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EFFECTS OF ZEOLITE ON SOME PHYSICAL PROPERTIES AND FORMALDEHYDE RELEASE OF MEDIUM DENSITY FIBERBOARD

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Abstract:
In this study, effects of Zeolite on some properties of medium density fiberboards (MDF) were investigated. Control and Zeolite modified (1.5%, 10kg/m³)) MDF boards were manufactured in Kastamonu Entegre Factory. Mixture of the beech (40%), oak (30%), and Scots pine (30%) wood chips was used for fiber production. Boards with dimensions of 500x490x14mm were manufactured. Thickness, density, moisture content, thickness swelling, water absorption, and formaldehyde gas emissions were determined after the acclimatization process at 20±2°C and 65±5% relative humidity. IB700 laboratory testing machine was used for performing tests. According to results, Zeolite significantly decreased (50.3%) the Formaldehyde emission and increased the water absorbtion with about 84.4% and thickness swelling with about 15.3%, and moisture content with about 8.2% of the MDF panles. Statistical analyses show that Zeolit had no significant influence on the density (0.4% increase) (P: 0.15) and thickness (0.5% decrease) (P: 0.25). Zeolit could be used as additive to decrease formaldehyde emission.

Key words: *medium density fiberboard; Zeolite; physical properties; formaldehyde.*

INTRODUCTION

In the production of Medium Density Fiberboard, lignocellulosic fibers, inorganic minerals and chemicals can be added to achieve some improvements on properties in comparison with standard values. Zeolite, natural or industrially produced aluminosilicate minerals that have microporous structure, is one of these modification additives. Structure of Zeolite and its areas of use were investigated by Mishra and Jain (2011). Deodorizing effect of zeolite on cellulose fibers was evaluated by Lim et al. (2006).

Effect of zeolite and different fire-retardant chemicals used in particle boards or MDF on their fire resistance performance was evaluated by Istek et al. (2013), Özdemir and Tutuş (2016). Donmez Cavdar et al. (2019) investigated the fire retardant effect of ammonium zeolite and ammonium phosphate fillings used in thermoplastic composites.

The influences of sepiolite, dolomite and perlite and ground calcium carbonate on the properties of MDF were analyzed by Özdemir (2019) and Ozyhar et al. (2020), respectively. Ozdemir (2019) stated that water absorption and thickness swelling increases with the increase in mineral amount. On the contrary, Ozyhar et al. (2020) stated that mineral filling to MDF up to 10 wt.% have no influences on the strength properties and thickness swelling. Furthermore, any notable effect was not observed for the formaldehyde emission. However, exceeding the 10 wt. % might increase the emissions. Kalantarifard et al. (2016) modified clinoptilolite zeolite using granite, bentonite and starch, and compared with the formaldehyde holding capacity of natural zeolite. Bellat et al. (2019) compared the selective adsorption properties of formaldehyde and water vapors in NaY and NaX zeolites.

Taghiyari and Nouri (2015) produced MDF containing nano-wollastonit additive and determined the physical and mechanical properties. Donmez Cavdar (2020) used Zeolit as filing agent (4, 8 and 12%) in production of MDF with UF melamine formaldehyde (MF) and evaluated its effect on modulus of rupture, modulus of elasticity, the thickness swelling, water absorption, limiting oxygen index (LOI), and thermal properties. Wang et al. (2016) produced MDF using vermiculite additive and performed mechanic tests, LOI and thermal (thermogravimetry-TG and differential scanning calorimetry-DSC) analysis. Kaymakçı et al. (2017) evaluated the some physical, mechanical and thermal properties of wood plastic composite (WPC) manufactured using pine wood flour, harmonizing medium, zeolite, and polypropylene. Salari et al. (2012) investigated the effect of organo-modified montmorillonite (MMT) on the properties of Oriental Strand Board (OSB) produced using underutilized low quality paulownia wood.

Wang et al. (2019) evaluated the effects of alkalinity and acidity rates of the natural Zeolite on hydrophobicity and hydrophilicity. They stated that “the alkali and acid treated zeolites with ascending

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SiO2/Al2O3 ratio exhibited decreasing water vapor adsorptions per unit area and increasing hydrophobicity". Therefore, using such a modified zeolite in the production of MDF could reduce the swelling properties.

