EFFECTS OF HEAT TREATMENT ON CALABRIAN PINE (*PINUS BRUTIA* TEN.) WOOD

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In this study, the effects of heat treatment on some physical, mechanical, chemical properties, and cellulose crystallinity of calabrian pine (*Pinus brutia* Ten.) were evaluated. Wood specimens were treated with heat under atmospheric pressure at three different temperatures (130, 180, and 230 ^{o}C) and two different time levels (2 and 8 h). Air-dry density (D_m), oven-dry density (D_0), shrinkage (β), swelling (α), fiber saturation point (FSP), compression strength parallel to grain ($\sigma_{c//}$), bending strength (σ_b), modulus of elasticity (MOE) in bending, equilibrium moisture content (EMC), holocellulose, and alcohol solubility were decreased, whereas 1% NaOH solubility and lignin content were increased, depending on the heating temperature and time. Cellulose crystallinity of the samples was not changed significantly. 130 ^{o}C showed a minimal effect; on the other hand, 230 ^{o}C showed a maximum effect on all properties of the treated wood. That's why, for the heat treatment process, 130 ^{o}C for 2 h should be applied in situations where mechanical properties such as modulus of elasticity, compression strength, bending strength, and hardness are important. However, 230 ^{o}C for 2 h should be used in situations where it is preferred to obtain favorable physical properties, such as density, shrinkage, swelling, and moisture content.

Key words: Calabrian pine; Heat treatment; Physical; Mechanical; Chemical properties; FT-IR; Crystallinity

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INTRODUCTION

Wood has been used for many applications because of its many excellent characteristics (such as a good strength to weight ratio, aesthetic appearance, etc.). However, wood also suffers a number of disadvantages, because wood is a hygroscopic material. Many studies have been done in order to ameliorate the disadvantageous properties of wood (Boonstra et al. 1998; Bekhta and Niemz 2003; Gündüz et al. 2008; Korkut and Guller 2008). The methods brought out based on the results of these studies are commonly called "wood modification methods" "Heat treatment" is a wood modification method, too (Hill 2006).

Heat treatment changes some physical, mechanical, and chemical properties of wood, i.e. dimensional stability, EMC, color of wood, bending strength, compression strength, hardness, amount of wood polymers, biological durability, etc. (Mazela et al. 2004; Yıldız et al. 2006; Gündüz et al. 2008). In this process, hemicelluloses start to decompose, lignin softens, and cellulose and hydrophilic groups become modified (Bekhta and Niemz 2003). As a result, treated wood with high temperatures loses its capacity to reabsorb water, contrary to hydrophilic behavior of the conventionally dried wood (Kocaefe et al. 2007). All these changes are achieved by heat-treatment process without any added chemicals. Thus, heat-treated wood has been considered as an ecological alternative material to impregnated wood (Kamdem et al. 2000; Gündüz et al. 2008). The mechanical properties of wood strongly depend on moisture content, increasing with decreasing moisture content below the fiber saturation point. Since heat-treated wood is less hygroscopic than untreated wood, its mechanical properties in service conditions may even be higher than at constant moisture content (Borrega and Karenlampi 2008).

Studies on the effects of heat treatment on properties of Turkish native trees are rather limited. The aim of this study was to determine the effect of heat treatment on some physical, mechanical, and chemical properties in calabrian pine (*Pinus brutia* Ten.) wood, which is the most common naturally grown wood species in Turkey.

EXPERIMENTAL

Material

The calabrian pine (*Pinus brutia* Ten.) trees were randomly selected with a breast height diameter (DBH) of 30–40 cm, average tree ages in the range 40-45, and obtained from forestlands of the Muğla province, Turkey. The lumbers were cut in parallel to grain directions from the five logs' heartwood sections according to Turkish Standard (TS), TS 4176. For each experiment, 10 samples were prepared. Afterwards, lumber samples were air-dried until they reached approximately 12% moisture content. The average air-dried density of the samples was 0.53 g cm^{-3}.

