (Li et al. 2016).

Transparent wood is a composite of delignified wood and transparent polymer, like poly(methyl methacrylate) (PMMA). The first reported study on transparent wood the modification was conducted in order to facilitate wood morphology studies (Fink 1984). Later on, engineering use of transparent wood was suggested by combining mechanical strength considerations with optical transmittance studies (Li et al. 2016). Many studies followed later around similar engineering use considerations (Li et al. 2019).

Transparent wood shows lower density than glass (approx. 1.2 g/cm^3), high optical transmittance (over 80%) and haze (over 70%), good mechanical performance, and potential for multi-functional modifications (Li et al. 2017b). Wood materials have good properties and are suitable for large-scale structures. Transparent building structure is such an

exemplification towards the future use of transparent wood, where light transmittance can be designed so that artificial light can be partially replaced by sunlight. Transparent wood roofs can be designed for some buildings, which will provide more uniform and comfortable illumination compared with conventional glass (Li et al. 2019). Another application for transparent wood is furniture making, where both aesthetical and functional properties are sought in modern homes and offices. There is possibility of diffusing luminescence by embedding quantum dots in a transparent wood panel. This is advantageous for planar light sources and luminescent construction elements or furniture (Li et al. 2017b).

Currently the established and most commonly used approach to prepare wood templates for transparent wood is a delignification process with sodium chlorite ($NaClO_2$), which causes oxidative aromatic ring-opening reactions to form acidic groups and make lignin degradation products soluble in water (Li et al. 2017a). This process usually takes place at a temperature around 80 °C, while samples thickness usually does not exceed 1 mm.

Another delignification method consists of lignin modification process through alkaline hydrogen peroxide (H_2O_2) treatment, which selectively reacts and removes chromophore structures, while the bulk lignin is preserved (Ramos et al. 2008). In other studies, the wood samples were submerged in the lignin-modifying solution at 70 °C, until wood became white (Li et al. 2017a).

According to earlier studies on pinewood, it was noted that the process of delignification generally leads to a higher porosity of wood, as the entire density was reduced from 440 kg/m³ in the reference samples to 330 kg/m³ after delignification (Frey et al. 2018). Delignification process typically removes around 25 % of wood tissue mass (Li et al. 2017b), which is consistent with the above values of density, when no changes in dimensions take place.

The purpose of this work was to investigate the action of delignifying and oxidizing agents on the following wood parameters: mass, volume, density and colour. This is the initial stage in the development of transparent wood production technology, preceding the use of delignified wood material as filler in transparent plastics. In order to conduct the research, lime and poplar wood were selected, having lignin content of about 18% and 20% respectively, according to literature (Prosiński 1984).

There are many reports on bleaching methods used in papermaking (e.g. Biermann 1996), but very few scientific reports on colour determination of bleached solid wood. Csiha & Papp (2013) investigated bleaching beech wood using sodium percarbonate and observed changes in all colour parameters of CIE Lab space. General information on wood bleaching can be found in a report by Forest Products Laboratory (1967). Kadir & Jantan (2016) studied colour changes of rubberwood under the bleaching, and found colour difference (ΔE) in the range of 5 to 18 units.

MATERIALS

Wood discs were taken from European lime (*Tilia cordata* Mill.) and white poplar (*Populus alba* L.) trees at the breast height. The cubic samples having dimensions of 15×15×15 mm were cut from the respective discs. Two solutions were prepared for each wood species: delignifying and bleaching ones. The mass and the volume of the samples were measured at room temperature before treatment. The bleaching solution was prepared in conical flasks by mixing 0.08 g of sodium hydroxide (NaOH) and 200 cm^3 of 30 % hydrogen peroxide solution. The delignifying solution was prepared in conical flasks by mixing 200 cm^3 of distilled water, 10 g of sodium chlorite ($NaClO_2$) and 0.08 cm^3 of glacial acetic acid (CH_3COOH). The samples of both species were placed in the appropriate flask, supplied with a reflux condenser, and placed in a water bath heated to 80 °C. The treated samples of both species were collected at subsequent time intervals 1, 3, 6 and 20 hours of treatment.

