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Relations between chemical changes and mechanical properties of thermally treated wood

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Abstract

Thermal treatments of wood (*Fagus sylvatica* and *Fraxinus excelsior*) were examined. The temperature load on wood causes characteristic changes in the chemical composition, which were determined by means of several defined methods. The results confirm that in addition to the degradation of polyoses lignin, known as the thermally most stable compound, also shows significant thermal alterations. In addition, mechanical properties of the specimens were examined in order to correlate these results with the effects of chemical changes of thermally treated wood. It was shown, e.g., that the decomposition of the polyoses can affect the strength properties both positively and negatively.

Keywords: ash; beech; chemical analyses; FTIR; NIR; physical and mechanical properties; thermal treatment.

Introduction

Thermal wood modification has become a topic of great interest since the first heat-treatment plant was built in Finland in the early 1990s. During the past few years more and more producers have joined the thermally modified timber (TMT) community and the production volume of thermally modified wood in Europe increased from approximately 100 m^3 in 1995 to approximately 130.800 m^3 in 2007 (Scheiding 2008). An important consequence of the increasing production is that in November last year the European Committee for Standardization (CEN) drew up the first technical specification (TS) on thermally treated wood (CEN/TS 2007: 15679).

The challenges for the production of thermally treated wood are (1) the increasing demand for outdoor applications of wood, (2) requirements for the substitution of tropical wood species, (3) alternatives for chemically preserved wood, as well as (4) the improvement of important application properties (e.g., desired effects on properties are higher durability, higher dimensional stability, reduced hygroscopicity, and different, especially darker, colors). Because no chemicals are involved, thermal treatment can be seen as a contribution to environmental protection, even though an energy input is necessary for the production of thermally treated wood (Hill 2006). Typical applications are, e.g., garden furniture, deckings for balconies, terraces or swimming pool borders, as well as spa areas.

There are different types of thermal modifications and therefore the results of previously published chemical investigations (e.g., Kacik et al. 1992; Tjeerdsma et al. 1998; Wienhaus 1999; Zaman et al. 2000; Kamdem et al. 2002; Nuopponen et al. 2004; Hill 2006; Boonstra et al. 2007; Boonstra 2008; Esteves et al. 2008 and literature cited therein) are not comparable in each case, because the changes and their extent are due to the special treatment conditions, such as temperature and atmosphere during the treatment or duration of the treatment. Moreover, chemical behavior of the specimens themselves is an important factor for the different reactions caused by the treatment. In general, however, it is well known that chemical changes are caused by autocatalytic reactions and that changes starting with hydrolysis of polyoses mainly depend on the applied temperature. Afterwards, cellulose and lignin are affected by the treatment as reported in numerous papers (e.g., Fengel and Wegener 2003; Fuchs 2006; Hill 2006; Windeisen et al. 2006, 2007; Esteves et al. 2008 and literature cited therein). Due to the various chemical nature of wood species, it is nevertheless difficult to make prevailing predictions of the treatment results in detail.

In combination with the chemical changes, other properties, such as color, hygroscopicity, dimensional stability, strength properties, and natural durability of thermally treated wood, become modified from those of untreated wood. Depending on the duration and the strength of the process, thermally treated wood shows improved rot-resistance properties and also demonstrates increased resistance to both fungi and climatic influences (Kamdem et al. 2002; Boonstra et al. 2007). To warrant the natural durability, it must be ensured, however, that the samples have no contact to the ground (Hofer et al. 2007). Furthermore, its dimensional stability and creep behavior can be improved (Tjeerdsma et al. 1998; Boonstra et al. 2006; Epmeier et al. 2007), as well as its adhesion property against hydrophobic materials (Follrich et al. 2006). Moreover, darker tints, which are normally characteristic for tropical wood species only, can be achieved (Ayadi et al. 2003; Schnabel et al. 2007).

Although considerable knowledge on thermally treated wood is available in the literature, there are still several

deficits. First of all, varying properties due to the multiplicity of different thermally modified assortments can be found. Although the first standard exists (CEN/TS 2007: 15679), missing standardization and quality control for market products sometimes lead to a lack of confidence of potential customers. Furthermore, there is still a lack of knowledge about the mechanisms of modification and application restrictions due to varying strength properties.

