EFFECTS OF CHEMICAL MODIFICATION ON WOOD PROPERTIES

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Abstract: Chemical modification can be used to improve the properties of wood. Effect of melamine formaldehyde modification on the physical and mechanical properties of Scots pine and Chestnut was investigated in this study. Wood samples were impregnated with melamine formaldehyde (MF) resin under 3 bar pressure for 10 or 30 min and were cured at a temperature of 150 °C for 20 min in an oven. Weight percent gain, water uptake, volumetric swelling, Brinell hardness, modulus of rupture and modulus of elasticity values of the samples were determined according to relevant standards. Modification with MF reduced the water uptake and the volumetric swelling of the woods. Anti-swelling efficiency of the modification were approximately 66 % and 57 % in chestnut and scots pine, respectively. MOE increased in scots pine (3% - 17 %) while unchanged in chestnut but MOR decreased significantly by modification in both chestnut (2.5% - 17.9%) and scots pine (26.2% - 32.7%). Also, MF modification increased the Brinell hardness of the wood, slightly.

Keywords: Wood modification, Melamine formaldehyde, Physical and mechanical properties

Introduction

Wood has many desirable characteristics required for a variety of end uses such as construction, furniture, and tools. However, wood also has properties that, in relation to specific applications, can be regarded as disadvantages. One main disadvantage of wood is its inherent moisture sensitivity, a major cause for fungal decay, mold growth and dimensional instability, resulting in decreased service life as well as costly maintenance (Gindl et al. 2003; Epmeier et al. 2004). Therefore, suitable technologies are needed to improve woods' properties, i.e., the dimensional stability, durability, mechanical strength, and hardness, to meet specific end-use requirements (Cai 2007; Hochmanska et al. 2014). Different methods, involved chemical and thermal modification, have been developed over many years to overcome these disadvantages. Major research approach has been carried out to improve physical properties. Physical properties could be improved, but the mechanical properties of wood decrease during the modification process (Poncsak et al. 2006; Gündüz and Aydemir 2009). Chemical modification of wood can be defined as a process of bonding a reactive chemical to a reactive part of a cell wall polymer to form a covalent bond between them (Rowell 2006).

The treatment of wood, with different types of chemicals or resins, has been widely studied with the end goal of enhancement. Melamine formaldehyde (MF) and phenol formaldehyde (PF) are two common resins for wood-related applications. Melamine formaldehyde (MF) resin, commonly used in thermosetting, has applications in coatings, adhesives, and both paper and textile treatments (Pittman et al. 1994). Various types and grades of MF resin are available for the impregnation of wood. Gindl et al. (2003) examined the factors were selected that influenced the uptake of MF resin into the cell wall of softwood. Impregnation of solid wood with water-soluble MF resin has led to a significant improvement in the surface hardness (Miroy et al. 1995; Gindl et al. 2004) and the modulus of elasticity (MOE) (Deka and Saikia 2000; Deka et al. 2007). Epmeier et al. (2003) and Deka et al. (2007) reported that modification of wood with MF has led to a decrease in swelling (30% - 75%) and equilibrium moisture of content (EMC) (20%) of the wood. Although many studies have been focused on MF modification, it has not been widely applied in an industrial setting because of its higher cost than other polymerizable monomers and pre-polymers (Deka et al. 2007). Epmeier et al. (2004) compared the physical and mechanical properties of 9 different modified woods and reported that the acetylation and furfurylation were the most effective modification methods for achieving a high dimensional and stiffness stability and a low EMC.

The main purpose of this study is improving the properties of wood by using chemical modification to produce value-added material. To achieve this purpose, the effects of melamine-formaldehyde (MF) modification on the physical and mechanical properties of Scots pine and Chestnut wood was investigated.

Materials and Methods

Materials

Scots pine (*Pinus silvestris* L.) (SP) and chestnut (*Castenea sativa* Mill.)(CH) were used as wood material in this experiment. Commercially available melamine formaldehyde resin (Almin-65), provided by the Gentaş Kimya Inc., Tuzla, Turkey, was used for the modification. The properties of the resin are given in Table 1, based on the manufacturer's information.

Table 1: Properties of Melamine Formaldehyde Resin

Appearence	Clear, colorless liquid
Solid content % weight	51±1
Viscosity (sn F.C.4 20 °C)	15 - 20
pH(20 °C)	9.6 - 10.5
Dansity (g/cm3 20 °C)	1.220 - 1.240
Water tolerance (20 °C)	1/1,0 - 1/2,0
Gel time (min. 130 °C)	35.00 - 40.00

Methods

Wood samples cut into dimensions according to relevant standard and were acclimatized before testing at a temperature of 20 ± 3 °C and a relative humidity (RH) of 65%. The weight and the volume of the samples were determined. Then the samples were oven-dried at a temperature of 103 ± 2 °C and the oven-dried densities were calculated before chemical modification.