Preparation of Samples for Physical and Mechanical Tests

Clear specimens of calabrian pine lumber were planed and then chopped up for determination of air-dry density (D_m), oven-dry density (D_0), moisture content (MC), equilibrium moisture content (EMC) (20×20×30 mm), shrinkage (β), swelling (α) (30×30×15 mm), compression strength to parallel grain ($\sigma_{c//}$) (20×20×30 mm), bending strength (σ_b), modulus of elasticity (MOE) in bending (20×20×320 mm), and Brinnel-hardness (H_B) (50×50×50 mm) according to TS 2470. All the experiments were conducted according to Turkish Standards to determine density (TS 2472), MC, EMC (TS 2471), β (TS 4083), α (TS 4084), $\sigma_{c//}$ (TS 2595), σ_b (TS 2474), MOE (TS 2478), and H_B (TS 2479). The fiber saturation point (FSP) was calculated by using the following equation:

$$\text{FSP} = \text{Volumetric shrinkage } (\beta_v) / \text{Basic density } (D_b)\ (\%) \qquad (1)$$

Heat Treatment

The temperature of the oven was increased to the temperature at which the actual heat treatment occurs. This heating period was taken as 1 h for all trials. An excessive amount of splitting and color differences may occur if the moisture content of the material is too high (MC>10%) before heat treatment (Syrjanen 2001). Therefore, specimens were conditioned to 7% moisture content at 25±2 °C and 35±5 % relative humidity to minimize such defects.

Heat treatment applications were conducted in a temperature-controlled small heating unit. Three different temperatures (130, 180, and 230 °C) and two different durations (2 and 8 h) were applied to specimens under atmospheric pressure. Because entrance of fresh air was prevented after starting the process, wood samples were subjected to heat treatment without oxygen to realize the pyrolyses. After treatment, the temperature was decreased to room temperature, a process that takes about 24 hours. The same procedure was conducted for all experiments. After heat treatment, the moisture contents of samples were measured.

Preparation of Test Samples for Chemical Analyses

Before the chemical analyses heat-treated and untreated (control) wood samples were cut to a length of 1–2 cm and ground in a Wiley mill to a homogeneous meal. Wood powder was sieved and used between 40 and 60 mesh. To remove low molecule weight carbohydrates, degraded celluloses and polyoses, 1% NaOH solution was applied to control and treated wood samples according to TAPPI T-212 om-88. Alcohol syclohegzane solubility (TAPPI T 204 om-88) was applied to extract oils, waxes, resins, non-volatile compounds, low molecule weight carbohydrates, salts, and other dissolvable compounds. Additional alcohol solution (TAPPI T 204 om-88) was applied to remove some other extractives such as tannins, pigments, and stilbenes. Holocellulose analysis was carried out according to Wises's sodium chlorite method (Wise et al. 1946). Lignin content was determined as acid-insoluble Klason lignin by the Runkel method (Runkel and Wilke 1951) using 72% sulfuric acid and 40% hydrobromic acid. In this procedure lignin is left as an insoluble residue and recovered by filtration, and the amount is gravimetrically determined.

FT- IR Spectroscopy

Before analyses, heat-treated and control samples were ground in a Wiley mill to a homogeneous meal. Control and heat-treated wood powder samples were used for Fourier Transform Infrared (FT-IR) spectroscopy measurement. The dried samples were embedded in potassium bromide (KBr) pellets and analyzed by using a Nicolet 20SX FT-IR spectrophotometer. They were recorded in the absorption mode in the range of 4000-400 cm^{-1} with an accumulation of 64 scans, resolution of 4 cm^{-1}. These spectra were normalized at 2900 cm^{-1} (C–H stretching vibration).

RESULTS AND DISCUSSION

The specimens were visually checked after the heat treatment process. The defects were found to be at a minimum level. The changes were obtained by calculating the property difference between heat treated wood and untreated same species as a percentage of untreated wood property.

Figure 1 shows color changes on heat treated specimens with heat treatment. The color became significantly darker with increasing treatment temperature and time, compared with control samples. An increase in lignin content with heat treatment temperature and time justifies these results.

