ORIGINAL

Crystalline structure of heat-treated Scots pine [*Pinus sylvestris* L.] and Uludağ fir [*Abies nordmanniana* (Stev.) subsp. *bornmuelleriana* (Mattf.)] wood

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Abstract The aim of this study was to determine changes in crystallinity and crystalline unit cell type of heat-treated Scots pine (*Pinus sylvestris* L.) and Uludağ fir (*Abies nordmanniana* stev. subsp. *bornmuelleriana* Mattf.) wood samples by means of FT-IR spectroscopic method. Heat treatment was applied on the test samples in an oven at three different temperatures (120, 150, and 180°C) and for two different periods of time (6 and 10 h) under atmospheric pressure. It was designated that crystallinity of both Scots pine and Uludağ fir wood samples increased during heat treatment depending on the duration. However, monoclinic structure in crystalline unit cells of Scots pine and Uludağ fir wood samples converted to triclinic structure when heat treated. It was estimated that monoclinic structure was dominant in the crystalline unit cell. It was established that the crystalline structure of Scots pine wood samples was more affected by heat treatment than that of Uludağ fir wood samples.

Introduction

Wood is subjected to heat treatment for many reasons. Heat treatment of wood contributes to the thermal degradation of its constituents and changes

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the crystallinity, influences the elasticity, absorptive capacity, and other industrially valuable physical properties of the fiber. Researchers have reported on the change of crystallinity of cellulose after heat treatment, but all their studies were carried out under oven-dried condition. The properties of wood are affected by the presence of moisture during heat treatment. It is assumed that crystallization in wood cellulose might be affected by moisture at the time of heat treatment, and activated energies can give us a clear concept on the effect of moisture (Bhuiyan 2000).

Temperatures above 150°C alter the physical and chemical properties of wood permanently. They reduce the shrinkage and swelling of the wood and improve the equilibrium moisture content of the wood. At the same time the strength properties start to weaken. Very high temperatures improve the resistance to rot and also reduce the susceptibility to fungal decay (Järmsä and Viitaniemi 2001).

A considerable research effort has been done over the last decades to improve the dimensional stability of wood and wood products. According to Hillis (1984) the change in moisture content causes changes in bond configuration of the noncrystalline regions of adjacent cellulose molecules and polyoses, resulting in swelling and shrinking. Nonuniformity of these dimensional changes accounts for warping, cupping, honeycombing, face-checking, and grain-raising of many wood species (Hillis 1984). Despite the many positive characteristics of wood (availability, variety, costs, renewability, strength in relation to weight, size, etc.) these defects restrict its use for certain exterior-type applications. Furthermore, wood is susceptible to biological degradation by fungi and bacteria above a moisture content of 21%. Such biological degradation results in an unacceptable loss of mechanical properties, which will affect its structural characteristics. Heat treatment has been reported to be an effective method to improve wood dimensional stability and/or its durability. In the last decade several research groups developed heat treatment methods suitable for industrial applications (Boonstra and Tjeerdsma 2005).

In this study, we investigated how the crystallinity and estimations of relative monoclinic (I_β) and triclinic structure (I_α) content of Scots pine (*Pinus sylvestris* L.) and Uludağ fir (*Abies nordmanniana* Stev. subsp. *bornmuelleriana* Mattf.) wood samples were changed by heat treatment at 120, 150, and 180°C. The selected treatment times were 6 and 10 h. Fourier transform infrared (FT-IR) spectroscopic method was used for analysis.

Materials and methods

Heat treatment

Scots pine (*Pinus sylvestris* L.) and Uludağ fir (*Abies nordmanniana* stev. subsp. *bornmuelleriana* Mattf.) wood samples were obtained from Bolu region in Turkey. The woods were cut in parallel to grain directions and sawn into

specimens. Conditioning to 12% moisture content was performed at 20 ± 2°C and 65 ± 5% relative humidity. Heat treatment was then applied on the test samples in an oven controlling the temperature ±1°C sensitivity, at three different temperatures (120, 150, and 180°C) and for two different periods of time (6 and 10 h) under atmospheric pressure and in the presence of air. Before analyses heat-treated and untreated (control) wood samples were ground in a Wiley mill to homogeneous meal.

FT-IR spectroscopy

Wood samples used in this study were Scots pine and Uludağ fir. Control and heat-treated wood powder samples were used for FT-IR spectroscopy measurement. The dried samples were embedded in potassium bromide (KBr) pellets, and were analyzed by using a Perkin Elmer Spectrum One FT-IR spectroscopy model 2000. They were recorded in the absorption mode in the range of 4,000–400 cm^{-1} with an accumulation of 32 scans, resolution of 2 cm^{-1}. These spectra were normalized at 2,900 cm^{-1} (C–H stretching vibration).

