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THE INFLUENCE OF HEAT TREATMENT
ON THE PHYSICO-CHEMICAL PROPERTIES
OF PINEWOOD (*PINUS SYLVESTRIS* L.)

Pinewood (Pinus sylvestris L.) was thermally modified at temperatures of 160ºC and 200ºC for 2, 6 and 10 hour periods, respectively. The severe conditions of the heat treatment resulted in decreased mechanical properties (compressive strength and modulus of elasticity) and a decrease in the degree of cellulose polymerization. A comparison of selected mechanical properties and the degree of cellulose polymerization indicated that there was a relationship between them and the temperature and duration of the heat treatment.

Introduction

The properties of thermally-modified wood have been examined since 1930s. One of first research studies was conducted by Stem and Hansen [1937] and concerned the dimensional stability of wood. Numerous technologies to obtain thermally-modified wood have been created, of which the best-known are: Dutch PlatoWood®, German Thermoholtz®, Finnish Thermowood® and French RectificatedWood®. These processes differ as regards the conditions in which the treatment is conducted. Some of the physical properties of thermally-modified wood change irreversibly. In addition to changes in the durability of the wood, the heat treatment of wood results in a change of wood colour [Schneider and Rusche 1973; Viitaniemi and Jämsä 1996; Kubojima et al. 2000]. The high temperature also causes a number of changes in the structural composition of the wood and, in particular, in the polysaccharide contents

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[Zawadzki et al. 2007; Gawron et al. 2011, 2014]. Furthermore, a number of chemical processes take place [Rowell et al. 2002; Yildiz and Gumuskaya 2007].

Only higher temperatures lead to a significant decrease in the degree of cellulose polymerization, which is connected with its degradation. The processes and reactions result in an alteration of the structural and non-structural substances content in the wood [Yildiz et al. 2006]. More visible changes can be observed where such treatment is conducted with the use of superheated steam or oxygen (e.g. in atmospheric conditions) as compared to the modification of dried wood in the presence of an inert gas. Mitchell [1988] found that the heat treatment of wood in the presence of atmospheric oxygen additionally influences the process of carbohydrate depolymerisation. The objective of this work was to discover whether the treatment of pine wood under oxygen conditions allows a correlation between the degree of cellulose polymerization obtained from the wood, particularly at a temperature of 200ºC and heat treatment times of 6 and 10 hours, and the mechanical properties.

Materials and methods

A pinewood (*Pinus sylvestris* L.) board, without defects, was used for the analysis. Samples were collected from the sapwood zone and measured $20 \times 20 \times 30$ mm (the longest edge parallel to grain). There were 38 samples in each group.

The first group of samples was stored at room temperature and no further action was taken with them. The second group was dried at 105ºC for 12 hours. The following three groups were dried first and then thermally modified at 160ºC for periods of 2, 6 and 10 hours, respectively. Similarly, the last three groups underwent heat treatment at 200ºC for periods of 2, 6 and 10 hours, respectively.

The treatment process

1. Raising the temperature to 105 ±1ºC; maintaining the temperature for a period of 12 hours.
2. Raising the temperature to the final level of 160 ±1ºC or 200 ±1ºC; maintaining the temperature for the given period of 2, 6, or 10 hours.
3. Taking the samples out and achieving constant weight in a desiccator.

Preparation of samples for chemical analysis

The pinewood control samples and samples after heat treatment were ground, obtaining a sawdust fraction of 0.5-1.0 mm used for testing. The sawdust underwent extraction using a chloroform and ethanol mixture $(93:7)_w$ [Antczak et al. 2006]. From the samples which had undergone heat treatment, the cellulose was separated with the use of the Kürschner-Hoffer method.

Following this, 3 cm^3 of water was added to a test tube containing 15 mg (0.015 g) of cellulose, and the suspension of cellulose in water was left for 12 hours. After this time, the water was separated from the swollen cellulose using a syringe and 2.5 cm^3 of methanol was added. After 45 minutes, the methanol was filtered using a syringe and replaced with a new portion of the solvent. The cellulose was then washed twice with 2.5 cm^3 of DMAc at identical time intervals. Following the addition of 2.5 cm^3 of DMAc for the third time, the suspension of cellulose in DMAc was left for 12 hours. After the removal of the DMAc, 1.25 cm^3 of 8% (w/v) LiCl/DMAc was added to dissolve the cellulose. After complete dissolution of the sample, it was diluted to a concentration of 1% (w/v) LiCl/DMAc [Dupont and Mortha 2004]. Subsequently, all the samples were analyzed with a SHIMADZU LC-20 liquid chromatograph. During the test, a Nucleogel M-10 (Macherey-Nagel) column was used. For all the analyses, identical conditions were applied: eluent – 0.5% solution of LiCl in DMAc, filtered through the 0.2 μm PTFE membrane; eluent flow rate was 1.5 cm³/min and temperature 80ºC. For the purpose of calibration, polystyrene standards with a molar mass from 580 Da to 6850 kDa were used. A Mark-Houwink universal calibration was used to establish the molar mass distribution, with the application of the following properties:

