MECHANICAL AND CHEMICAL BEHAVIOR OF BEECH WOOD MODIFIED BY HEAT

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ABSTRACT

In this study the effects of heat treatment on compression strength of beech wood (*Fagus orientalis*) were examined, and changes in the chemical structure of the treated wood were determined by analyzing contents of cellulose, hemicellulose, and lignin.

Heat treatment was applied on the test samples in an oven at four different temperatures (130°C, 150°C, 180°C, and 200°C) and three different durations (2, 6, and 10 h) under atmospheric pressure.

The results indicate that the effects of heat treatment on compression strength values generally exhibited a decrease with increased duration and temperature as expected. In the chemical properties, it was seen that hemicelluloses were the wood-cell components most degraded by the heat treatment.

Keywords: Heat treatment, *Fagus orientalis*, thermal degradation.

INTRODUCTION

Wood is subjected to very different conditions and environments in its wide field of use. In many processing procedures, wood is submitted to high-temperature treatment which usually does not exceed 200°C, since thermal degradation is not intended. However, it is not the temperature alone that causes change in wood substance. Additional factors such as time of treatment, pressure, atmosphere, or other forms of treatments influence thermal degradation. Thus, under certain conditions, changes in wood can be observed, even at 100°C (Kwasniakova et al. 1996).

Heat treatment of timber is used to modify the properties of wood to resist dimensional changes in humidity, to achieve better heat insulation, improved decay and weather resistance, reduced moisture deformation, and new shades of color as an alternative to tropical hardwood. All these changes are achieved with heat-treatment process without any added chemicals. Therefore, heat-treated wood has been considered as an ecological alternative to impregnated wood ma-

terials. It can also be used for several other purposes, e.g. for garden, kitchen, and sauna furniture; floors and ceilings; inner and outer bricks; doors and windows; and also for musical instruments. However, weathering of wood is not avoided in exterior cladding, and joinery use of heat-treated conifer timber and impregnation or painting is suggested (Manninen et al. 2002).

The higher the treatment temperature, the better the wood's biological durability. However, at the same time wood's mechanical properties are more weakened. A negative consequence is that the wood becomes more brittle, and bending and tension strength decrease by 10% to 30%. No changes have been found in compression and impact strength and surface hardness. However, the dry knots become loosened, the use of heat-treated wood in load-bearing constructions is restricted (Jamsa andViitaniemi 2001).

Heat treatment of timber has been studied since the 1920s and the recent industrial-scale heat treatment process of wood was developed in the Technical Research Centre of Finland (VTT) in the early 1990s. Industrial output of heat-treated timber in Finland has been about 40.000 m_/year; but during the next few years, the production of heat-treated timber multiplied because of several newly established companies (Manninen et al. 2002). Recent efforts in thermal treatment of wood lead to the development of several processes introduced to the European market during the last few years. The total production capacity of heat-treated wood in 2001 is estimated as approx. 165.000 m_ (Militz 2002).

In Turkey one of the most common wood species naturally grown and intensively used in the forest product industry is beech (*Fagus orientalis*). This study is the first pioneer research project about the subject and provides a new data base for commercial producers in Turkey using the temperature rise period. The improved characteristics of heat-treated timber of beech wood will potentially offer the timber products industry many interesting opportunities. Certain mechanical properties are reduced by thermal modification but the dimensional stability and the biological durability of wood can be in-creased without adding outside chemicals/biocides to the wood. (Yildiz 2002).

The objectives of this study were to investigate the effects of heat treatment on compression strength and changes in the amount of cellulose, hemicellulose and lignin proportions in heated beech wood.

MATERIAL AND METHODS

Preparation of mechanical test samples

Raw material beech wood (*Fagus orientalis* Lipsky) was obtained from the Black Sea Region in Turkey. Beech wood was cut in parallel to grain directions and sawn into specimens measuring 2 x 2 x 3 (tangential x radial x longitudinal) cm. Specimens were stored in 12 treatment groups, and 20 test and 20 control samples for each group were used.