Results and discussion

Wood is a complex composite material consisting mainly of cellulose, hemicelluloses, and lignin. Cellulose represents the crystalline parts of the wood, while the structure of hemicelluloses and lignin are amorphous. The main mechanical function of hemicelluloses and lignin is to buttress the cellulose fibrils (Wikberg and Maunu 2004). The strength properties of cellulosic materials are intrinsically related to the interactions between the cellulose molecules, and an understanding of the molecular structure of cellulose is therefore extremely important (Hinterstoisser and Salmén 1999). The fiber texture and the complex chemical composition of wood complicate the crystallinity determination. Furthermore, the separation of amorphous background from the diffraction pattern of cellulose crystallites is difficult because the cellulose crystallinity of wood cannot be determined accurately (Andersson et al. 2003).

The chemical analysis of woods after thermal treatment at various temperatures shows relatively good stability of the components up to 100°C and up to a treating time of 48 h. At higher temperatures the content of polysaccharides (holocellulose) decreases more and more, the hemicelluloses reacting obviously more sensitively than cellulose. Alpha-cellulose of softwood contains a relatively high amount of hemicelluloses and residual lignin; the decrease of alpha-cellulose which begins at 100°C can be reduced to the loss of these accompanying compounds, so that the content of pure cellulose remains constant up to 150°C even if softwood. The lignin content too remains constant in a wide temperature range; above 150–160°C the lignin content increases (Fengel and Wegener 1989).

Scots pine and Uludağ fir wood samples were heat treated at 120, 150, 180°C for 6 and 10 h. Using FT-IR spectroscopy method crystalline structure properties of these wood samples were designated. We used different methods for determination of crystallinity of wood samples in FT-IR spectroscopy method. The first approach for determination of crystallinity of wood cellulose was the ratio of the peaks areas at 1,370 and 670 cm^{-1} (A_{1370}/A_{670}) proposed by Richter (1991) in FT-IR spectra of wood samples. This method actually uses the ratio of the combined areas of the three peaks at 1,370, 1,335, and 1,315 cm^{-1}, which have called the 1,370 cm^{-1} peak (CH bending) to that of the peak at 670 cm^{-1} (C–OH out of plane bending mode). Spectra were recorded in absorbance modes using KBr discs containing a constant amount of the samples (Evans et al. 1995). According to this method, crystallinity of both Scots pine and Uludağ fir wood samples increased by raising the temperature from 120 to 180°C during thermal treatment depending on the duration. It was found that the increase in crystallinity of Scots pine wood samples is higher than that of Uludağ fir wood samples, as can be seen in Figs. 1a and 2a.

The ratio of peak heights at 1,429 and 897 cm^{-1} (H_{1429}/H_{897}), and at 1,372 and 2,900 cm^{-1} (H_{1372}/H_{2900}) in FT-IR spectra of wood samples was used as a second approach for the determination of crystallinity of cellulose in wood samples (Åkerholm et al. 2004). In this study, higher H_{1372}/H_{2900} ratio for Scots pine wood samples was estimated than for Uludağ fir wood samples. It was determined to decrease the H_{1372}/H_{2900} ratio for Scots pine wood samples at 150°C (10 h) and for Uludağ fir wood samples at 180°C (10 h), as is shown in Figs. 1b and 2b.