$k_{PS} = 17.35 \times 10^{-3}$ cm³/g, $\alpha_{PS} = 0.642$ – for polystyrene [Timpa 1991]
$k_{cel} = 2.78 \times 10^{-3}$ cm³/g, $\alpha_{cel} = 0.957$ – for cellulose [Bikova and Treimanis 2002].

Preparation of samples for mechanical properties test
The mechanical properties of the samples collected from the sapwood zone which underwent heat treatment were measured, as well as those of the control samples which had been stored in ambient conditions. The compressive strength and elastic modulus of the wood compressed in the direction along the fibres were measured.

The consolidated results of the physical and mechanical properties – the density, compressive strength and elastic modulus of the pinewood samples, according to treatment temperature and time, were presented in an earlier publication [Zawadzki et al. 2013].

Results and discussion

The weight average molar mass was established with regard to the cellulose contained in the pinewood which underwent heat treatment with the application of different durations and temperatures. It is possible to observe, on the basis of the data provided in figure 1, that the temperature and time of the wood treatment influenced the degree of cellulose degradation. Changes in the weight average molar mass of the cellulose extracted from the pinewood occurred in both cases – at a temperature of 160ºC and 200ºC.
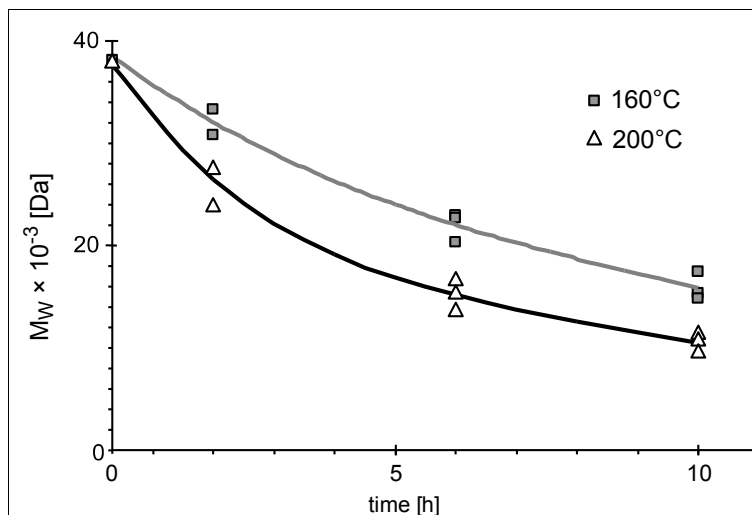
Fig. 1. Changes in the weight average molar mass of cellulose molecules contained in pinewood during heat treatment

The duration of the heat treatment also influenced the degree of cellulose polymerization. The extension of the heat treatment time from 2 h to 6 h, and then to 10 hours, at the given temperatures consequently resulted in a decrease in the weight average molar mass of the cellulose. In relation to 380 kDa molar mass of cellulose in reference samples, the influence of a treatment temperature of 160ºC and 10 h time resulted in its decrease to 180 kDa, i.e. a decrease of 53%. Treatment temperature of 200ºC and 10 h duration caused a decrease in the weight average molar mass of the cellulose molecules to 120 kDa, i.e. a decrease of approx. 69%. The results obtained correspond well with the results of Kacikova et al. [2013].

Similar results were obtained by Fengel [1967], who tested Norway spruce wood which was subjected to thermal modification for 24 hours. The degree of cellulose polymerization remained almost unchanged up to 120ºC, however, at a temperature of 200ºC, it rapidly decreased to 40% of initial value.