Application of heat treatment and compression strength

Prior to the test, the dimensions were measured to the nearest 0.001 mm, and their weights were recorded to the nearest 0.01 g. Conditioning to 12% moisture content was done at 21°C and 65% relative humidity. Heat treatment was then applied on the test samples in an oven with ±1°C sensitivity, at four different temperatures (130°C, 150°C, 180°C, and 200°C) and three different durations (2, 6, and 10 h) under atmospheric pressure and in presence of air. The compression strength parallel to grain values for control samples (untreated) and test samples, both conditioned to 12% equilibrium moisture content, were recorded at Universal Test Machine according to the Standard Methods of Testing Small Clear Specimens of Timber (ASTM D 143, 1988).

Percentage of compression strength (CS) parallel to grain was calculated from the following formula;

$$CS = \frac{P}{a \times b} \text{ (kp/cm\_);} \qquad (1)$$

where P is the force applied on wood specimen (kp); a is the width of the sample (cm); and b is

TABLE 1. *Heat treatment conditions and the results of compression strength for heat-treated and untreated (control) samples.*

Conditions		Test			Control		
Temperature (°C)	Duration (h)	Average CS kg/cm_	SD*	Homogeneity groups**	Average CS kg/cm_	SD*	Homogeneity groups**
130	2	559.20	29.72	A	560.99	21.41	A
	6	558.95	29.77	B	554.65	33.87	B
	10	582.35	37.22	C	604.98	43.25	C
150	2	658.23	41.42	D	676.36	37.97	D
	6	631.06	34.99	E	656.30	43.99	E
	10	537.05	37.89	F	565.37	43.08	F
180	2	569.47	39.29	G	602.98	43.51	G
	6	549.95	40.66	H	593.70	43.70	H
	10	533.78	38.13	I	576.67	36.42	I
200	2	522.83	37.24	J	596.89	19.51	X
	6	350.97	39.85	K	576.17	28.21	M
	10	364.08	37.45	L	572.67	18.14	T

* Standard Deviation
** Means with the same letter are not significantly different at $p < 0.05$. Comparisons were done between the each control and its test.

the height of the sample (cm). The results are given in Table 1.

Preparation of chemical test samples and application of experiments

Before the chemical analyses, heat-treated and untreated (control) wood samples were chopped to a length of 1–2 cm and ground in a Wiley mill to a homogeneous meal. Holocellulose analysis was done according to Wises's sodium chlorite method, cellulose was determined by Kurschner-Hoffner's nitric acid method, and lignin content was determined as acid-insoluble Klason lignin. Hemicellulose content was found by subtracting cellulose content from holocellulose content.

RESULTS AND DISCUSSION

Table 1 shows the effect of heating in different temperatures and durations on CS as compared to control groups. The rates of CS loss are shown in Fig. 1.

The data were statistically evaluated by one-way ANOVA to demonstrate the effect of heat-treated and untreated wood samples on CS. Differences between test and control groups were not statistically significant at 0.05 level.

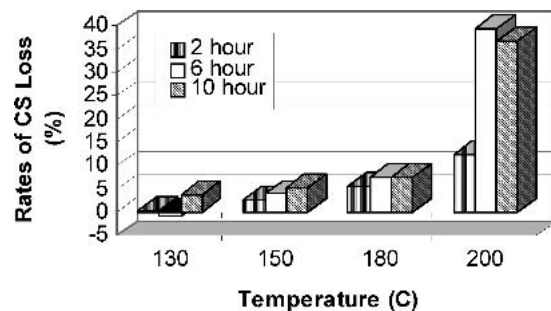As can be seen from Table 1, when heated at

FIG. 1. The rates of CS loss

130°C for 6 h, the CS value was found a little bit higher on heat-treated wood than on unheated wood. At the same temperature for 2 and 10 h, the CS decreased compared to the control group. The rate of CS loss for 10 h was 3.74% (Fig. 1).

Heating at 150°C and 180°C for 2, 6, and 10 h, the diminutions in CS were extended with increasing temperature and duration of heating. The rates of CS loss at 150°C, for 2, 6, and 10 h, were 2.68%, 3.85%, and 5.00%. The rates of CS loss at 180°C, for 2, 6, and 10 h were 5.55%, 7.37%, and 7.44% respectively (Fig 1).

The lowest CS values were obtained from the variation at 200°C for 6 h–10 h (350.97–364.08 kp/cm_). The CS losses at 200°C for 6 h and 10 h were 39.09% and 36.42%, respectively (Fig. 1).