Melamine formaldehyde resin was used in two grades. One group was modified with melamine formaldehyde resin which was diluted by 50% with distilled water (MFW) while the other group was modified with MF without further modification. Impregnation was performed in a stainless steel vacuum chamber at 3 bar pressure for 10 or 30 minutes and impregnated samples cured in an oven at a temperature of 150 °C for 20 minutes. The impregnation was performed separately for each treatment level and a new resin solution was used for each of the different variations. Before physical and mechanical analysis testing, the samples were cut into various dimensions, according to the specifications of the testing standard. Ten replicates were prepared for each experiment, and the samples were acclimatized at a temperature of 20 ± 3 °C and a RH of 65%. The experimental design was given in Table 2, and the modification process was summarized in Figure 1.

Table 2: Experimental design

Modification groups (Codes)	Wood species	Chemical	Distilled water	Impregnation duration (min)	Pressure	Number of samples
SP-C		Control	-	-	-	10
SP-MF-10			-	10	3 bar	10
SP-MF-30			-	30	3 bar	10
SP-MFW-10			% 50	10	3 bar	10
SP-MFW-30			% 50	30	3 bar	10
CH-C		Control	-	-	-	10
CH-MF-10			-	10	3 bar	10
CH-MF-30			-	30	3 bar	10
CH-MFW-10			% 50	10	3 bar	10
CH-MFW-30			% 50	30	3 bar	10

The oven-dry densities of the samples, before and after the modification treatment, were determined according to the testing standard, TS 2472 (1976). The weight percent gain (WPG) of the samples was calculated according to the following equation:

$$WPG = \frac{m_i - m_0}{m_0} \times 100 \quad (1)$$

where m_o is the oven-dry weight of the samples before the modification in grams and m_j is the oven-dry weight of the samples after the modification in grams.

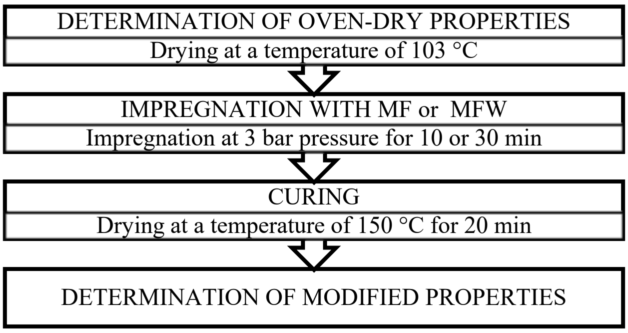

Figure 1: Chemical modification process

To determine the effect of the modification on the dimensional stability, the water uptake (WU), swelling (S), and anti-swelling efficiency (ASE) values of the samples were determined. According to the testing standard, TS 4086 (1983), 20 × 20 × 30 mm (T×R×L) samples were immersed in distilled water for 4 wk. After immersion, the dimension and the weight of the samples were recorded, and the dimensional stability values were calculated according to equations 2 through 4:

$$WU = \frac{m_w - m_i}{m_i} X100 \quad (2)$$

where m_w is the weight of the samples after water immersion in grams and m_i is the oven-dry weight of the samples after the modification in grams;

$$S = \frac{V_W - V_i}{V_i} X100 \quad (3)$$

where V_w is the volume of the samples after water immersion in cm^3 and V_i is the oven-dry volume of the samples in cm^3; and

$$ASE = \frac{S_m - S_u}{S_u} X100 \quad (4)$$

where S_m is the swelling ratio of the modified samples as a percentage and S_u is the swelling ratio of the unmodified samples as a percentage.

The mechanical properties of the MF modified samples, including the modulus of rupture (MOR), modulus of elasticity (MOE), and Brinell hardness (BH) were determined according to the TS 2474 (1976), TS 2478 (1976), and TS 2479 (1976) testing standards, respectively.

The data were analyzed statistically using an SPSS software system (SPSS17, IBM Corp., Armonk, NY). An analysis of variance (ANOVA) model was used to determine the effect of the MF resins on the mechanical and physical properties of wood. Duncan’s multiple range tests were used for pairwise comparisons when the overall ANOVA model was significant. Data for Scots pine and chestnut woods were analyzed using separate models.

Results and Discussion

The oven-dry densities of the MF modified wood, and the change as a percentage compared to the unmodified control samples were given in Table 3. Modification with MF or MFW increased the oven-dry density of the both wood species. The highest density increase was determined as 27.2% in Scots pine modified with MFW for 30 min. The density increase in Scots pine were higher than that of chestnut and the change increased with the increasing impregnation duration. Modification with MFW resulted in a higher density increase than modification with MF.