There are regulations for the limitation of formaldehyde emission of the MDF published different authorities such as California Air Resources Board (CARB), United States Environmental Protection Agency (US EPA), European Regulations, etc. And, according to CARB Phase 2, thickness of the MDF defines the limit of parts per million (ppm). For example; 0.13 ppm for thin MDF (thickness of the board is 8mm or less) and 0.11 ppm for MDF (Csondes 2008). Furthermore, such regulations have been put into practice for the formaldehyde emission by some of the foremost countries in this field. Therefore, reducing the formaldehyde gas emission of MDF is an important issue not only for wood-based material manufacturer but also for consumer. In this study the applicability of Zeolite in the production of MDF and its effects on the physical properties and reduction of formaldehyde emission were evaluated.

MATERIAL AND METHOD

Raw Material

Beech (*Fagus orientalis* L.), Oak (*Quercus robur* L.), and Scots pine (*Pinus sylvestris* L.) wood were used for MDF production. They were harvested from Kastamonu, Western Black sea, and Bolu stands, respectively.

Adhesive

Urea-formaldehyde (UF) adhesive (1:1:17 mole) was provided by the Kastamonu Entegre Adhesive Plant located in Kastamonu Organized Industrial Zone in Turkey. Properties of the produced adhesive were presented in Table 1.

Table 1

Properties of used adhesive

Solid content	Mole ratio (U/F)	Density at 20°C (g/cm³)	Viscosity at 25^{0}C (cps)	Gel time (100°C) (20%(NH4)$_2$SO$_4$)	pH	Free Formaldehyde (%)	Metilol groups (%)	Shelf time (day)
62 ± 1	1.17	1.227	20-35 mPa/s	20 - 45 s	7-8.5	0.2	12 -15	75

Hardening agent

Ammonium sulfate, $(NH_4)_2SO_4$, (purchased from a local supplier in İzmit city and prepared as 20% solution) was used as hardener for UF. Density and pH values were 0.95g/cm^3 and 6.5, respectively.

Paraffin

Paraffin (off-white, 60% solid matter content, 9-10 pH, 12-23sn viscosity, 0.96g/cm^3 density) was provided by Mercan Kimya Ltd., Denizli, Turkey, and used as water-resisting agent.

Zeolite

Natural zeolite (clinoptilolite), purchased from Rota Mining Ltd. in İzmir city, was used in this study. Chemical formulae of Zeolite is Ca, K_2, Na_2, $(Mg)_4Al_8Si_{40}O_{96}\cdot 24(H_2O)$. Properties of the Zeolite are presented in Table 2.

Table 2

Properties of Zeolite

Pore diameter	Melting point (°C)	Density (g/cm³)	Particle size (µm)
4 Å	1300	0.6-0,8	275

Production of MDF boards

Mixture of the hardwood (70%) and softwood (30%) fibers were used to produce experimental boards. Control boards without zeolite were produced using 100% biomass fibers (40% beech wood, 30% oak wood, and 30% pine wood) and defined by (R). R, expresses the consumed wood fibers for 1m³ board material. Beside the control boards, 1.5% Zeolite boards were manufactured and were defined by Z. Z, expresses 1m³ board material including; 275µm Zeolite, 1:1.17 mole UF adhesive, 20% ammonium sulfate hardener in solution phase, and 1.8% (0.95g/cm³) liquid paraffin.

Beech (40%), oak (30%), and Scots pine (30%) wood species were used as raw material for MDF production. Woods were chipped in chipping unit according to species. They were separately stored in silos. Mixture of the species was adjusted following the silo discharging. Non-standard constituent parts in the mixtures were sorted out by the roller screening system. Chips were processed along 3.5 minutes by the Andritz Refiner and Defibrillator units using 7.9 bar steam pressure and 182°C temperature. Plastified chips at the end of the refiner were transformed into the fibers (between the Defibrator segments) and graded. Liquid paraffin, ammonium sulphate hardener, and UF adhesive were sequentially added in the Blowline section. UF, hardener, and paraffin were added by 11%, 0.72%, and 1.8% in percentage by weight of dried wood fibers, respectively. Fibers were dried up to 11% moisture content and then they were picked up from laying station.

At first, natural fibers were cold pre-pressed (forming the board to reduce the volume and improve the contact of fibers for further processes) in a 500x500x400mm press cabin. Also, 1.5% Zeolite applied another batch of cold-press application was performed. Then, control and Zeolite modified MDF boards (five for each) were produced using laboratory type press machine (195ºC temperature, 32kg/cm² pressure, and 300 seconds). Experimental boards of 500x490x14mm MDF boards were stored for five days in the storage and then top and bottom surfaces of the MDF boards were sanded using 40 and 80 grid sand papers. All the MDF boards were acclimatized at 20±2°C and 65±5% relative humidity in accordance with ISO 554 (1976). Workflow diagram of the MDF production is presented in Fig. 1.