The diminutions in the strength properties are related to the rate of thermal degradation and

losses of substance after heat treatments (Rusche 1973). The decrease in strength mainly is due to the depolymerization reactions of wood polymers, as a notable loss of carbohydrates does not occur at temperatures below 100°C. At temperatures above 100°C the inter-molecular and intra-molecular chemical bonds begin to break. The rate at which the bonds are broken intensifies as the temperature increases. Between 100°C and 200°C, noncombustible products, such as carbon dioxide and water vapor, and also traces of organic compounds, are produced. Above 200°C, the cellulose starts to break down, producing tars and flammable volatiles (Kotilainen 2000). As can be seen from the chemical analysis, the primary reason for the CS loss is the degradation of hemicelluloses, which are less stable to heat than cellulose and lignin. Heat in the presence of air also tends to promote degradation reactions, because the rate of thermal degradation is also dependent on the surrounding atmosphere, especially in regard to the presence or absence of oxygen (Mitchell 1988). Stamm (1956) demonstrated that the thermal degradation of wood heated in the presence of oxygen is more rapid than that of wood heated in an oxygen-free atmosphere. Rosa and Fortes reported (1988a) on the effects of heating cork in air at temperatures in the range of 100–300°C. According to them, compression strength is diminished, the decrease being more pronounced for compression in non-

radial directions. This change becomes more pronounced with increasing temperature/time, but is virtually accomplished (for specimens of moderate dimensions) in the first 15 min of heating. Similar results were observed following heating in a vacuum.

The results of the cellulose, hemicellulose and lignin content determination are shown in Table 2. The cellulose contents of heat-treated wood samples were similar as compared to each other almost in all variations or to untreated wood. A linear correlation between increasing temperature and duration of heating and cellulose content changing between 53% and 56% was not observed. Analysis of variance (ANOVA) showed that there was not a statistically significant difference (P≤0.05) between the test and control group relating to content of cellulose. Therefore, it can be concluded that the effects of temperature and duration were not a cause of degradation of cellulose; furthermore, it improved the cellulose content in some variations compared to the control sample. According to the researchers; crystalline structure of cellulose is not changed (Kotilainen 2000; Runkel and Wilke 1951) but can even improve up to a certain temperature, which may be as high as 200°C, depending on the conditions involved. The crystallinity of the alkali-resistant cellulose from thermally treated spruce wood increased up to a temperature of 200°C because of a degra-

TABLE 2. *Heat treatment conditions and the chemical composition of heat-treated and untreated samples.*

Temperature (°C)	Duration (hour)	Cellulose (average %)		Hemicellulose (average %)	Lignin (Average %)	
		X	SD*	X	X	SD*
130	2	56.13	0.36	22.56	21.29	0.00
	6	55.45	0.26	23.24	21.56	0.27
	10	53.76	0.45	24.67	21.73	0.19
150	2	55.85	0.94	23.87	20.57	0.07
	6	56.65	0.14	22.69	20.69	0.43
	10	53.97	0.71	25.00	21.28	0.50
180	2	53.54	0.21	25.90	20.16	0.12
	6	53.34	0.80	14.57	20.79	0.73
	10	54.40	0.29	6.51	33.44	0.00
200	2	55.17	0.15	4.24	36.92	1.10
	6	54.40	0.00	2.38	40.13	0.00
	10	53.67	0.00	1.71	42.02	0.15
Control		54.19	1.09	24.66	22.25	0.00

* Standard Deviation

dation of the less ordered molecules. The annealing of stretched rayon fibers at 200°C initiates a growing of the cellulose crystallites and an increase in the degree of crystallinity (Fengel 1967). According to the thermogravimetric analysis, the first change observed in the heating of cellulose, which occurs at about 100°C, is the elimination of adsorbed water (Kotilainen 2000). By raising the temperature above 200°C, the thermal degradation of cellulose and formation of volatile products proceed rapidly. Levoglucosan is frequently said to be the most important primary degradation product, but other anhydroglucoses, furan, and furan derivates are also produced (Manninen et.al. 2002; Fengel and Wegener 1989).