The increase in crystallinity may be explained as crystallization in quasi-crystalline amorphous regions due to rearrangement or reorientation of cellulose molecules inside these regions; the higher crystallization in wood cellulose may be due to the crystallization in hemicelluloses. Wood cellulose contains more quasicrystalline regions than pure cellulose. In a previous study, Bhuyian et al. (2000) currently tried to verify the cause of more crystallization
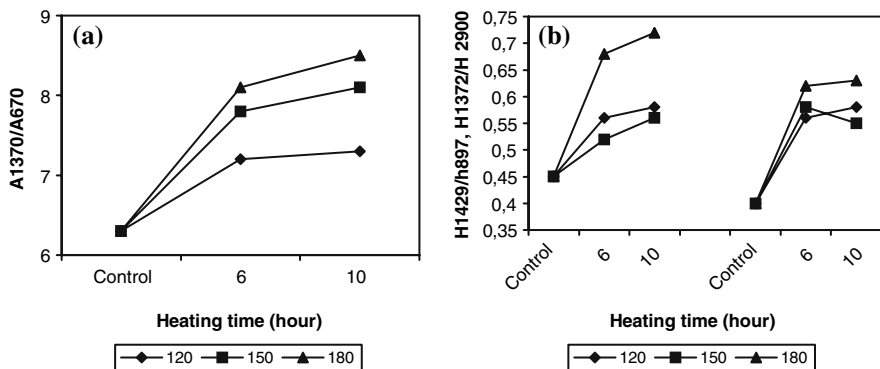
Fig. 1 Changes in crystallinity of Scots pine wood samples with heat treatment
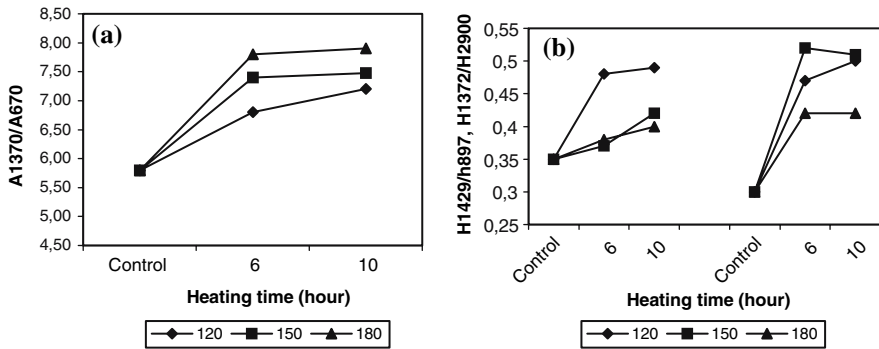
Fig. 2 Changes in crystallinity of Uludağ fir wood samples with heat treatment

in wood cellulose. There are evidences that xylan and mannan are capable of crystallizing. Therefore, in the present study, in addition to crystallization in quasicrystalline regions, crystallization might have occurred in xylan and mannan owing to the heat treatment, which results in more crystallization in wood cellulose than in pure cellulose. At the later stages of heat treatment, the glucosidic linkage is believed to be cut, and depolymerization occurs. In addition to depolymerization, thermal degradation occurs in both the crystalline and noncrystalline regions; and a decrease in crystallinity is observed in both wood species (Bhuiyan et al. 2000).

Crystalline unit cell type in wood samples was determined by using FT-IR spectroscopy. In previous studies, according to Sassi et al. (2000), Wada and Okano (2001), bands at 750 and 710 cm^{-1} for cellulose in wood and pulp samples were assigned to I_α (triclinic) and I_β (monoclinic) phases, respectively. I_α and I_β may have a different H-bonding pattern since their FT-IR spectra are not identical in the OH stretching region (Wada et al. 1993).

As can be seen in Tables 1 and 2, I_α/I_β ratio established 34/66 for Scots pine wood sample and 39/61 for Uludağ fir wood samples. It was determined that crystalline unit cell converted from I_β to I_α in two wood samples by heat treatment. The alteration of crystalline unit cell in two wood samples was clear at all temperatures after 6 h.

Table 1 Estimations of relative content I_α/I_β in heat treated Scots pine wood samples

Temperatures (°C)	Time (h)	I_α (%)	I_β (%)
Control	–	34	66
120	6	42	58
	10	48	52
150	6	44	56
	10	49	51
180	6	50	50
	10	48	52

Table 2 Estimations of relative content I_α/I_β in heat treated Uludağ fir wood samples

| Temperatures (°C)	Time (h)	I_α (%)	I_β (%)
Control	–	39	61
120	6	45	55
	10	44	56
150	6	42	58
	10	46	54
180	6	48	52
	10	49	51

Fengel and Wegener (1989) reported an increase of crystallinity in thermally treated cellulose up to temperatures of 120–160°C followed by a decrease. The temperature at which the maximum value was reached depended on the water content of the cellulose sample. The thermal degradation of cellulose is not restricted to the cleavage of molecular chains, but there are additional dehydration and oxidation reactions. Chain cleavage and dehydration follow a zero-order reaction whereas oxidation is a first-order reaction. Heating in air causes oxidation of the hydroxyl groups resulting in an increase of carbonyl and subsequently of carboxyl groups.

Peak shoulder at 1,635 cm^{-1} (adsorbed water) for Scots pine wood and Uludağ fir wood samples decreased by rising heating temperature and time, as can be seen in Figs. 3 and 4. Band at 1,635 cm^{-1} came closer to band at 1,740 cm^{-1} (C = O valance vibration of COOH group) for both Scots pine and Uludağ fir wood samples with heat treatment.

When the band at 1,426 cm^{-1} (CH$_2$ bending for cellulose) for Scots pine wood samples moved up with heat treatment according to control wood samples (Fig. 3), these spectra for Uludağ fir wood sample decreased (Fig. 4). Peak shoulder at 1,510 cm^{-1} (C = C stretching aromatic ring for lignin) for Scots pine and Uludağ fir wood samples was not changed by heat treatment, evidently. The band at 1,163 cm^{-1} (asym. bridge C–O–C stretching for cellulose) increased in Scots pine wood samples with heat treatment according to control wood sample, but this increase was not clear for Uludağ fir wood samples. The band at 1,163 cm^{-1} for Uludağ fir wood sample moved up clearly at 150°C (Fig. 4).