The samples were then washed three times by boiling in distilled water, while the water was exchanged every hour. Reference samples were not treated by solutions, but were boiled in water as well, for comparison and determination the effect of washing. All the samples were dried at 105 ± 3 °C for 48 h before further measurements. Mass and dimensions of each sample were measured, and then their density was calculated. Colour changes of the samples were measured using BYK Spectro-guide gloss 45/0 spectrophotometer in CIE Lab colour space.

RESULTS

Average mass loss of the samples in series is shown in the Figure 1. In the case of poplars wood, the difference in mass loss between both agents tested was significant over the entire period of experiment, reaching over 28 % in chlorite solution. In peroxide bath after initial loss to about 15 % within 8 hours, the changes in the next stage were negligible. The samples of poplar wood in chlorite bath showed constant mass loss in the same time. In the case of lime wood mass loss trends with both agents were more similar to poplar wood in peroxide bath. The changes in peroxide bath did not reach a plateau, featuring small, but still increase. On the other hand, in chlorite bath lime wood mass loss reached the level of poplar wood in chlorite bath and similarly the stage of stabile mass was observed.

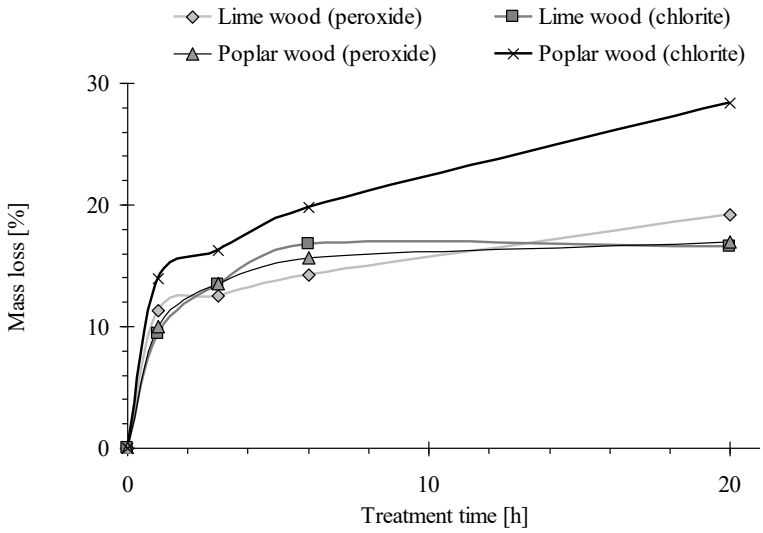

Figure 1. Dependence of changes in mass of the samples on treatment time.

Clear differences in the behaviour of both tested wood species were observed when volume changes were measured. In the case of lime wood, a significant increase in sample volume was observed at the initial stage, which can be associated with swelling of the test material. In the case of poplar wood, however, volume loss was observed from the very beginning. Thus, despite the swelling, the mass loss of poplar wood was large enough to be accompanied by a volume loss. In the case of lime wood treated with hydrogen peroxide solution, at the initial stage there was a strong increase in volume, while at prolonged treating the volume of samples dropped, reaching the initial average value within 20 h. In the case of the sodium chlorite solution, the volume of lime wood samples increased at the initial stage of treatment and remained near unchanged until the end of the experiment. In the case of poplar wood treated with the hydrogen peroxide solution, overall volume loss was observed about 2 to 3 %, while after 3 hours of treatment a temporary deviation towards larger decrease was found. In the case of the sodium chloride solution, the volume loss of poplar wood samples

was very strong, in spite of changes of the trend, which was observed for the first 6 hours. 12% volume loss found was the biggest decrease among all the series tested.

