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ORIGINAL ARTICLE

Detection of the effective refractive index of thermally modified Scots pine by immersion liquid method

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Abstract The purpose of this study was to determine the effective refractive index of thermally modified Scots pine (*Pinus sylvestris* L.) wood specimens as a quantitative measure regarding the change of wood density which is due to the thermal modification. The refractive index of thermally modified Scots pine wood was obtained by introducing pine wood powder into an immersion liquid and measuring light backscattering with a homebuilt multifunction spectrophotometer. The present method provides useful information that in principle can be applied, for example, in the optimization of the thermal modification process and inspection of the quality of thermally modified wood.

Keywords Immersion liquid method · Refractive index · Thermally modified pine

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Introduction

Thermal modification at a typical temperature of 180–220°C is an industrial treatment applied for almost 100,000 m^3 of sawn timber in Finland annually (Thermowood® production statistics 2010) [1]. Thermal modification of wood aims at improving wood's resistance against mold and decay fungi, dimensional stability, weather resistance, and appearance [2–4]. The improved dimensional stability is derived from the decrease of the hydroxyl groups that increases the hydrophobicity of wood and reduces the absorption of water [5]. This results in lowered equilibrium moisture content. A majority of the extractives is removed from the wood, and its porosity is increased as the treatment temperature and time increase [6]. Furthermore, wood's colour turns to brown throughout the cross section. There is a practical need for easy-to-use, inexpensive and rapid analysis method that could be applied for defining the treatment temperature from wood specimens after the thermal modification. This would help monitoring the quality of thermally modified wood in the markets.

Wood consists mainly of cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses are polysaccharides while lignins are highly complex, mainly aromatic polymers of phenylpropane units. Wood also contains small amounts of extractives such as resin and fatty acids, fats, fatty alcohols, waxes, phenols, terpenes, and steroids [7]. The crystalline cellulose contains long-chain polysaccharides composed of β-1,4-linked D-glucose rings that cause rotation of linearly polarized light, which results from the birefringence of uniaxial cellulose crystal [8]. The extraordinary refractive index of cellulose n_e is 1.5956 and the ordinary refractive index n_0 is 1.5312 and thus the positive birefringence is 0.0643 (concentration of water is zero) for the sodium D-line [9]. In the literature, an

estimate of 1.557 is given for the effective refractive index of cellulose [10]. Since any wood has various constituents that have different refractive indices the refractive index obtained by measurement is a weighted average of the constituents, and it is called the effective refractive index.

A variety of measurement techniques for determining optical properties of wood material such as the refractive index and birefringence have been developed. These include, e.g., ellipsometry [11], interferometry [12], polarized light microscopy [13], reflectometry [8], X-ray diffraction [14], ultrasound [15], and terahertz techniques [16]. Unfortunately, many of these measurement techniques require rather expensive devices and good specimen quality in terms of homogeneity and smoothness [17, 18].

The objective of this study was to investigate the refractive index of thermally modified Scots pine (*Pinus sylvestris* L.) wood by an immersion liquid method. The immersion method has been popular for determination of the refractive index of microscopic minerals, identification of unknown solids [19], and inspection of the heterogeneity of the cell population in microbiology [20]. In addition, immersion method has been utilized in tissue measurements in medicine. Anisotropic minerals have been studied with the immersion method [21]. Wood, which has a much more complicated structure than a mineral, has also anisotropy in its structure. The advantages of the immersion method are that it is independent of the shape and size of a particle, and the measurement is relatively easy and fast to perform [17]. The principle of the immersion method is to match the refractive index of solid particles with that of the immersion liquid. In the event of a perfect match between the index of the light non-absorbing particles and the immersion liquid, the light transmittance will be 100% and the scattering intensity of light will be zero. However, in the presence of insoluble birefringent (double refraction of light) particles, which form a two-phase system with the immersion liquid, the light transmission measurement method usually fails in situations where the particle density is high and a relatively long optical path is required for the measurement of the transmittance. On the contrary, another type of measurement method that can be used for the detection of the effective refractive index of birefringent particles, namely the light backscattering measurement technique which was exploited in this study, is free from such problems.

In the previous studies we have used a homebuilt multifunction spectrophotometer (MFS) for the measurement of refractive index of liquids. Furthermore, the MFS has been useful for the measurement of the refractive index of isotropic, and also effective refractive index of anisotropic (birefringent) pigments by using the immersion liquid method [22–24]. The advantages of the MFS over conventional devices that are used for the refractive index measurement of particles are: (1) refractive indices of both the immersion liquid and the pigment can be estimated using only one device; (2) measurement can be done both in the light transmission or scattering mode; and (3) the probe wavelength can be freely chosen in the UV–visible spectral range.

In this study, the effective refractive index of thermally modified Scots pine wood was measured for different treatment temperatures. The effective refractive index is proportional to the porosity of the wood.

Experimental

The thermal modification of the specimens was performed according to the Thermowood® process [25]. Scots pine sawn timber with dimensions of 63 (R) × 75 (T) × 2000 (L) mm were treated at 180, 200 and 230°C with actual heat treatment time of 3 h in the maximum temperature. The boards were sawn from trees that had grown in Central Finland, approximately between 64–65°N and 27–28°E. The boards contained both heartwood and sapwood.