The aim of this work was to investigate and compare mechanical properties and basic chemical changes in beech and ash wood during industrial thermal modification. In addition, NIR spectroscopy is tested as a method for quality assurance.

Experimental

Wood samples ($20\times20\times360$ mm^3) were obtained after thermal treatment at different temperatures (180–220°C) for 4–6 h under oxygen exclusion by wood gas evolved in an industrial process. To determine the changes, the heat-treated specimens (Beech: B-180, B-200, B-220; Ash: A-180, A-200, A-220) were analyzed and compared to untreated reference samples.

Physical and mechanical properties

Determination of physical and mechanical properties were carried out according to several standards: equilibrium moisture content DIN 52 183, bending strength: modulus of elasticity (MOE) and modulus of rupture (MOR) DIN 52 186. Determination of compression strength was adapted from DIN 52 192.

Wet-chemical analyses

Prior to chemical analyses, the samples were cut into small pieces and then ground with a mill (particle size <0.75 mm) under cooling conditions by adding solid CO_2. The analysis of polysaccharides after hydrolysis with trifluoroacetic acid (TFA) according to Fengel and Wegener (1979) at different temperatures and different concentrations of TFA was carried out by means of ion-exchange chromatography. A gravimetric method for the determination of lignin was carried out according to the Runkel method with H_2SO_4/HBr (Runkel and Wilke 1951). Lignin analysis by means of thioacidolysis was carried out according to Lapierre et al. (1986) and Rolando (1992). Treatment of the samples with boron trifluoroetherate and ethanethiol leads to the depolymerization of lignin. The detection of the cleaved lignin units is limited to monomeric compounds, owing to the subsequent determination of the TMS derivatives by means of GC and/or GC/MS. In the diagram in Figure 2, only the clearly identified main products of G-lignin and S-lignin were evaluated. The determination of acetyl groups was carried out according to Månsson and Samuelsson (1981) by means of an aminolysis with pyrrolidine and subsequent GC analysis. Determination of phenolic hydroxyl groups was performed after acetylation and again by means of an aminolysis with pyrrolidine and subsequent GC analysis. This method has been developed by Månsson (1983) to determine the OH content of several lignins.

In general, by using standard methods it is possible to describe principal changes, keeping in mind that the applied methods may not yield absolute information on the chemical changes.

FTIR spectroscopy

Samples were embedded in KBr pellets (1 mg/300 mg). The FTIR analyses were carried out on an FTS-40 (Biorad) with a resolution of 4 cm^{-1} (16 scans). The spectra are baseline corrected and normalized at the band at 1505 cm^{-1}.

NIR spectroscopy

NIR spectra were obtained by a Bruker MPA spectrophotometer equipped with an integrating sphere using a resolution of 8 cm^{-1} (32 scans). Ten single spectra per sample were averaged. Mean normalization and second derivative mode (Savitzky-Golay, 15 points) were performed.

Results and discussion

Chemical analyses

As expected, chemical analyses showed that during thermal treatment different reactions in beech and ash occur due to the respective composition of the two wood species.

A first impression of the thermal induced changes is given in Figure 1 with the decrease of xylan and other polyoses (hemicelluloses) after thermal treatment. Glucan content is hardly affected.

Noticeable differences can also be seen in the modification of the lignin. The changes of lignin after thermal treatments were determined by means of acid insoluble portion of wood (according to the Runkel method) and thioacidolysis (Figure 2). The latter method shows the decrease of monomeric degradation products, which is due to the reduction of structural units linked by arylglycerol-β-ether bonds. Initially, the determination of the so-called Runkel lignin only means that this portion of the wood is acid insoluble or can be condensed with acid and is not already present in condensed form. Nevertheless, it can be assumed that lignin units have already cross-linked among themselves or, if possible, with degradation products of the polyoses (e.g., furans) and, as a consequence, these products are no more detectable by means of GC or thioacidolysis.