Colored byproducts formed during the degradation of hemicelluloses might have a contribution to this change in appearance (Kocaefe et al. 2008). Thermal treatment always results in darkening of the wood (Ayadi et al. 2003; Sundqvist 2002). Heat-treated woods acquire a darker color similar to most tropical woods, which is an aesthetical advantage for some applications (Bekhta and Niemz 2003; Mitsui 2006).

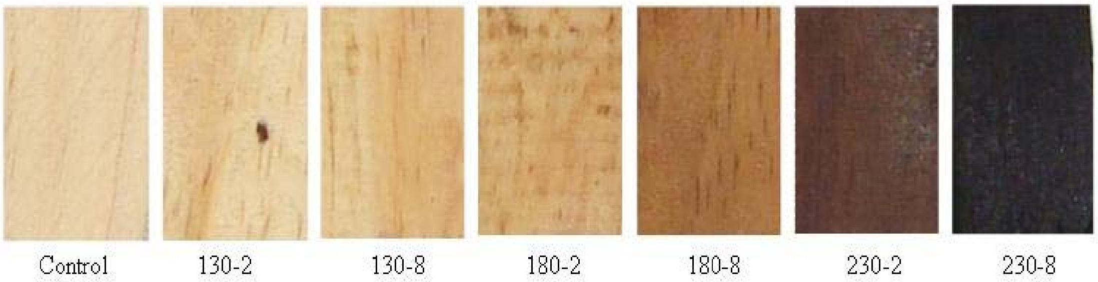

Fig. 1. Color change with increasing heat treatment temperature and time

Treatment temperature was highly correlated with all physical, mechanical, and chemical properties of calabrian pine wood, and the differences were statistically significant ($P<0.01$) except in the case of alcohol-cyclohexane solubility. However, treatment time was only correlated with compression strength, MOE, bending strength and 1% NaOH solubility ($P<0.01$). Heat-treatment time was also correlated with D_0, lignin and holocellulose ($P<0.05$) (Table 1).

Figure 2 displays the changes as percentage on D_m, D_0, β_t, β_r, β_v, α_t, α_r, α_v, fiber saturation point (FSP), and EMC of heat-treated calabrian pine wood at 130 ^{o}C, 180 ^{o}C, and 230 ^{o}C for 2 h and 8 h. All values of the physical properties were decreased with temperature and duration of process, and physical properties were strongly affected negatively by treatment temperature. But, the effects of time were not significantly (Table 1). In this case, it can be said that temperature might have greater effect on physical properties than time.

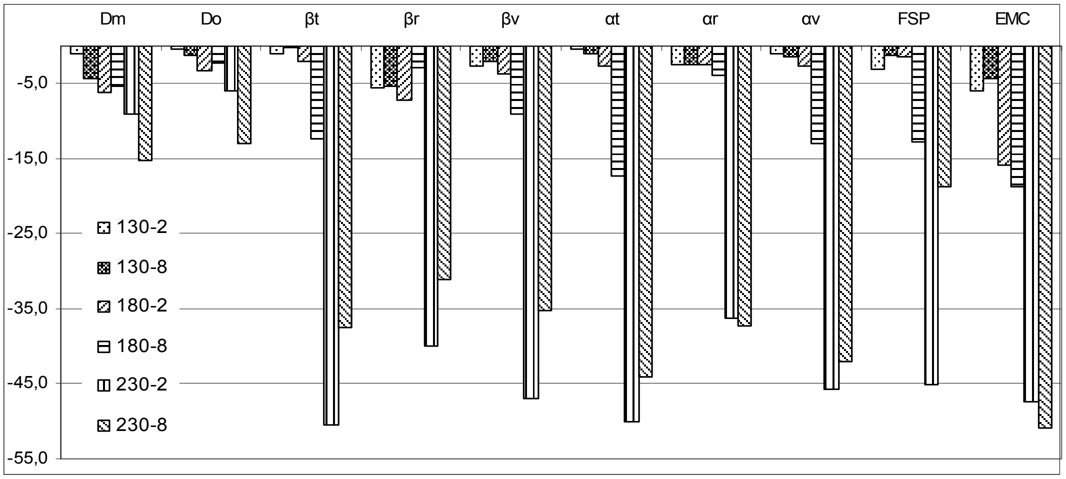

Fig. 2. Percent changes in physical properties as a function of treatment temperature and time