The weight of the samples before and after modification, and WPG values of the modification were shown in Table 4. The WPG values varied from 17.83% to 46.53%. Although the greatest WPG was observed in modification with MFW for 10 min (46.53%), there was no statistically significant difference between the 10-min and 30-min impregnation durations in Scots pine. It has been found that WPG alters more chestnut than Scots pine. This could be attributed to the relatively low permeability of chestnut. Dieste et al. (2013) noted that the average water vapor permeability of chestnut was lower than that of pine, and this low permeability is attributed to the wood extractives, which reduce the void space and hindered condensation. Chestnut wood has different vapor sorption and vapor permeability than conifers normally used in construction.

Table3: The oven-dry densities of the modified woods

Wood species	Chemical	Distilled water	Impregnation duration (min)	Oven-dry density (g/cm^3)	Change (%)
	Control	-	-	0.451	-
		-	10	0.514	14.0
		-	30	0.541	20.1
		50%	10	0.529	17.4
		50%	30	0.573	27.2
	Control	-	-	0.539	-
		-	10	0.592	9.8
		-	30	0.621	15.3
		50%	10	0.603	12.0
		50%	30	0.614	13.9

Table 4: Weight percent gain values of the modified wood

Modification groups	m_o (g)	m_i (g)	WPG (%)	HG
SP-MF-10	12.49	15.89	26.91	a
SP-MF-30	12.39	16.47	32.75	ab
SP-MFW-10	11.36	16.63	46.53	c
SP-MFW-30	11.72	16.92	44.38	c
CH-MF-10	13.19	15.54	17.83	x
CH-MF-30	12.94	16.42	26.96	y
CH-MFW-10	13.05	16.81	28.91	y
CH-MFW-30	12.97	17.29	33.34	z

HG: Homogenity groups. Means within a column with different subscripts differ ($P < 0.05$)

WPG were higher in MFW than MF in both wood species. These results showed that MF or MFW impregnated both the cell lumens and the cell walls. It was reported that an aqueous melamine formaldehyde solution can penetrate the secondary cell wall of Scots pine or larch wood (Gindl et al. 2002) and the amorphous region of cellulose fibrils (Hua et al. 1987).

Table 5: Water uptake values of modified and unmodified wood

Modification groups	Water Uptake (%)	Change (%)	HG
SP-C	82.1	-	a
SP-MF-10	72.3	11.9	ab
SP-MF-30	65.0	20.8	bc
SP-MFW-10	69.8	15.0	abc
SP-MFW-30	54.3	33.9	c
CH-C	98.0	-	x
CH-MF-10	68.3	30.3	y
CH-MF-30	63.9	34.7	z
CH-MFW-10	62.8	35.8	z
CH-MFW-30	62.1	36.5	z

HG: Homogenity groups. Means within a column with different subscripts differ ($P < 0.05$)

The WU values of the modified with MF and MFW, and unmodified wood were given in Table 5. Reductions in the WU varied from 11.9% to 36.5%. The average decrease in the WU in modified chestnut was about 35%, and there was no statistically difference between them except in modified with MF for 10 min (30.3%). But the difference among the modified pine groups was more evident. It was determined that the impregnation duration was quite effective on the WU in Scots pine; longer impregnation duration caused about twice a decrease.

The volumetric swelling and the ASE values of the modified wood were shown in Table 6. Modification with MF or MFW decreased the volumetric swelling of Scots pine and chestnut. The ASE values of the MFW-modified samples were higher than that of MF-modified samples. Deka et al. (2007) reported a 17.5% increase in ASE for MF-modified Norway spruce. In this study, higher ASE values of 57% and 67.5% for MFW-modified Scots pine and chestnut, respectively, were achieved. Deka et.al. (2007) indicated that this dimensional stability might be due to blocking of water accessible OH groups of wood component with MF resin, which was perceived even after repeated wetting and drying of wood. Since, the MF resin caused volumetric swelling of wood (Militz et al, 1997), it could be inferred that the resin could easily penetrate the wood substrate to reach OH groups of the cell wall components for dimensional stability.