The presented results confirm that already a temperature load of 200°C causes strong alterations in the lignin structure of the investigated hardwood species ash and beech. The stronger effects of the thermal treatment on ash wood are also demonstrated by a significant increase in free phenolic groups (Figure 3). As a consequence of the decomposition of polysaccharides, demonstrated in Figure 1, a decrease of acetyl groups after thermal treatment takes place (Figure 3). The lower pH value of

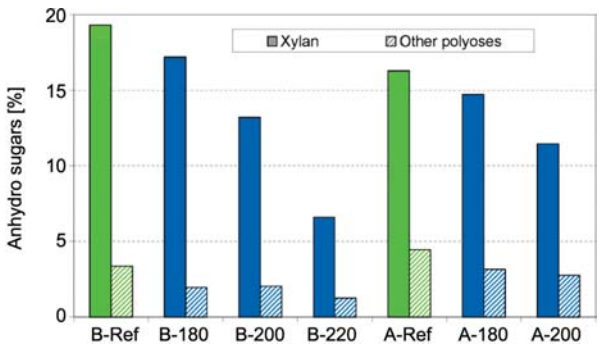

Figure 1 Sugar content (xylan and other polyoses calculated as anhydro sugars) before and after thermal treatment.

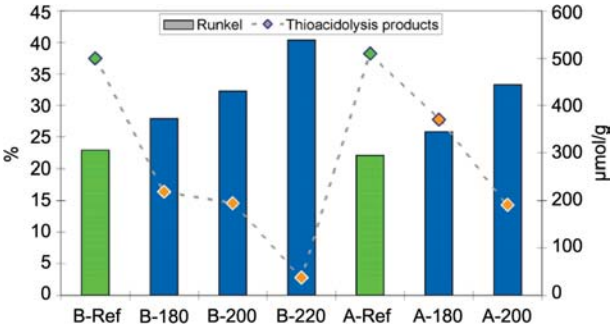

Figure 2 Determination of lignin content by means of different methods before and after thermal treatment.

approximately 4 of the thermally treated samples is also an indication for the occurrence of acetic acid (Hill 2006).

The loss of acetyl groups is obvious from Figure 4, which shows the FTIR spectra of thermally treated ash wood samples demonstrating that a noticeable decrease of the C-O band at 1245 cm^{-1} occurs, which is characteristic for acetyl groups in hardwoods. The corresponding carbonyl absorption at approximately 1730 cm^{-1} is not diminished to the same extent, but this might be due to the generation of new carbonylic groups. This is consistent with the results of Kotilainen et al. (2000) who found an increase of this absorption band for spruce and Scots pine, and with the results of Schwanninger et al. (2003) for beech, and of Tjeerdsma and Militz (2005) for beech and Scots pine. Additionally, all peaks concerning C-O and C-H absorptions decrease due to the loss of polyoses in comparison to the lignin absorptions, used for the normalization of the spectra. But the peaks ascribed to the aromatic structures show slight shifts (1600, 1505 cm^{-1}), which again provides evidence for the modification of lignin.

In the NIR spectra, a baseline shift to higher wave numbers with increasing temperature can be observed (Figure 5a). This is due to the darker colors of the samples. Thermal treatment can also be observed in the second derivative mode of the NIR spectra, which is presented in two expanded views (Figure 5b and c). There is a decrease of the band at 5800 cm^{-1}, the first overtone of CH stretching vibrations, which is caused by the degradation of polyoses and/or deacetylation of xylan. This can also be observed by a decrease around 8300 cm^{-1}, the second overtone of CH stretching vibrations (Figure 5a). The increase of the band around 5950 cm^{-1}, the first

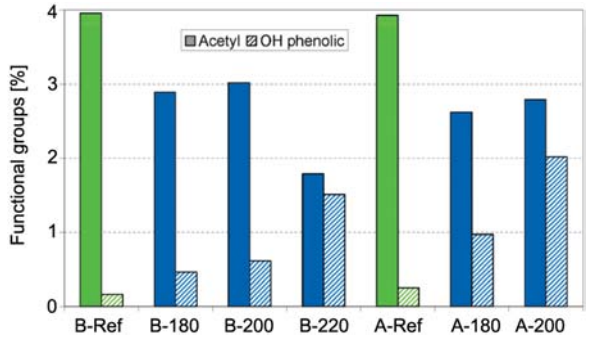

Figure 3 Determination of functional groups before and after thermal treatment.