The lowest D_m, D_0, α_r, and EMC were obtained at 230 ^{o}C for 8 h, and maximum reductions were obtained as 15.3%, 12.9%, 37.2% and 50.9%, respectively. Also, maximum variations for β_t, β_r, β_v, α_t, α_v, and FSP were obtained at 230 ^{o}C for 2 h as 50.4%, 40.0%, 46.9%, 50.1%, 45.6%, and 45.0% compared with the control sample, respectively. While the maximum effect of heat treatment was recorded at 230 ^{o}C, the minimum effect was recorded at 130 ^{o}C for both time levels. Similarly, Gündüz et al. (2008) studied the effects of heat treatment on physical properties and surface roughness of Camiyanı black pine (*Pinus nigra* Arn. subsp. *pallasiana* var. *pallasiana*) wood. Their research indicated that reduction in density, swelling, compression strength, Janka-

Table 1. Correlation Matrix for the Parameters Characterizing Heat Treatment Temperature and Time with the Parametric Pearson's Correlation

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature (1)	1,000	0,457**	-0,639**	-0,706**	-0,723**	-0,816**	-0,764**	-0,626	-0,817**	-0,562**	-0,471**	-0,393*	-0,779**	0,612**	0,790**	0,060
Time (2)		1,000	-0,362*	-0,126	-0,223	-0,263	-0,455**	-0,509**	-0,577**	-0,197	-0,070	-0,042	-0,374*	0,392*	0,838**	0,056
D_0 (3)			1,000	0,693**	0,756**	0,801**	0,829**	0,436**	0,596**	0,770**	0,693**	0,669**	0,817**	-0,846**	-0,387*	-0,503**
β_v (4)				1,000	0,965**	0,937**	0,699**	0,473**	0,694**	0,775**	0,824**	0,757**	0,913**	-0,821**	-0,278	-0,433**
α_v (5)					1,000	0,963**	0,783**	0,507**	0,752**	0,836**	0,848**	0,792**	0,963**	-0,882**	-0,325	-0,519**
EMC (6)						1,000	0,849**	0,535**	0,782**	0,851**	0,830**	0,759**	0,975**	-0,893**	-0,418*	-0,503**
Compression strength (7)							1,000	0,574**	0,733**	0,837**	0,698**	0,580**	0,869**	-0,843**	-0,530**	-0,461**
MOE (8)								1,000	0,796**	0,415*	0,312	0,211	0,579**	-0,487**	-0,596**	-0,081
Bending strength (9)									1,000	0,622**	0,465**	0,510**	0,821**	-0,715**	-0,687**	-0,297
Tangential Brinell-hardness (10)										1,000	0,791**	0,694**	0,863**	-0,835**	-0,203	-0,626**
Radial Brinell-hardness (11)											1,000	0,794**	0,821**	-0,837**	-0,072	-0,578**
Cross-section Brinell-hardness (12)												1,000	0,785**	-0,834**	0,005	-0,751**
Holocellulose (13)													1,000	-0,929**	-0,442**	-0,598**
Lignin (14)														1,000	0,332	0,678**
1% NaOH sol. (15)															1,000	-0,211
Alcohol-cyclohexane (16)																1,000

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

hardness, and surface roughness values were observed with the increase in heat treatment time and temperature. Another study showed similar results for Scots pine (*Pinus sylvestris* L.) and beech (*Fagus orientalis* Lipsky) wood (Korkut et al. 2008). Also, Korkut and Guller (2008) reported a reduction in physical properties, oven-dry density, air-dry density and swelling, and surface roughness of wood.