Though lignin is seen to be the thermally most stable component of wood, various changes were observed even at temperatures below 200°C. The determination of the lignin content in thermally treated woods gave evidence of an increase in nonhydrolyzable residue with increasing temperature up to 200°C. Regarding the degree and shape of fiber swelling as criteria of thermally caused changes, researchers found no change in lignin up to 155°C. Heating at 175°C caused a lignin condensation which increased with heating temperature up to 240°C (Fengel and Wegener 1989).

Yıldız and Gümüşkaya (2007) reported that the crystalline index for cellulose in spruce and beech wood samples increased with thermal modification. Yet, crystalline index (A_{1370}/A_{670}) for cellulose in beech wood samples
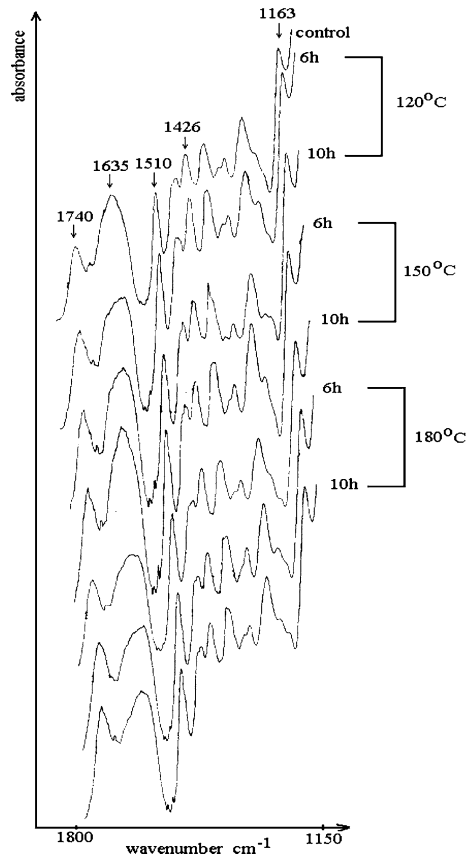
Fig. 3 FT-IR spectra of heat-treated Scots pine wood samples

decreased to remain from 6 to 10 h at 200°C. They found that crystalline structure of cellulose in spruce wood samples was more affected by thermal modification than in beech wood samples.

Conclusion

It was concluded that crystallinity of Scots pine (*Pinus sylvestris* L.) and Uludağ fir *(Abies nordmanniana S*tev. subsp. *bornmuelleriana* Mattf.) wood samples increased during heat treatment at 120, 150, and 180°C for 6 and 10 h. It was determined that changes in crystallinity related to not only heating temperature but also to time. Monoclinic structure ratio in crystalline unit cell converted triclinic structure with heat treatment, but monoclinic structure was dominant in crystalline unit cell. It was designated that crystalline structure of Scots pine wood samples was more affected by heat treatment than Uludağ fir wood samples.
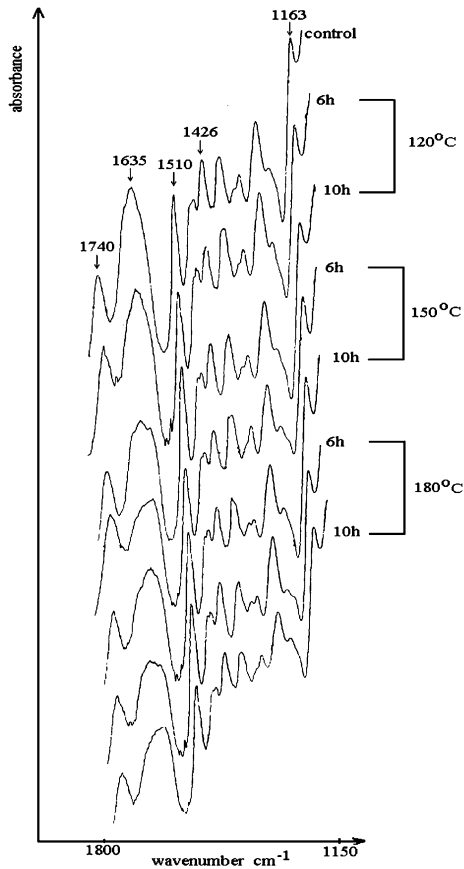
Fig. 4 FT-IR spectra of heat-treated Uludağ fir wood samples

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