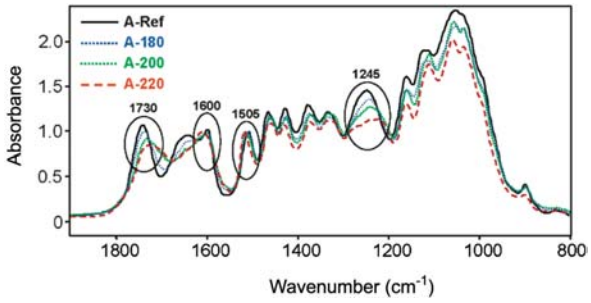

Figure 4 FTIR spectra of ash wood samples before and after thermal treatment.

overtone of aromatic skeletal CH stretching vibrations, may be due to a relative increase and structural variation of lignin. Moreover, there is an increase of the absorption band around 6900 cm^{-1}, which can be assigned to the phenolic hydroxyl groups originating from lignin and to a decrease of the absorption band assigned to the amorphous region in cellulose at 7000 cm^{-1} (Schwanninger et al. 2003; Inagaki et al. 2008; Mitsui et al. 2008).

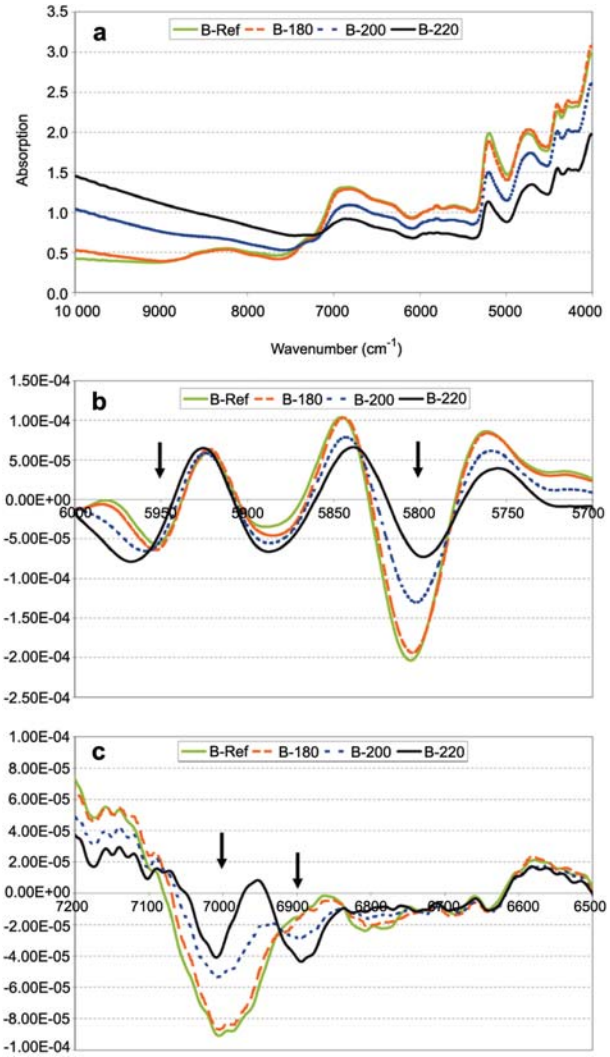

Figure 5 (a) NIR spectra of beech samples before and after thermal treatment. (b) NIR spectra (5700–6000 cm^{-1}) of beech samples before and after thermal treatment. (c) NIR spectra (6500–7200 cm^{-1}) of beech samples before and after thermal treatment.