Wood subjected to high temperatures loses its capacity to reabsorb water (Kocaefe et al. 2007). An average decrease in hygroscopicity of 40 % has been found (Tjeerdsma et al. 1998; Boonstra et al. 1998). Also, Esteves et al. (2007) reported an EMC decrease (46% for pine and 61% for eucalyptus), and a dimensional stability increase (maximum anti-shrinking efficiency in the radial direction of 57% and 90% for pine and eucalyptus, respectively).

Heat-treated wood at high temperature has lower hygroscopicity than untreated wood. Due to a decrease of hydroxyl groups on carbohydrate chains, the cell wall of heat-treated wood absorbs less water. As a consequence of the reduced number of hydroxyl groups, swelling and shrinking are being lower.

Figure 3 shows the changes on $\sigma_{c//}$, MOE in bending, σ_b, and H_B (tangential-H_{Bt}, radial- H_{Br} and cross-section-H_{Bc}) of treated samples in comparison to the control samples. To compare the strength properties of heat treated and untreated wood samples, moisture adjustment at 12% were applied for all data. Also, the Pearson's correlations between mechanical properties and treatment temperature and time were given in Table 1. As can be seen from Table 1, all mechanical properties of calabrian pine wood were negatively correlated with treatment time and temperature.

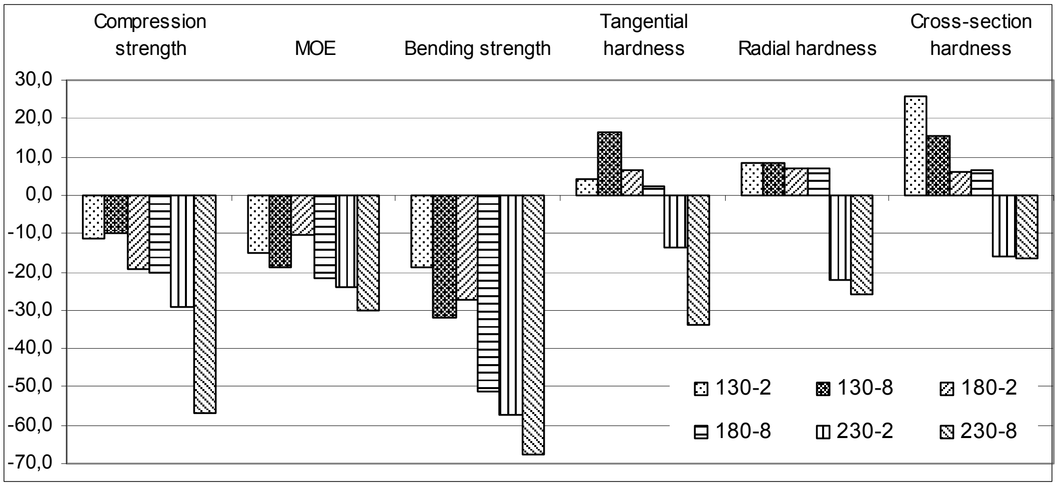

Fig. 3. Changes on mechanical properties as a function of treatment temperature and time

The values of all measured mechanical properties decreased, except for hardness, with increasing temperature and time (Fig. 3). This is probably due to the break-up of the hemicelluloses and cellulose polymers. The hardness slightly increased with both temperature and time up to 230 °C compared with the control sample, and then it showed a decreasing trend due to the further structural degradation.

For all mechanical properties, maximum decreases were recorded at the treatment of 230 °C for both 8 h and 2 h. Compared to the control sample, total loss in $\sigma_{c//}$, MOE, σ_b, H_{Bt}, H_{Br}, and H_{Bc} were obtained as 57.1%, 30.3%, 67.7%, 34.0%, 26.1%, and 16.6%, respectively. However, minimum reductions were obtained at 130 °C for $\sigma_{c//}$, MOE, and σ_b. While increasing H_B value at 130 °C and 180 °C, it decreased at 230 °C for all sections of the samples for both time levels. The maximum hardness value was obtained as 5.00 kgf mm^{-2} at 130 ^{o}C for 2 h.