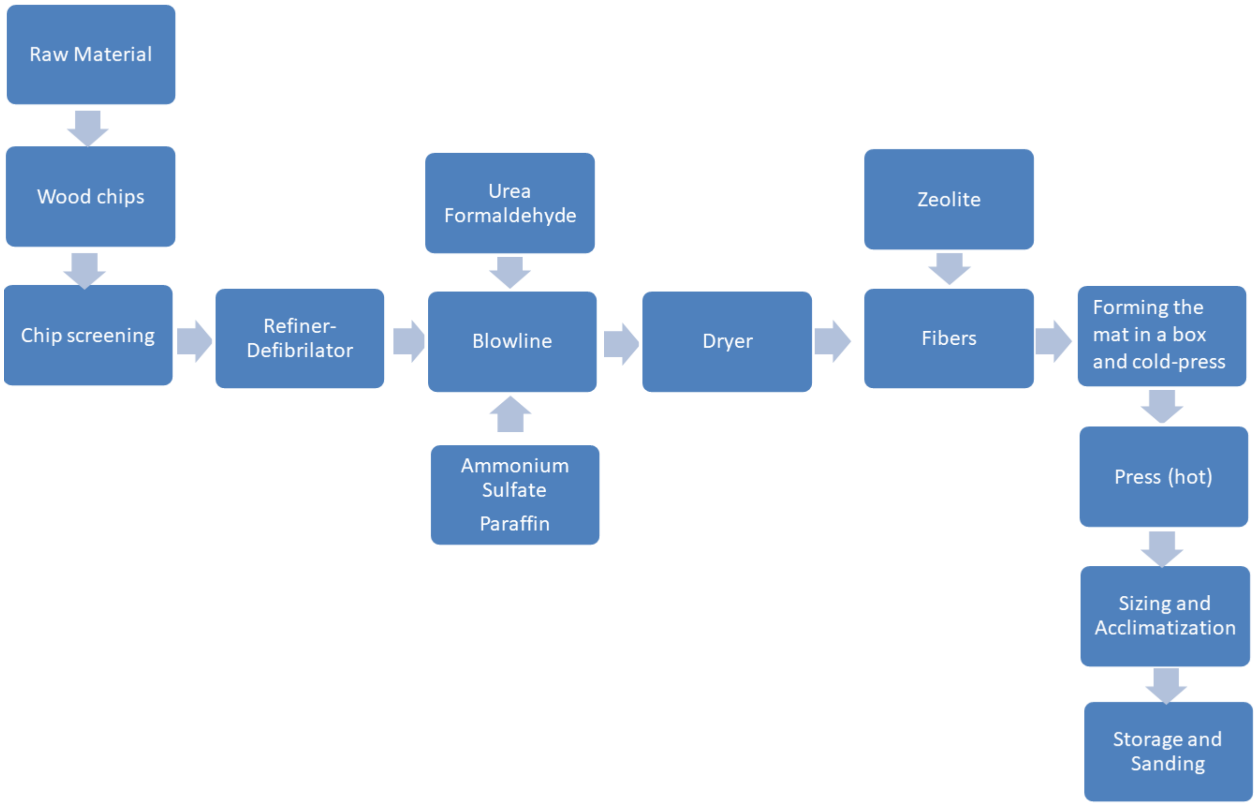

Fig. 1.
Workflow diagram of the test samples production.

Physical Properties

The experimental boards meet the general requirements of ISO 9424 (2003) and EN 622-5 (2009) standards. Density and moisture content (MC) of boards were determined using TS EN 323 (1993) and TS EN 322 (1999) standards, respectively. TS EN 317 (1993) standard was used to determine the thickness swelling (TS, 24 hours) and water absorption (WA, 24 hours). Boards' properties were tested using laboratory testing machine, IB700 (IMAL SRL, Italy), in compliance with standards.

Formaldehyde Emission Analysis

EN 717-2 (1994) standard was used to determine formaldehyde release of control and Zeolite modified boards by Gas analysis method.

Statistical Analysis

Independent samples T test (Mann-Whitney U) and ANOVA were used to compare means using SPSS software. Linear regression analysis ($p < 0.05$) was performed to identify relation between results of R and Z boards.

RESULTS AND DISCUSSION

Thickness

According to statistical analysis ($t_{0.05:8}$=1.234), seen in Table 3, no statistical significant differences between the thicknesses of control and Zeolite modified boards were seen. However, control boards were 0.55% thicker than the modified boards.