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Physical and mechanical properties

The mass loss (Figure 6) and the decrease of the equilibrium moisture content (Figure 7) are caused predominantly by the degradation of the polyoses. However, the extent of the mass losses does not correspond in all cases to the results of the analyses of neutral sugars (Figure 1), e.g., the mass loss of B-220 is not as high as the reduction of detectable xylan would let assume and otherwise the mass loss of A-200 is higher than expected. This again provides evidence that changes during thermal treatment, especially of the polyoses, are strongly dependent on the wood species, and furthermore that the polyoses are not just decomposed but can be partially converted to other substances, mainly furan derivatives (Fengel and Wegener 2003). The reduced hygroscopicity is important for applications in wet areas.

It can be seen in Figure 8a that heat treatment results in the case of beech wood in an increase in MOE up to 200°C, which remains constant at above 200°C, while ash wood already shows a slight reduction at 200°C. This is in accordance to earlier investigations, e.g., Rusche (1973), who had already found that the decrease in MOE only became significant when the mass loss exceeds 8%. It was assumed that the change in the MOE is related to the formation of new chemical bonds with a higher binding energy than the cleaved hydrogen bonds as well as to the rapprochement of cellulose chains, which is, however, only possible up to a certain level, where no further increase of MOE can be observed. This leads to a decrease in equilibrium moisture content (EMC) due to the reduction of hydrogen bonding and a decrease in free accessible hydroxyl groups. The moisture content is known to affect the strength properties of wood and lower EMC of the treated beech samples could jointly be responsible for the increase of MOE up to 200°C. Boonstra (2008) also found an increase in MOE in the case of pine and spruce wood and a two-stage thermal treatment at 195°C, whereas Johansson (2008) found a slight MOE loss for birch, pine, and spruce wood at 200°C.

Unlike MOE, there is no increase in bending strength (MOR) when wood is thermally treated. The reduction in MOR increases with the severity of thermal treatment (Figure 8b). Again, ash wood is more strongly affected at 200°C in comparison to beech wood. Due to the fact that the MOR is the equivalent stress in fibers at the point of failure, it is related to the ultimate bending strength of the wood. The reduction of MOR or the bending strength is

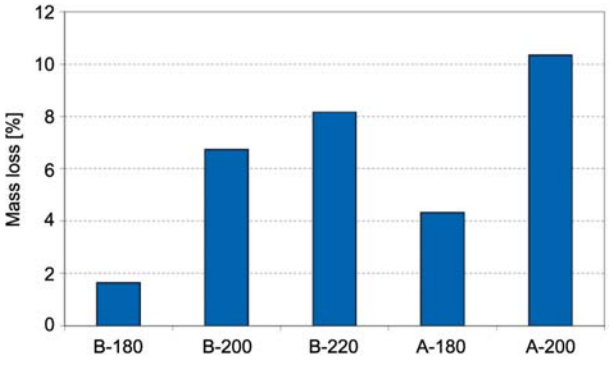

Figure 6 Mass loss after thermal treatment.

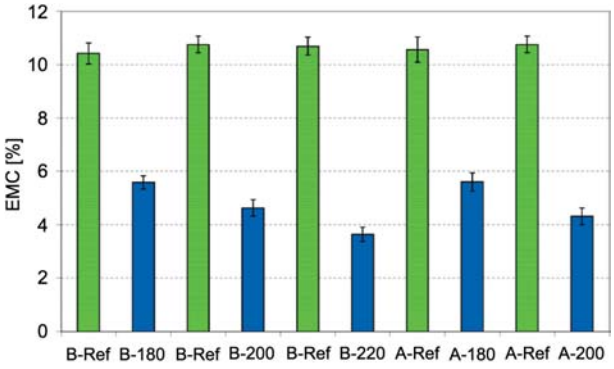

Figure 7 Equilibrium moisture content (EMC; 20/65) before and after thermal treatment.

one of the limiting facts of thermally treated wood for the utilization as building material.

Along with the loss of bending strength (MOR), there is an accompanying loss of xylan and other polysaccharides (Figure 1), which is consistent with the results by Winandy and Rowell (2005). The greatest loss is in xylose content, which may be the causative effect leading to strength loss. The slight rise of the compression strength values (Figure 9) may be explained by the relative increase and the condensation of lignin.