These results can be explained in terms of material losses in cell wall and hemicelluloses degradation depending on the applied high temperature after heat treatments. Decrease in strength is mainly due to the depolymerization reactions of wood polymers (Kotilainen, 2000). Furthermore, the wood density can play a role in the mechanical properties.

Similar results for reductions in mechanical strength properties of heat-treated wood were reported by Santos (2000), Poncsak et al. (2006), Shi et al. (2007), and Unsal and Ayrilmis (2005). Also, Esteves et al. (2007) reported increasing mass losses with treatment time and temperature for pine and eucalyptus woods. Besides, little effect on modulus of elasticity (5% for pine and 15% for eucalyptus) and reducing bending strength (by 40% for pine and 50% for eucalyptus) were recorded by Esteves et al. (2007).

Changes on some chemical contents of the heat-treated calabrian pine wood samples relative to the control sample are shown in Fig. 4.

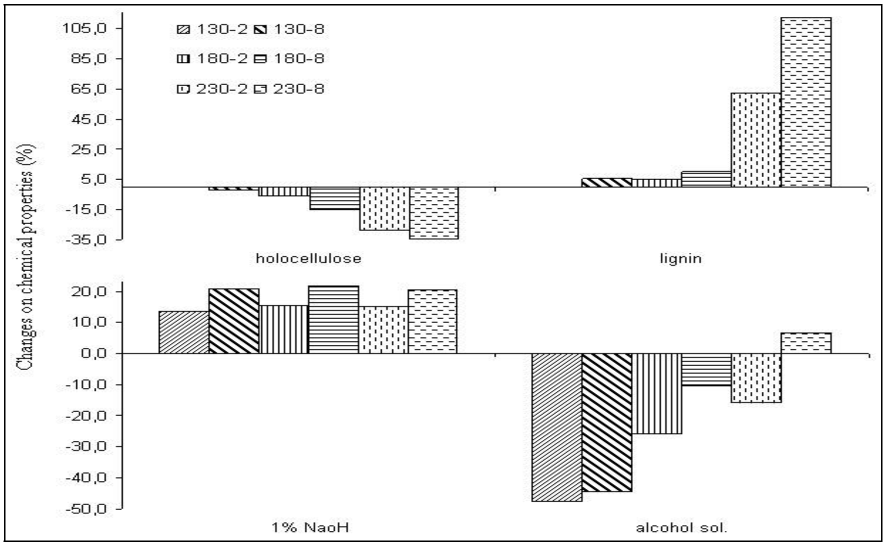

Fig. 4. Changes in chemical properties as a function of heat treatment and time

Holocellulose content changed negatively with increasing temperature and time. Similarly, according to the Pearson's correlations results shown in Table 1, holocellulose content was correlated negatively with temperature and time of heat treatment as R =0.78 (P<0.01) and R =0.37 (P<0.05) respectively.

A maximum decrease in holocellulose content was found at 230 ^{o}C for 8 h as 34.3% and a minimum decrease was obtained at 130 ^{o}C for 2 h as 0.1%. Heat treatment significantly degraded the wood carbohydrate, suggesting depolymerization and alterations through the cleavage of acetic acid from the acetyl side chains (Kartal et al. 2008).

Lignin values increased with rising treatment temperature and time, as justified by the Pearson's correlations results (Table 1). Lignin content was correlated positively with temperature and time of heat treatment as R = 0.61 (P<0.01) and R = 0.39 (P<0.05), respectively. The highest lignin contents were obtained at 230 ^{o}C for both 2 h (40.83%) and 8 h (53.26%). This result confirmed most of the conclusions stated in the literature (Kartal et al. 2008; Boonstra and Tjeerdsma 2006; Kamdem et al. 2002). According to another viewpoint, an increase in lignin content during the thermal treatment can be explained by the fact that some of the thermal degradation products of carbohydrates may be retained in the lignin fraction with Klason lignin analyses (Yildiz et al. 2006). Shrinkage and swelling behavior of the heat-treated wood has been affected positively with increasing of lignin ratio. However, this improvement not only depends on the increasing lignin ratio but also non-damaged carbohydrates with crystalline structure. In addition, color darkening occurs with increasing lignin amount in heat treated wood structure. Figure 1 shows this effect.

