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Changes in mechanical and chemical wood properties by electron beam irradiation

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ABSTRACT

This study deals with the influence of various electron beam irradiation (EBI) dosages on the Brinell hardness of Norway spruce. The results of the hardness measurements and the FT-IR spectroscopic analysis show different effects of the EBI at dosages of 25, 50, 100 and 200 kGy. It was assumed that the lignin and carbohydrates undergo different altering mechanisms due to the EBI treatment. New cleavage products and condensation reactions of lignin and carbohydrates lead to better surface hardness of low irradiated wood samples. These results provide a useful basis for further investigations on the changes in wood chemistry and material properties due to electron beam irradiations.

1. Introduction

The modification of physical properties of wood surfaces is as old as wood research. Hill [1] gave a detailed overview of the methods and processes for wood modification. Indeed the modification methods were focused on the surface layers in respect of ecological and economic reasons in the last few years [2]. The effectiveness of current used surface modifications processes of wood were critically analysed by Petrič [3]. Different modification processes improve the material properties as desired (e.g. dimensional stability or durability). On the other hand some properties can be degraded due to these treatments (e.g. mechanical strength).

Ionising irradiation is one possible method to alter the wood properties [4–7]. The irradiated wood undergoes various changes in properties. The modifying mechanisms are very complex and influenced by many factors. High energy irradiation of cellulose causes depolymerisation, a reduction in crystallinity and an extensive decomposition with increasing dose levels [8,9]. As a function of the dose level (10–100 kGy) the degree of polymerisation changes to lower values, simultaneously the number of functional groups increases in the cellulose. Irradiation of lignin (MWL) does not change the aromatic hydroxyl groups and conjugated carbonyls [10]. To protect wood against the negative effects of electron beam irradiation, ionic liquids present one possible opportunity to inhibit the formation of free radicals [11]. Fischer and Goldberg [10] claimed that condensation reactions between the aromatic nucleus and the side chain occur during low irradiation doses. Moreover, there is a risk of material destroying, when the electron beam irradiation dose is too high for the wood material. A systematic study of the effects of high energy electron beam radiation on wood surfaces to influence the surface hardness is not available.

The resulting effects of the electron beam radiation (EBI) on wood properties may improve the surface hardness due to chemical changes in wood components. This was the central hypothesis of the present work. The objective was to analyse the effect of electron irradiation doses on the surface hardness of Norway spruce wood samples. The influence of electron beam irradiation was verified using the established method of Brinell hardness measurements and additionally the effective FT-IR-ATR spectroscopy method.

2. Materials and methods

In this study, samples from Norway spruce (*Picea abies L. [Karst.]*) were cut to dimension of 150 mm × 75 mm × 20 mm providing a radial face for analysis.

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2.1. Electron beam irradiation (EBI)

For the EBI treatment at doses of 25, 50, 100 and 200 kGy an Electrocurtain® LAB Unit CB 175/15/10L electron accelerator was used with accelerating voltage of 150 kV. Five spruce samples were irradiated under nitrogen atmosphere for each EBI dose. Higher electron beam doses than 50 kGy were achieved by repeating the irradiation process a 50 kGy. The low radiation energy applied effectuates only a surface treatment. Jagrović et al. [12] mentioned that the penetration depth of electron is a function of accelerating voltage and material density, and is limited to approximately 500 μm using the accelerating voltage of 150 kV. Therefore, only one surface of the wood samples was irradiated and the opposite side of the samples was used as reference for the further analysis and comparison. This procedure guaranteed low influences of the heterogeneity of wood properties on the mechanical and chemical investigations.

2.2. Surface hardness (Brinell hardness) tests

For the hardness test the samples were stored in a climatic chamber (20 °C and 65% RH) before and after the electron beam irradiation. The samples were tested according to EN 1534 [13]. Using the EMCO Test Automat M4U 075 a steel ball with 10 mm diameter was pressed with a defined force of 500 N into the material and remained there for 30 s. The Brinell hardness was calculated applying the press force, the diameter of the steel ball and the diameter of the impression. Nineteen measurements in transverse direction for each sample of each EBI dose were employed to determine the changes and the mean value of the results was used for the further analysis.

2.3. FT-IR spectroscopy

For the chemical analysis the wood samples were dried at 50 °C for one week to reduce the moisture content. The spectra were recorded in the range between 4000 and 600 cm^{-1}, with 32 scans and with the resolution of 4 cm^{-1} using a Frontier FT-IR spectrometer (Perkin-Elmer) equipped with a Miracle diamond ATR accessory with a 1.8 mm round crystal surface. All spectra were ATR corrected and three single spectra per sample were averaged. The spectra were baseline corrected in the wave number range between 600 and 4000 cm^{-1} and normalised using the unit vector normalisation.