A kinetic model of pseudo-zero-order reaction [Zou et al. 1994; Emsley et al. 1997] was used in order to examine the kinetics of the degradation process. Taking into account the dependence between the percentage yield and the degree of cellulose polymerization, an equation was obtained, which was used to interpret the experimental data. On the basis of the parameters of molar mass distribution of the cellulose from degraded samples (previously extracted from the wood which underwent heat treatment), the weight average polymerization degree (P_w) were determined and the kinetic model described above was applied. The dependence of the reciprocal polymerization degree of cellulose on the time of wood treatment is illustrated in figure 2.
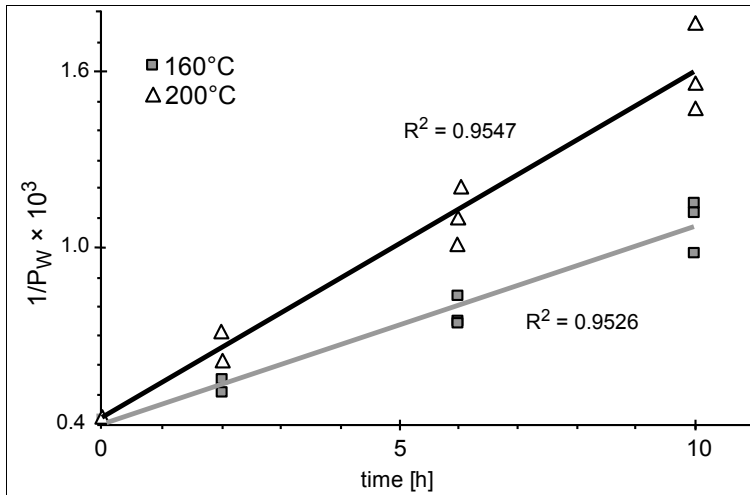
Fig. 2. The kinetic dependence of degradation of cellulose contained in thermally modified pinewood

The observed dependence seems to be linear, therefore the degradation mechanism may be interpreted as random.

The cellulose depolymerisation reaction constant was established on the basis of the observed dependence. For wood treatment at 160ºC, the following value was obtained: k = (1.85 ±0.16) × 10^{-8} s^{-1}. At 200ºC, the progress of cellulose degradation was faster: (3.25 ±0.27) × 10^{-8} s^{-1}, i.e. by 76%.

The Arrhenius equation in the logarithmic form gives linear dependence of the reaction rate constant on temperature. Knowing the process rate values of the experimentally determined degree of cellulose depolymerisation at the treatment temperatures 160ºC and 200ºC, it is possible to determine the activation energy of the cellulose degradation process. Under the conditions of the applied heat treatment process, it was (23.9 ±2.3) kJ·mol^{-1}. In most chemical reactions, the activation energy levels are between 50-300 kJ·mol^{-1}. In the case of cellulose, the activation energy of the thermal decomposition reaction changes significantly according to the experiment conditions. Hill et al. [1995] provides the values of 79-92 kJ·mol^{-1} for thermal decomposition, and higher values of 113-120 kJ·mol^{-1} for hydrolytic degradation. At the higher range of temperatures, between 300ºC and 360ºC, the activation energy for thermal degradation is higher and reaches up to 112 kJ·mol^{-1} [Zickler et al. 2007]. According to Strlič et al. [2001], values for the initial phase of decomposition at 180ºC, obtained on the basis of chemiluminescence measurements, are approx. 49 kJ·mol^{-1} under anaerobic conditions and 78 kJ·mol^{-1} under aerobic conditions. On the other hand, Ding and Wang [2008] concluded that the values obtained for sulphate paper degradation at temperatures under 100ºC depend on the environment. The activation energy was only 11.5 kJ·mol^{-1} in the presence of air, 34 kJ·mol^{-1} in oil,

and it reached 120 kJ·mol^{-1} after oxygen and humidity elimination. In addition, it should be stressed that in the case examined of the heat treatment of wood, the cellulose degradation process did not function as a closed system. Wood is a complex system, which comprises substances of various natures, such as resin acids or phenolic compounds (including lignin). These compounds may catalyze or inhibit cellulose reactions, thus significantly altering the activation energy.

It was decided that the interdependence between the physical and mechanical properties of the modified wood and the measured degree of cellulose polymerization extracted from the thermally modified pinewood would be analyzed.

The results of tests to determine the density, compressive strength and elastic modulus of the pinewood (*Pinus sylvestris* L.) samples are presented in an earlier publication [Zawadzki et al. 2013]. A significant decrease in the compressive strength and the modulus of elasticity was clearly visible at 200ºC and with a duration time of 10 hours; a large decrease in wood density was also visible under these conditions. The results obtained also correspond well with the results of Kacikova et al. [2013] and Yildiz and Gumuskaya [2007]. The resulting dependence between the level of cellulose polymerization in the pinewood after heat treatment and its compressive strength and elastic modulus is shown in figures 3 and 4.