Table 6: Volumetric swelling and ASE values of the modified wood

Modification groups	Volumetric Swelling (%)	HG	Anti-swelling Efficiency (ASE) (%)
SP-C	7,45	a	
SP-MF-10	4,46	c	
SP-MF-30	5,67	b	
SP-MFW-10	3,43	c	
SP-MFW-30	3,2	c	
CH-C	11,54	x	
CH-MF-10	7,92	b	
CH-MF-30	6,71	c	
CH-MFW-10	3,75	d	
CH-MFW-30	3,99	d	

HG: Homogenity groups. Means within a column with different subscripts differ ($P < 0.05$)

Table 7: MOR and MOE of the modified wood

Modification groups	MOE (N/mm^2)	HG	Change in MOE (%)	MOR (N/mm^2)	HG	Change in MOR (%)
SP-C	7566.8	a	-	93.3	a	-
SP-MF-10	8389.5	b	10.9	68.9	b	-26.2
SP-MF-30	8874.8	c	17.3	68.2	b	-26.9
SP-MFW-10	8038.1	ab	6.2	62.8	b	-32.7
SP-MFW-30	7928.1	ab	4.8	64.6	b	-30.8
CH-C	9616.2		-	105.5	x	-
CH-MF-10	9983.4		3.8	102.9	x	-2.5
CH-MF-30	9587.9		-0.3	90.4	y	-14.3
CH-MFW-10	9315.7		-3.1	86.6	y	-17.9
CH-MFW-30	10070.8		4.7	87.7	y	-16.9

MOR: Modulus of rupture; MOE: Modulus of elasticity
HG: Homogenity groups. Means within a column with different subscripts differ ($P < 0.05$)

The mechanical properties of the modified wood were determined and the results were summarized in Table 7. Modification with MF or MFW reduced the modulus of rupture (MOR) more in Scots pine than chestnut. The decrease in MOR was approximately 30% compared to unmodified Scots pine and there was no statistically significant difference among the modified groups. Decrease in MOR were varied by 2.5% to 17.9% in modified chestnut and there was no statistical difference among the modified groups except samples modified with MF for 10 min. Epmeier et al. (2003) reported an approximately 10% increase in MOR with the methylated melamine formaldehyde resin modification; however, acetylation and furfurylation were not significant. The reduction in the MOR of the MFW-modified samples was higher than that of the MF-modified samples. This reduction in the MOR might be caused by high temperature of the curing step of the modification process. A high treatment temperature causes strength loss in wood (Thermowood 2003;Lekounougou and Kocaefe 2014). Therefore, the process values must be selected carefully when exploiting heat in wood modification. Winandy and Rowell (2013) stated that the bending strength depends on many properties, like specific gravity and Weigl et al. (2012) found that the bending strength reduction is aligned with hemicelluloses degradation.

Modification with MF or MFW increased the MOE of the Scots pine. The highest increase was observed in samples modified with MF for 30 min as 17.3%. The increase was relatively low in the other groups and there was no statistically difference among them. Modification with MF or MFW slightly changed the MOE of the chestnut and there was no statistically difference compared to unmodified samples ($p=0.264$). Epmeier et al. (2004) indicated that although the MOE was affected by a change of density, an increase in density caused by chemical modification does not affect the MOE in the same manner.

Although chemical modification with MF and MFW slightly increased the HBR (Table 8), it was found that this increase was statistically insignificant. Gindl et al.(2002), Epmeier et al. (2003), Lande et al. (2004), and Deka et al. (2007) reported that the hardness of the wood notably increased by chemical modification at high weight percent gain levels. Deka et al. (2007) inferred that resin's adherence and/or reaction on the surface of treated wood caused increase in surface hardness considerably.

Table 8: Brinell hardness of the modified wood

Modification groups	HB N/mm^2	HG
SP-C	1,49	
SP-MF-10	1,76	
SP-MF-30	1,63	
SP-MFW-10	1,49	
SP-MFW-30	1,57	
CH-C	2,93	
CH-MF-10	3,23	
CH-MF-30	3,13	
CH-MFW-10	3,05	
CH-MFW-30	2,64	

Conclusion

Certain physical and mechanical properties of the wood modified with melamine formaldehyde (MF), and melamine formaldehyde diluted with water (MFW) were investigated. The results show that chemical modification affects the properties of wood in different ways. Based on the findings of this study, conclusions given below can be inferred:

- Chemical modification with MF increased the density of both Scots pine and chestnut,
- WPG values and density increase were higher in samples modified with MF diluted with water,
- Longer impregnation time resulted higher WPG and density increase,
- Modification with MF or MFW decreased the water uptake and swelling of wood significantly,
- ASE of the modification were higher in chestnut than that of Scots pine. ASE of the modification with MFW were higher than that of modification with pure MF. Approximately 55% and 65% ASE were determined in Scots pine and chestnut modified with MFW, respectively.
- Modification with MF or MFW decreased the MOR of Scots pine, significantly. (30%) Decrease in MOR were relatively lower in chestnut (17%).
- Modification did not affect the MOE in chestnut, significantly ($p=0.264$). But, modification with MF increased the MOE in Scots pine (10%-17%).
- Modification with MF or MFW did not affect the HB of the wood, significantly.

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