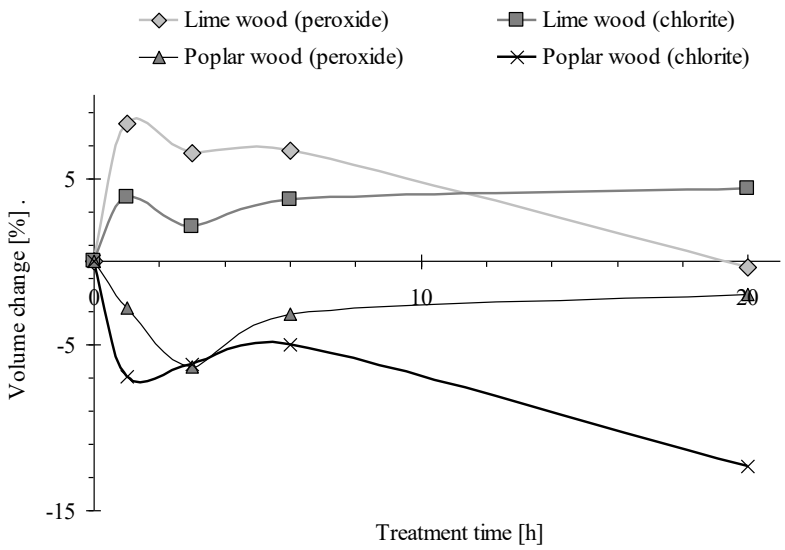

Figure 2**.** Dependence of changes in volume of the samples on treatment time.

The changes in density of wood samples, as the result of mass and volume changes, are presented in the Figure 3. Significant decrease at the first stages of the treatment and subsequent slowing down the changes was found in all cases, irrespectively of the direction of volume changes. The decrease of lime wood density was greater than of poplar wood, while the difference was greater in the case of peroxide treatment. Lime wood density decrease was generally uninfluenced by treatment method, and final decrease of approximately 10 % was observed. In the case of polar wood faster decrease was found for chlorite bath, reaching near 9 %, while in peroxide bath decrease did not exceed 7 %.

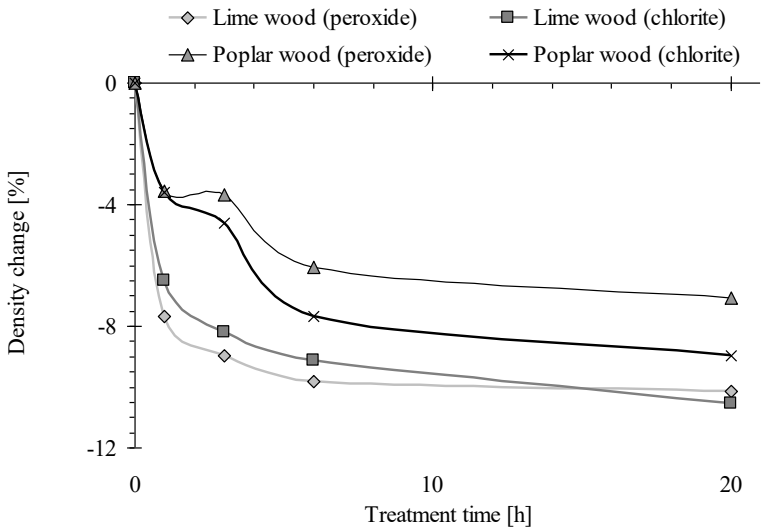

Figure 3. Dependence of density changes of the samples on treatment time.

Lightness (L) was found to gradually increase in most samples (Figure 4), except for the poplar wood in the hydrogen peroxide solution, which decreases slightly after initial growth. In contrast, Poplar in chlorite solution showed the highest level of brightness with

constant growth. Lime wood showed a similar increase, with hydrogen peroxide solution being the highest, reaching 0.7 units lower than poplar wood in chlorite solution.