According to Fig. 4, 1% NaOH solubility values of the samples increased with rising treatment time and temperature in comparison with the control sample. Since increase in the thermal degradation products of carbohydrates, 1% NaOH solubility products were increased, depending on temperature and time. This conclusion is justified by the Pearson's correlations (Table 1). However, the alcohol-syclohegzane+alcohol solubility of the samples decreased with rising treatment time and temperature in comparison with the control sample. As can be clearly seen in Table 1, changes of alcohol-syclohegzane+alcohol solubility with temperature and time were not statistically significant ($p<0.05$). It's well known that extractives are not structural components, and most of the compounds evaporate easily during the heat treatment.

FT-IR spectra were recorded for treated samples at 130, 180, and 230 ^{o}C for 2 and 8 h and for the control sample (Fig. 5). For calabrian pine wood samples, the band at 1426 cm^{-1} (CH$_2$ bending for cellulose) moved up with heat treatment relative to the control (Fig. 5). The peak shoulder at 1507 cm^{-1} (C=C stretching aromatic ring for lignin) for samples was not changed by heat treatment, evidently. The band at 1106 cm^{-1} (asym. bridge C–O–C stretching for cellulose) did not change to an obvious extent in samples as a result of heat treatment at 130 °C and 180 °C relative to the control wood sample. However, the band at 1106 cm^{-1} moved up distinctly at 230 ^{o}C (Fig. 5). Similar results were found by Akgül et al. (2006). At 1635 cm^{-1}, the peak shoulder increased with rising heating temperature and time. The bands at 1635 cm^{-1} and 1736 cm^{-1} (C=O valance vibration of COOH group) had almost the same absorbance value for all samples.

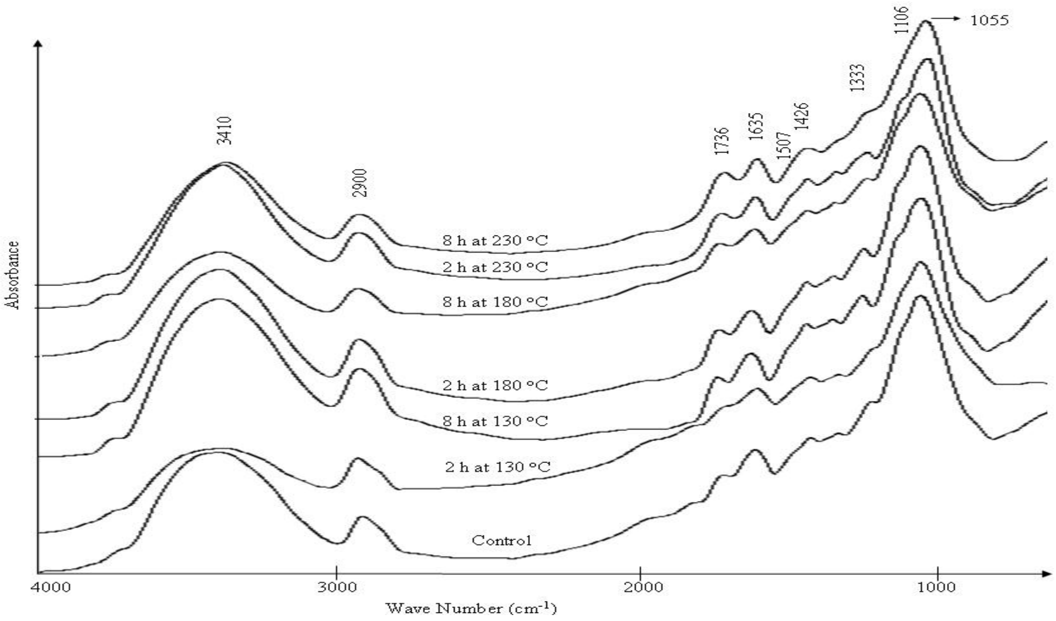

Fig. 5. FT-IR spectra of untreated and heat treated calabrian pine wood

The degree of crystallinity is one of the important parameters for polymers. The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity (Mo et al. 1994). An FT-IR spectroscopy method was used for determination of Relative Crystallinity Indexes (RCI) (Table 2).