In reality, it is usually difficult to adjust the measurement direction of the optical properties of wood with respect to an "optic axis" of a macroscopic wood specimen because the orientation of wood grains changes as a function of the thickness of the specimen. For instance, the birefringence of cellulose of wood is therefore usually detected from a fibre. In our study, the thermally modified boards were cut into approximately 5 × 5 × 5 mm pieces using a band saw. These pieces were ground in a refiner (CYCLOTEC 1093 Sample Mill) with 1.0-mm diameter circular holes. Finally, the powder obtained was dried at 103°C for 24 h and then put into a glass tube with cork closed for restoration. The higher thermal modification temperatures resulted in finer powders compared to the lower temperatures.

The effective refractive index of the specimens was determined by measuring the backscattering signal from wood suspension using the MFS. Schematic diagram of the apparatus is shown in Fig. 1. In the apparatus, the light source is a 150 W xenon lamp, and a monochromator is used for the selection of the probe wavelength. The wavelength can be scanned over the spectral range of 270–800 nm. The probe light is guided into a bifurcated optical fibre. The output end of the fibre can be considered as a point source, and when it is set at the focal point of a parabolic reflector, a collimated light beam is generated. Linearly polarized light beam propagates towards the prism and the sample interface. The angle of back scattering was set at 29.4° by a step motor. A more detailed technical description of the MFS can be found in a previous publication [26]. The whole system has an automatic operation.

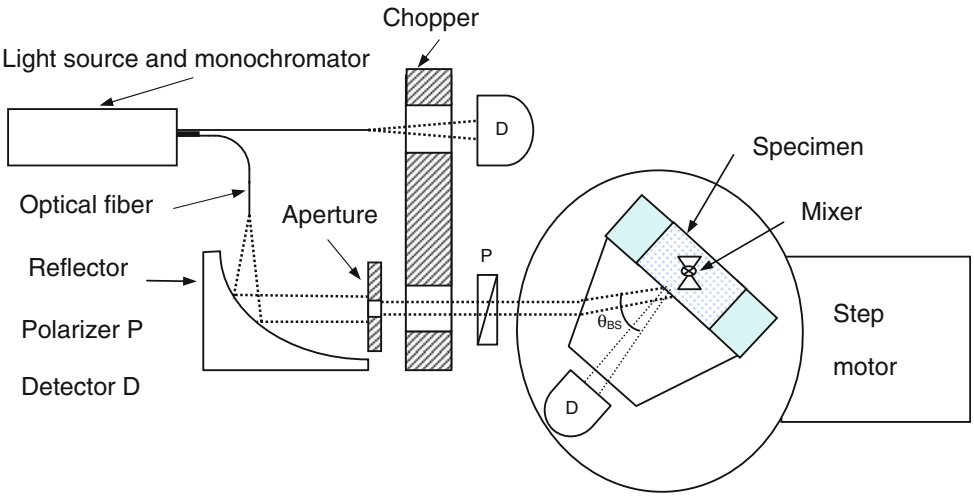

Fig. 1 Schematic diagram of the multifunction spectrometer, MFS

Using the MFS we measured the refractive index for both the set of immersion liquids as well as the effective index of the specimens of wood powder. The ground specimens were suspended in acetone–methylene iodide mixtures with varying refractive indices from 1.54 to 1.73 with a 0.05 step. The measurement wavelength and temperature were 589.6 nm and 22°C, respectively. The mass concentration employed were 0.250 g in methylene iodide (specimen volume of 15 ml) and 0.50 g in acetone (specimen volume of 30 ml). Density of wood samples was determined by measuring the weight and the dimensions of the samples.

The definition of the effective refractive index n of the immersion liquid is based on measurement of the volumes V_a and V_b of two liquids a and b, measurement of the refractive indices n_a and n_b with the MFS, and the use of the formula: [27]

$$n = \frac{V_a n_a + V_b n_b}{V_a + V_b}. \quad (1)$$

When measuring the index match between the particle and the immersion liquid, the accuracy of the assessment of the refractive index of the particle from the backscattering signal (BS) can be improved using, for example, the Gaussian-fitting procedure, which is assumed to hold for particles that have a Gaussian size distribution:

$$\mathrm{BS} = b - A\exp\left[-(n_{\mathrm{liquid}} - n_{\mathrm{wood}})^2/(2\psi)^2\right], \quad (2)$$

where b is the baseline, A is amplitude and ψ is related to the width of the normal distribution at the half maximum [28].