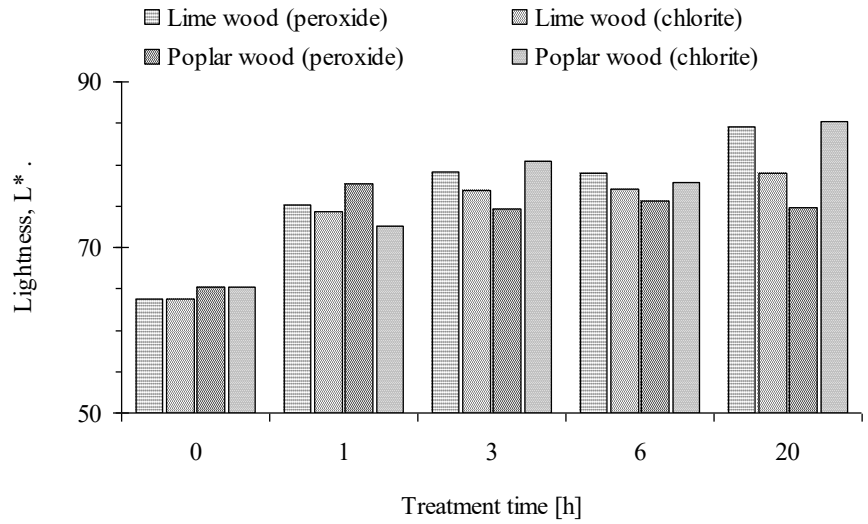

Figure 4. Dependence of lightness (L) changes of the samples on treatment time.

Figure 5 shows the average colour difference measured between the series reference samples and the treated ones. Such difference allows to better estimate the changes occurring due to the treatment, without the effect of soaking in water. Systematically increasing colour difference was found for lime wood treated with hydrogen peroxide. The same wood treated with chlorite solution featured an increase in colour difference as well, while the changes were significantly lower. In the case of poplar wood, treatment with hydrogen peroxide wood led to a clear difference for the first series of samples, collected after an hour of treatment, while in following measurements these differences were less significant. In the case of poplar wood treatment with chlorite solution, there was a growing trend of colour difference dependence on treatment time, in spite of a lower value of the ΔE parameter found after 6 hours. Due to the heterogeneity of the wood material, it can be argued that there are individual colour differences between the samples, which in turn can be sufficient explanation of trend fluctuations.

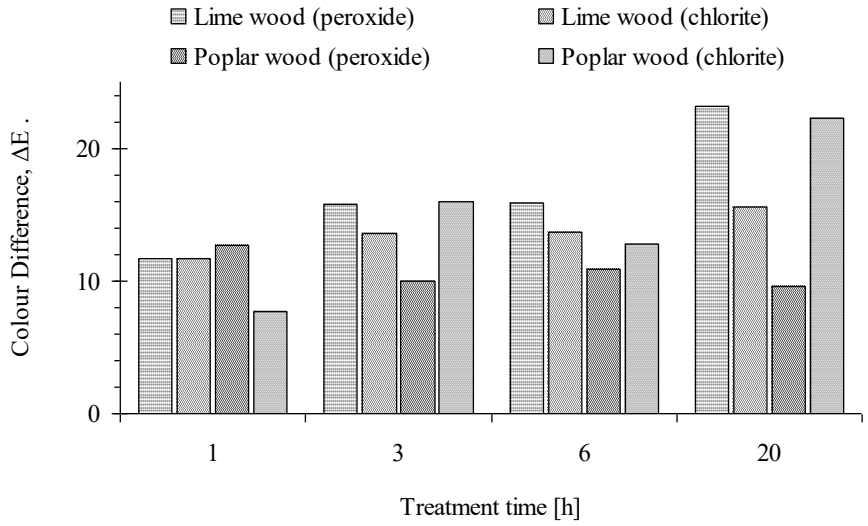

Figure 5. Dependence of changes of colour difference (ΔE) treatment conditions

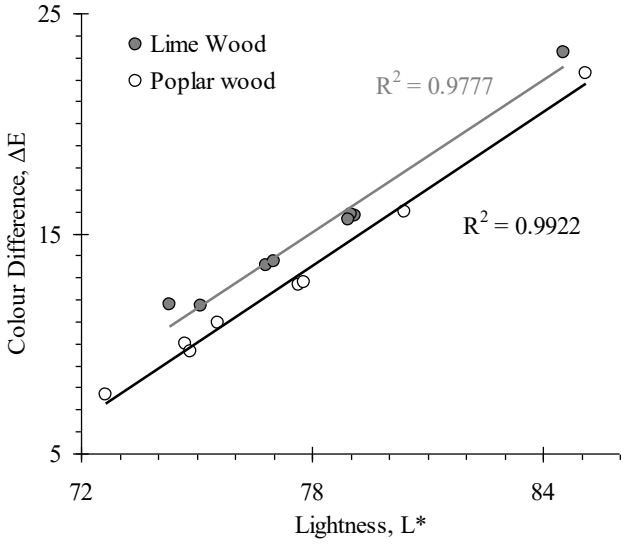

Figure 6. Correlation between colour difference (ΔE) and lightness (L*) for both wood species tested