Conclusions

The presented results show that the structural changes and decomposition of both polyoses and lignin affect the physical and mechanical properties. It is obvious that the effects are specific for the different wood species invest-

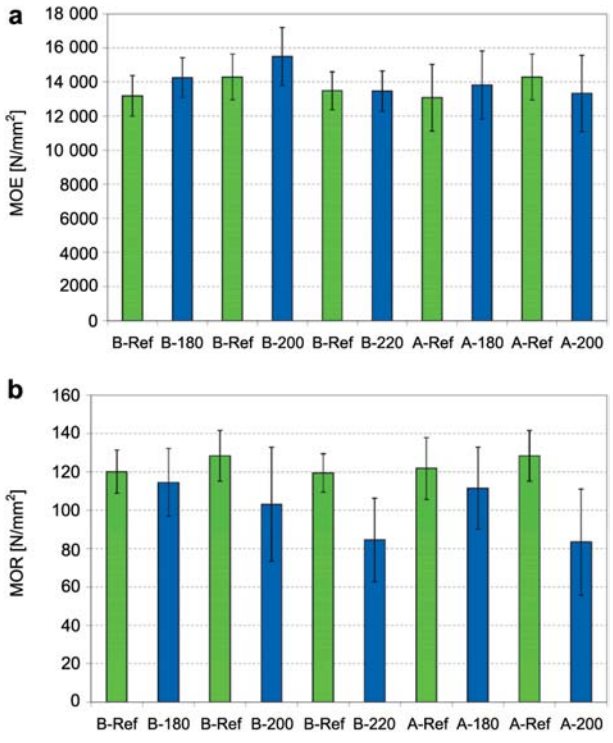

Figure 8 (a) Modulus of elasticity (MOE) before and after thermal treatment. (b) Modulus of rupture (MOR) before and after thermal treatment.

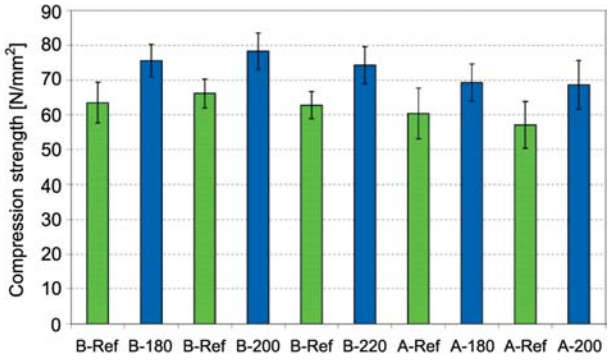

Figure 9 Compression strength before and after thermal treatment.

igated. Reduction of hygroscopicity (EMC) leads to mass loss. The decisive change already occurs at 180°C. Above 180°C, the reduction is more moderate. The decrease of EMC can be moderately correlated with the degradation of polyoses. The correlation between the decrease of xylan and the mass loss is obvious first, but the relation becomes weaker at higher temperatures. This implicates that the mechanisms which occur at higher temperatures cannot be explained by chemical routine analyses only. A loss of xylan leads to reduction of bending strength (MOR). The loss of xylan may be the causative effect leading to strength loss. The lignin content can also be associated with mass loss, but in contrast to the polyoses in the opposite direction. Therefore, there is an increase in the acid insoluble portion, meaning condensed structures in the Runkel lignin, accompanied with mass loss. A loss of alkyl aryl ether linkages in lignin but eventually also the cleavage of lignin-carbohydrate-complexes leads to reduction of bending strength (MOR). A further correlation is that the decrease in MOE only becomes significant when the mass loss exceeds 8%. The slight increase of the compression strength values may be explained alongside the decrease in EMC by the relative increase and the condensation of lignin. FTIR spectroscopy can be used for characterizing essential variations of functional groups, and NIR spectroscopy for monitoring of hydroxyl groups by means of second derivatives of the spectra. Furthermore, it has potential for quality control measurements.

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