With heating at 130°C, hemicellulose values showed an increase with increasing exposure duration, and at 150°C exhibited an unstable configuration. Until the variation of 180°C for 6 h, the hemicellulose values were similar as compared to each other or to the control sample. Reduction in the contents of hemicelulose started at temperatures and durations above 180°C for 2 h. The lowest hemicellulose contents were found to be 2.38% and 1.71% for the variations at 200°C for 6 h and 200°C for 10 h, respectively.

Because of the structural heterogeneity of hemicelluloses, it is a complex matter to reveal their thermal behavior. Xylan (pentosan) is the most reactive wood hemicellulose, and in general pentosans are very sensitive to degradation and dehydration reactions (Kotilainen 2000; Mannien et.al. 2002). The most intensive thermal degradation takes place in the temperature range 200-260°C. The lower thermal stability of hemicelluloses compared to cellulose is usually explained by the lack of crystallinity. In addition, more gaseous products and less charred residue are formed in the pyrolysis of hemicelluloses than that of cellulose (Kotilainen 2000).

Until the variation at 180°C for 10 h, a linear correlation between increasing temperature and duration of heating and lignin content changing between 20%–21% was not observed. Evaluated by analysis of variance (ANOVA), the lignin values revealed few significant differences at the 5% significance level. Therefore, it can be concluded that lignin values increased with an increase in treatment temperature and duration. Increase in the contents of lignin started at temperatures and durations above 180°C for 10 h. The highest lignin contents were obtained from the variations at 200°C for 6 h (40%) and 200°C for 10 h (42%). This result confirmed most of the conclusions reported in the literature (Kotilainen 2000; Fengel and Wegener 1989; Kollmann and Fengel 1965; Runkel and Wilke 1951). Kotilainen (2000) reported that as general trend, the relative mass proportion of lignin increased with both elevated temperature and extended treatment time, with a simultaneous decrease in the mass proportion of carbohydrates. On the other hand, some of the thermal degradation products of carbohydrates may be retained in the lignin fraction in Klason lignin determination.

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 (*Picea abies, Pinus sylvestris, Quercus robur*) gave evidence of an increase in non-hydrolyzable residue with increasing temperatures up to 200°C. The yield of ethanolysis products of spruce wood increased also, whereas the methoxyl content decreased after heating the wood at temperatures of 180°C and 200°C for 24 h. It should be pointed out that during pyrolysis, lignin and carbohydrates (polysaccharides) are gradually converted into volatiles and "extractives-like material," which in turn are partly degraded together with the original extractives, into various volatile products. In addition, the heating of carbohydrates probably led to some extent to the formation of unsaturated nonvolatile material (i.e., UV-detectable "lignin-like material") (Kotilainen 2000).

Avni et al. (1985) have reported a model for lignin thermal degradation. Relatively weak aliphatic bonds break down, and hydrocarbon fragments are released. As secondary reactions, hydrocarbon fractions are degraded further, and repolymerization occurs. Simultaneously, some of the functional groups are cleaved and gaseous

low-molecular mass products are evolved. Carboxylic groups from carbon dioxide, carbonyl groups carbon monoxide, hydroxyl groups water, methoxyl groups methanol, and aliphatic precursors light hydrocarbons.

CONCLUSIONS

The results of this study indicated that the compression strength values of beech wood were decreased with increasing the exposure durations and temperatures. The decrease in compression strength was correlated to the changes in chemical structure of wood components. Hemicelluloses was the most degraded wood-cell component during the treatment. This was determined through darkening of the wood samples dependent on heating temperature and duration of treatment. The color change in heat-treated wood samples observed was a consequence of the formation of degradation products containing different chromophoric moieties (Kotilainen 2000). The darkening of wood by heat treatment can be evaluated as an advantage in view of the decorative texture. It is also possible to control the degree to which the process changes the wood's natural color.

By this thermal modification, some mechanical properties of wood are reduced, but the most important property of heat-treated wood compared to untreated wood is that reducing the equilibrium moisture content of the treated wood and the consequenct shrinkage and swelling of the wood is also reduced without using any water repellents (Yıldız 2002). Therefore, heat-treated wood material is very suitable for coating applications. The best way of utilizing heat-treated timber is to make use of these improved properties. Wood species having no commercial value as such can be heat- treated and in this way a new use may be found for these species.

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