Changes in the wood chemistry during the EBI were monitored from the FT-IR differences (D) of absorbance (A) spectra according to Eq. (1)

$$D_{EBI} = (A_{EBI} - A_{EBI(NaOH)}) - (A_{ref.} - A_{ref.(NaOH)}), \quad (1)$$

where EBI corresponds to various electron irradiation doses, A_{EBI} conforms to the absorbance of EBI treated wood surface as well as $A_{EBI(NaOH)}$ complies with the IR spectrum of EBI treated wood after the NaOH treatment and respectively the $A_{ref.}$ and $A_{ref.(NaOH)}$ for their control samples without electron beam irradiation.

2.4. X-ray diffraction (XRD) analysis

X-ray diffraction measurements were carried out using a Rigaku S-Max 3000 SAXS/WAXS system equipped with a copper-target micro-focus X-ray tube MicroMax-002+ (45 kV, 0.88 mA), collimated through three pinholes (400, 200 and 700 μm) to achieve a beam diameter at the sample position of 210 μm (FWHM) and a Triton 200 2D multi wire gas-filled X-ray detector (200 mm diameter of active area, spatial resolution 200 μm). Data was acquired in the q-range from 3.3 to 26 nm^{-1} with a measurement time of 1000 s for each scattering pattern at vacuum conditions better than 10^{-2} mbar. The samples were prepared as 200 μm thick sections from the irradiated surface and were mounted free-standing in the beam path. Data was integrated using Fit2D and azimuthally integrated.

The radial intensity distribution I_0 was normalised using the X-ray transmission, *trans*. Furthermore the sample thickness d was calculated from the X-ray transmission and the X-ray attenuation length, l_{att} for chemical composition of spruce wood at the determined specimen density based on [14] and was also used for thickness correction based on the absorption.

The normalised intensity I_{corr} was calculated using the following formula:

$$I_{corr} = \frac{I_0 * trans}{-\ln(trans/l_{att})}$$

The crystallinity was determined by fitting and integrating the 101, $10\bar{1}$, 021 and 002 peaks of cellulose with two Gaussian distributions. The relative degree of crystallinity was obtained by dividing the sample crystallinity with the crystallinity of the untreated control samples.

2.5. Sodium hydroxide solution treatment

Thin wood layers were cut from the surface of the samples using a sharp knife and treated with a 0.1 M sodium hydroxide (NaOH) solution for 24 h at room temperature to show the effect of possible chemical reactions in the wood components. The residual sodium hydroxide in the samples was washed-out by water to decrease the range of the pH-value of 6.0–7.0. During the intensive water treatment the linked Na-ions were removed and the lattice of cellulose II was formed [5]. Then the samples were dried at 50 °C for one week for the IR spectroscopy.

3. Results and discussions

3.1. Changes in surface hardness (Brinell hardness)

Ionising irradiation can alter the ultrastructural of wood. These changes have a negative implication of the mechanical properties, as a decomposed structure and ruptures within the middle lamella and the secondary cell wall can occur [5]. However, De Lhoneux [15] and Polčin and Karánek [16] mentioned that no remarkable changes on gamma irradiated wood surfaces of the cell walls can be proved by using scanning electron microscope (SEM) micrographs. Only after chemical (e.g. DMSO extraction) or mechanical (e.g. grinding in a micro-vibration mill) treatments the differences in irradiated wood structures can be observed. Also, the gamma irradiation doses up to 300 kGy did not change the structure of bamboo [7]. Therefore, in this study the analysis of the wood microstructure was not the main objective.

Sell [17] identified 12 MPa as the average Brinell hardness perpendicular to grain of Norway spruce with moisture content (MC) between 10 and 12%. This value was also determined for the untreated spruce samples in this study and provided the base to show the changes. Fig. 1 shows the differences in Brinell hardness (MPa) of Norway spruce samples of the control group and after various doses of electron beam irradiations.

The surface hardness of the control group shows the expected natural variability of wood, while the median of this data is located at zero. With increasing electron beam irradiation doses the medians of the groups shift to higher values, which means the transversal surface hardness of wood increases. Lower irradiation doses influence positively the surface hardness, while this effect is not determinable at 200 kGy EBI dose.

The buckling of individual wood fibres is the starting point for the failure under compression [18]. Therefore, macro-surface hardness is limited by the critical stress of single cell walls. For the investigated samples the depth of indentation of the steel ball