Results and discussion

The curves of backscattering signal as a function of the refractive index of the immersion liquid for three thermally modified and one untreated Scots pine specimens are shown in Fig. 2. Table 1 presents the effective refractive indices that yield the minimum light scattering as obtained from Fig. 2. The first impression is that the effective refractive index of thermally modified Scots pine increases as a function of the treatment temperature. This would mean that the wood density has increased during the treatment. However, this is not the explanation, since we know that some material is removed during the thermal modification process, which means decrease in density. A more plausible explanation is that the immersion liquid has penetrated into the pores of the wood that are formed during the treatment process. Hence, the observed increase in the effective refractive index is a measure of the decrease of the density of wood. Or in other words, the increase of the effective refractive index is a measure of

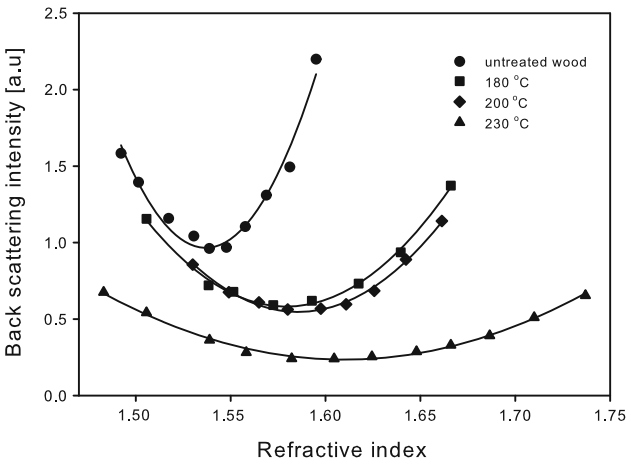

Fig. 2 Data of backscattering signal obtained from thermally modified Scots pine particles as a function of refractive index of the immersion liquid. The immersion liquid is a mixture of acetone ($n_a = 1.358$) and methylene iodide ($n_b = 1.73$). The angle of back scattering was 29.4° and the wavelength of the light was 589.6 nm. The *solid lines* present Gaussian line fittings

Table 1 Measurement results for the density, effective refractive index and loss of birefringence of thermally modified Scots pine

	Untreated	180°C	200°C	230°C
Density (kg/m^3)	562	392	528	487
Effective refractive index	1.553	1.578	1.587	1.596
Change of effective refractive index		0.025	0.034	0.043
Relative change of effective refractive index (%)		1.61	2.19	2.77

increase of the wood porosity. Based on Fig. 2, it is also evident that the BS is steeper for the untreated Scots pine wood as a function of mismatch of the refractive index, and being at its lowest for the treated specimen. Also this fact is assumed to result from the penetration of the immersion liquid inside the pores.

Based on Fig. 2, we can notice that the minimum level of the backscattering signal decreases in the vertical direction when the treatment temperature rises. Nevertheless, the BS is always higher than zero. This indicates that thermally modified Scots pine contains constituents that have different refractive indices. One such a constituent is the birefringent cellulose, and one explanation we propose as the reason for lowering of the minimum value of BS is the loss of birefringence of the cellulose due to crystal to amorphous deformation [29]. Thermal modifications of crystalline structure of cellulose of beech and spruce were studied in [30]. In that study, the cellulose was isolated and using KBr (alkali halide) disks to collect Fourier transform infrared (FT-IR) spectra. Our study is different from [27] because we studied Scots pine and did not use KBr matrix.

In our study, the untreated specimens had the highest BS, whereas the lowest BS was obtained for the specimens treated in the highest temperature. In Table 1, the change of the effective refractive index was calculated by subtracting the effective index of thermally modified specimen from that of untreated one. This value is proposed to be proportional to the loss of birefringence of cellulose. We remark that similar result was obtained in the article of Degushi [31], where cellulose in water at temperature around 320°C and at constant pressure of 25 MPa was investigated. We suggest that the backscattering signal, measured with the MFS, yields information on the crystal to amorphous change of cellulose in the thermal modification process of wood. In Table 1 is presented density and also the relative change of the effective refractive index of the treated wood with respect to untreated one. This percentage is suggested to show the change of density/porosity of the treated wood sample. The thermally modified pine samples of this study had a lower density than the untreated pine which is assumed to result from changes of the sample mass during the heat treatment process when wood loses its weight [1]. Naturally, for comprehensive statistical analysis the number of wood samples should be much higher than we measured because the density of the wood is a subject of variation not only among tree species but also among specimens of the same sample [1]. The complexity of the density, porosity and pore size distribution of thermally treated spruce and maple has been investigated [32].

Further research is needed in order to verify the results with larger set of specimens and different tree species. However, this preliminary study indicates that the refractive index shows high potential for defining the degree of thermal modification after the treatment process.

Conclusion

In this paper, we have presented a light backscattering technique and a multifunction spectrophotometer to obtain effective refractive index for thermally modified Scots pine wood. Our measurements were based on the immersion liquid method. In this study, the wavelength was fixed. However, it is possible to freely choose the measurement wavelength of the light. This can have importance in basic studies of wood and wood products such as paper. In the case of paper the refractive index information is important in the aim of improving the opacity of the paper. We suggest that the immersion method and the MFS are useful in the basic studies of optical properties of thermally modified wood. Using the index data it is possible to assess changes in the porosity and crystalline forms of cellulose of thermally modified wood as a function of temperature and the treatment time. The proposed method will have importance in the quality inspection of thermally modified wood, and help to monitor and develop the industrial treatment process for thermal modification of wood.

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