Table 2. The Relative Crystallinity Index (RCI) of Heat-treated Calabrian Pine Wood

RCI	Control	130 °C		180 °C		230 °C	
		2 h	8 h	2 h	8 h	2 h	8 h
A1427/A898	0.97	0.97	1.04	1.00	0.93	1.05	1.00
A1371/A2900	1.20	1.18	1.36	1.44	1.90	1.33	1.31
A1371/A670	0.96	1.03	0.96	0.97	0.93	1.04	1.02
A1371/A690	0.97	1.01	1.01	1.02	0.95	1.08	1.03

The absorbance peaks at 1430 cm^{-1} and 897 cm^{-1} were assigned to the CH_2 bending mode and deformation of anomeric CH_2, respectively (Kataoka and Kondo 1998). The ratios of the absorbency at A_{1430}/A_{897} and A_{1371}/A_{2900} have been used to measure the relative cellulose crystallinity (Hassan et al. 2000). Meanwhile, the ratios at A_{1371}/A_{690} and A_{1371}/A_{670} can be used as an indicator for of the transformation of cellulose I and cellulose II during alkaline treatment (Hassan et al. 2000; Akerholm et al. 2004). This method actually uses the ratio of the combined areas of the peaks at 1370, 1335, and 1315 cm^{-1}, which represented the CH bending, to that of the peak at 670 cm^{-1} (C-OH out of plane bending mode) (Evans et al. 1995).

While cellulose shows substantially crystalline structure, hemicelluloses and lignin show amorphous structure within the chemical composition of wood. Heating of wood modifies the cell wall components. The most effected compounds in the chemical structure are hemicelluloses, cellulose, and lignin, respectively. Similarly in this study a significantly decreasing holocellulose ratio and an increasing lignin ratio in the wood structure were determined. Carbohydrate compounds with amorphous characteristics were affected negatively by heat treatment. According to other researchers, the crystalline structure of cellulose is not changed (Yildiz and Gümüşkaya 2007) or even can improve up to a certain temperature, which may be as high as 200 °C, depending on the conditions involved. The present results confirm that relative crystallinity indexes of the celluloses are not affected by different heat treatment times and temperatures within the ranges that were considered (Table 2).

CONCLUSIONS

According to the experimental results, the air-dry density, oven-dry density, shrinkage (tangential, radial and volumetric), swelling (tangential, radial and volumetric), FSP, and EMC values decreased with increasing temperature and time of treatment. Similarly, compression strength parallel to the grain, bending strength, and MOE in bending values decreased. But hardness of wood decreased at only 230 °C for both sets of treatment times. However, while holocellulose ratio and alcohol solubility of the wood were decreased, 1% NaOH solubility and lignin content were increased, depending on heat treatment temperature and time. Relative cellulose crystallinity of the samples was not changed significantly.

The lowest decreases were determined at 130 ^{o}C for 2 h. Temperature was highly correlated with all physical, mechanical, and chemical properties of calabrian pine wood. Heat treatment can be considered as an environmentally friendly technique, because no chemicals are involved during the process.

In this case it can be said that temperature had greater influence on strength properties than time. For a heat treatment process, 130 ^{o}C for 2 h should be applied in situations where mechanical properties such as σ_b, H_B, $\sigma_{c//}$ and MOE are important. However, 230 ^{o}C for 2 h should be used in place where preferred physical properties of wood such as D_m, D_0, β, α, FSP and EMC are desirable. As a result, heat-treated woods can be utilized using proper time and temperature without any loses in strength values and chemical characteristics in areas, where woodworking and stability are important.

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