According to the data provided in figures 3 and 4, the degree of cellulose polymerization changed as a result of the heat treatment applied. The temperature of 160ºC and heat treatment durations of 2, 6 and 10 hours did not significantly influence the compressive strength and modulus of elasticity, though the process of cellulose degradation took place and the degree of polymerization fell from 2000 to approximately 1000. The increase in treatment temperature to 200ºC resulted in a significant decrease in the degree of polymerization. This change was particularly apparent at a temperature of 200ºC and 10 hours of heating time. In such conditions, a significant decrease in the durability and elastic properties was observed, which was a result of the decrease in the degree of cellulose polymerization to 650.

According to the data provided, there was a direct dependence between the degree of polymerization of the cellulose extracted from the thermally modified pinewood and the examined mechanical properties of the wood. This dependence resulted, among other things, from the changes in the composition and amount of cellulose, which was subjected to degradation under the heat treatment conditions.
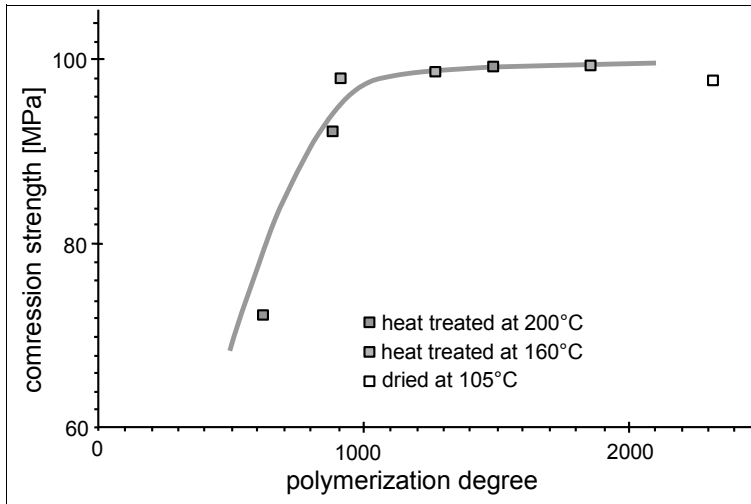
Fig. 3. Dependence between the degree of cellulose polymerization in pinewood after heat treatment and its compressive strength
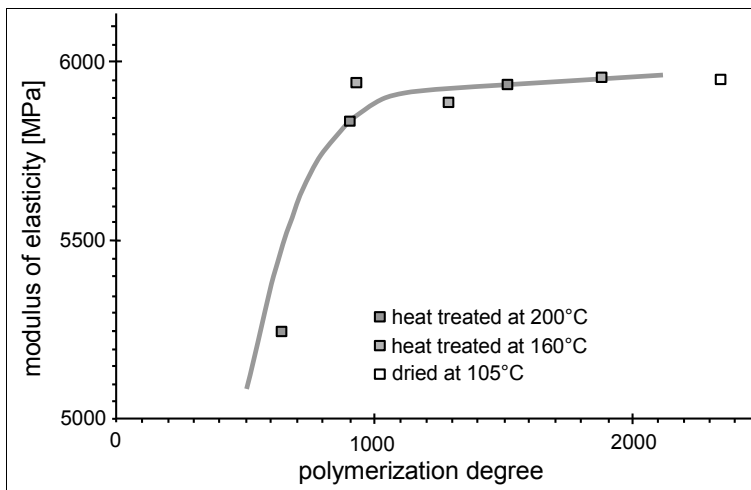

Fig. 4. Dependence between the degree of cellulose polymerization in pinewood after heat treatment and its elastic modulus

Conclusion

To sum up, it can be stated that temperatures of 160ºC and 200ºC and the duration of the process, resulted in changes in the wood and the mechanical properties of the cellulose. A change in the molar mass and decrease in the degree of cellulose polymerization could be observed, as well as the lower compressive strength and elastic modulus of the pinewood. There was a direct and strong correlation between these data.

Increasing the treatment duration from 2 to 10 hours significantly influenced the degree of cellulose polymerization. The temperature of the heat treatment influenced the degree of cellulose polymerization more than the duration of the process. The decrease in the degree of cellulose polymerization did not cause a significant decrease in the compression strength and modulus of elasticity. For this reason, the heat treatment at a temperature of 160ºC with duration up to 6 hours did not cause a decrease in the polymerization degree below 1000. Therefore, such a wood may still be used as construction wood but with increased resistance to biological factors.