Figure 6 shows the correlation between lightness and colour difference for both wood species. An excellent correlation was obtained for poplar wood, with an R^2 coefficient of 0.9922, while the correlation for lime wood was very good as well, with R^2 of 0.9777. It can be concluded that changes in colour are primarily associated with the brightening of samples, while their hue changes were of minor significance, both for red-green, and yellow-blue directions.

CONCLUSIONS

Based on the research results, the following conclusions can be drawn. Agents used for both wood species caused rapid weight loss in the initial stages and in later handling the weight loss stabilized. The maximum mass loss was 28 % for poplar wood treated with chlorite solution, while Li *et al.* (2017) found mass loss during the delignification process about 30 wt% of wood tissue for various wood species.

Both tested wood species show different behaviour as the volume of lime samples increased while poplar wood samples shrinked. Their behaviour overtime was also different when using different oxidise agents. In the hydrogen peroxide solution, the lime wood mass after initial growth dropped continuously and in the case of poplar wood, such a situation occurred with the use of sodium chloride solution. This treatment method caused severe deformation of the samples, causing analytical difficulties. When a potential application is considered, possibility of dimensional change and deformation should be taken into account and appropriate method of further machining should be provided. Surprisingly, the density of the samples comparably decreased in each case. Larger mass loss was compensated by larger volume drop, while poplar wood showed a little higher density decrease in average.

Non-uniform changes were found in wood colour during treatment. In general, wood of both species was still brighter over the experiment, in spite of some fluctuations. The colour differences, measured at the various stages of treatment against blind probes are clear except for samples of poplar wood in hydrogen peroxide solution. The colour difference for all samples after the first series was above five units of ΔE, which means that the average observer has the impression of a different colour from the reference samples (Budzyński et al., 2015). Another significant colour change is observed between 6 hours and 20 hours exposure of poplar wood treated with the hydrogen peroxide solution and poplar wood treated with sodium chlorite solution. Comparison of ΔE values with directly measured lightness of

the samples showed excellent correlation and confirmed a naked-eye observation, that all samples became brighter without significant change in their hue.

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Streszczenie: *Badanie przydatności środków utleniających do odbarwiania drewna lipowego i topolowego w pierwszym etapie wytwarzania przezroczystego drewna.* Przygotowano serie próbek drewna lipowego i topolowego i poddano je obróbce utleniającej w celu odbarwienia drewna w całej objętości. Jako reagenty zastosowano roztwór chlorynu sodu w środowisku rozcieńczonego kwasu octowego oraz alkaliczny roztwór nadtlenku wodoru, po czym próbki poddawano intensywnemu płukaniu w wodzie i suszeniu. Zbadano wpływ warunków delignifikacji drewna, takich jak czas obróbki i zastosowany odczynnik. Mierzono zmiany masy i wymiarów próbek, i obliczono zmiany gęstości. Zmiany koloru mierzono za pomocą kolorymetru w przestrzeni kolorów CIE Lab. W przypadku drewna lipy zaobserwowano pęcznienie próbek na pierwszym etapie, wraz z utratą masy, co prowadziło do zmniejszenia gęstości o 10% po 20 godzinach obróbki. W przypadku drewna topolowego stwierdzono kurczenie się próbek, ale z powodu znacznej utraty masy gęstość końcowa była zbliżona do drewna lipowego. Zmiany koloru korelowały głównie z parametrem jasności próbek. Istotne różnice barwy stwierdzono nawet po najkrótszym czasie obróbki.

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