References

Antczak A., Radomski A., Zawadzki J. [2006]: Benzene Substitution in Wood Analysis. Annals of Warsaw Agricultural University, Forestry and Wood Technology 58: 15-19

Bikova T., Treimanis A. [2002]: Problems of the MMD analysis of cellulose by SEC using DMA/LiCl: A review. Carbohydrate Polymers 48: 23-28

Ding H.-Z., Wang Z.D. [2008]: On the degradation evolution equations of cellulose. Cellulose 15: 205-224

Dupont A.L., Mortha G. [2004]: Comparative evaluation of size-exclusion chromatography and viscometry for the characterization of cellulose. Journal of Chromatography A 1026: 129-141

Emsley A.M., Heywood R.J., Ali M., Eley C.M. [1997]: On the kinetics of degradation of cellulose. Cellulose 4: 1-5

Fengel D. [1967]: On the changes of the wood and its components within the temperature range up to 200ºC Part IV. The behaviour of cellulose in spruce wood under thermal treatment. Holz als Roh und Werkstoff 23: 102-111

Gawron J., Grześkiewicz M., Zawadzki J., Zielenkiewicz T., Radomski A. [2011]: The influence of time and temperature of beech wood (*Fagus sylvatica* L.) heat treatment in superheated steam on the carbohydrates content. Wood Research 56: 213-220

Gawron J., Antczak A., Borysiak S., Zawadzki J., Kupczyk A. [2014]: The study of glucose and xylose content by acid hydrolysis of ash wood (*Fraxinus exclesior* L.) after thermal modification in nitrogen by HPLC method. BioResources 9: 3197-3210

Hill D.J.T., Le T.T., Darveniza M., Saha T. [1995]: A study of degradation of cellulosic insulation materials in a power transformer, part 1. Molecular weight study of cellulose insulation paper. Polymer Degradation and Stability 48: 79-87

Kacikova D., Kacik F., Cabalova I., Durkovic J. [2013]: Effects of thermal treatment on chemical, mechanical and colour traits in Norway spruce wood. Bioresource Technology 144: 669-674

Kubojima Y., Okano T., Ohta M. [2000]: Bending strength and toughness of heat treated wood. Journal of Wood Science 46: 8-15

Mitchell P. H. [1988]: Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen. Wood and Fiber Science 20: 320-355

Rowell R., Lange S., McSweeny J., Davis. M. [2002]: Modification of wood fiber using steam. Wood Science and Engineering Department, Oregon State University, Corvallis, USA

Schneider A., Rusche H. [1973]: Sorption-behaviour of beech- and sprucewood after heat treatments in air and absence of air. Holz Als Roh- und Werkstoff 31: 313-319

Stem A.J., Hansen L.A [1937]: Minimizing wood shrinkage and swelling: Effects of heating in various gases. Industrial and Engineering Chemistry 29: 831-833

Strlič M., Kolar J., Pihlar B., Rychlý J., Matisová-Rychlá L. [2001]: Initial degradation processes of cellulose at elevated temperatures revisited – chemiluminescence evidence. Polymer Degradation and Stability 72: 157-162

Timpa J.D. [1991]: Application of universal calibration in gel permeation chromatography for molecular weight determinations of plants cell wall polymers; cotton fibre. Journal of Agricultural and Food Chemistry 36: 270-275

Viitaniemi P., Jämsä S., (1996). Modification of Wood with Heat Treatment. VTT Research Report Publications 814, VTT, Finland, 53

Yildiz S., Gumuskaya E. [2007]: The effects of heat treatment on crystalline structure of cellulose in soft and hardwood. Building and Environment 42: 62-67

Yildiz S., Gezer E.D., Yildiz U. [2006]: Mechanical and chemical behavior of spruce wood modified by heat. Building and Environment 41: 1762-1766

Zickler G.A., Wagermaier W., Funari S.S., Burghammer M., Paris O. [2007]: In situ X-ray diffraction investigation of thermal decomposition of wood cellulose. Journal of Analytical and Applied Pyrolysis 80: 134-140

Zou X., Garnugul N., Uesaka T., Bouchard J. [1994]: Accelerated ageing of papers of pure cellulose – mechanism of cellulose degradation and paper embrittlement. Polymer Degradation and Stability 43: 393-402

Zawadzki J., Grześkiewicz M., Gawron J., Zielenkiewicz T. [2007]: Chemical behavior of pine wood (*Pinus silvestris* L.) modified by heat. Annals of Warsaw University of Life Sciences, Forestry and Wood Technology 62: 380-383

Zawadzki J., Radomski A., Gawron J. [2013]: The effect of heat treatment on selected physical properties of wood of Scots pine (*Pinus sylvestris* L.). Wood Research 58: 243-250

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