Table 3

Statistics analysis for thickness of boards

Boards		**N**	**Average**	**Standard Deviation**	**Standard Error of the Mean**	**t (95% CI*)**	**df**	**p**
Thickness (mm)	R	5	14.64	0.11	0.05	1.234	8	0.252
	Z	5	14.56	0.09	0.04			

**Confidence Interval*

Density

As seen in Table 4, no statistically significant differences (P: 0.154) between the density of the control and Zeolite modified boards were observed. According to t test result ($t_{0.05:5.79}$ =-1.63), it's seen that the variances were not homogeny and density of the Zeolite modified boards were 0.4% higher than the control boards. However, densities of the both MDF boards were in the range of standard (0.65 <MDF <0.80g/cm³).

Table 4

Statistics for density of boards

Boards		**Average**	**Standard Deviation**	**Standard Error of the Mean**	**t (95% CI)**	**df**	**p**
Density (kg/m³)	R	712.60	3.44	1.54	-1.639	5.797	0.154
	Z	715.40	1.67	0.75			

Moisture Content (MC)

According to the t-test results ($t_{0.05:5.014}$=-11.690), seen in Table 5, there are statistically significant differences between the MC of the control and modified boards. MC of the Zeolite modified boards was 8.2% higher than the control boards. Therefore, it's seen that Zeolite tends to absorb further moisture. But, it should be taken into account that, one of the most affecting factors on the mechanic properties of wood or wood based materials is moisture (Aydın and Yılmaz Aydın 2020).

Table 5

Statistics for MC properties of boards

Boards		**Average**	**Standard Deviation**	**Standard Error of the Mean**	**t (95% CI)**	**df**	**p**
MC (%)	**R**	4.210	0.022	0.010	-11.690	5.014	0.000
	Z	4.556	0.062	0.027			

Thickness swelling (TS)

According to t-test result ($t_{0.05:8}$=-3.395), seen in Table 6, it's seen that there are statistically significant (P: 0.009) differences between the thickness swelling of control and Zeolite modified boards. However, Zeolite modified boards swelled much more than control boards. Therefore, 15.3% increase in swelling may become meaningful due to absorbance tendency of the Zeolite as seen in MC properties. Furthermore, same behavior was reported by Camlibel and Akgul (2020) for calcite added MDF boards and according to Ozdemir (2019) thickness swelling of the boards increases when the amount of the additive mineral increases. On the contrary, Donmez Çavdar (2020) reported that modification of MDF using Zeolite (ammonium and natural) improved the TS, and therefore dimensional stability. According to Kaymakçı et al. (2017) thickness swelling of WPC (pine wood flour, harmonizing medium, zeolite, and polypropylene) advanced with the increase in zeolite content.

Table 6

Statistics for thickness swelling properties of boards

Boards		**Average**	**Standard Deviation**	**Standard Error of the Mean**	**t (95% CI)**	**df**	**p**
Thickness Swelling (in Water) (%)	**R**	27.360	2.059	0.921	-3.395	8	0.009
	Z	31.540	1.827	0.817			

Water Absorption (WA)

According to the t-test results ($t_{0.05:8}$=-16.99), seen in Table 7, there are statistically significant (P: 0.00) differences between the water absorption of control and Zeolite modified boards. Remarkable increase (84.4%) in water absorption was observed when MDF panles modified using Zeolite. As aforementioned in thickness swelling, Camlibel and Akgul (2020) and Ozdemir (2019) reported increases in water absorption of the boards when modified using calcite and mineral additives, respectively. However, according to Donmez Çavdar (2020), ammonium Zeolite and natural zeolite have positive effects on WA of the modified MDF boards. Positive effect of zeolite on WA was reported by Kaymakçı et al. (2017) for WPC boards.

Table 7

Statistics for water absorption properties of boards

Boards		Average	Standard Deviation	Standard Error of the Mean	t (95% CI)	df	p
Water absorption (24 Hours) (%)	**R**	42.750	3.004	1.343	-16.994	8	0.000
	Z	78.850	3.679	1.645			

Formaldehyde emission

According to the t-test results ($t_{0.05:8}$=49.78), seen in Table 8, there are statistically significant differences between the formaldehyde gas emissions of control and Zeolite modified boards. However, there are differences (Sig. (2-tailed) <0.05) between the groups. As seen in Table, 1.5% Zeolite usage in MDF production provided significant reduction (50.3%) in formaldehyde emission when compared to control result. 84.4% and 331.2% decreases in formaldehyde emission of 3% and 9% zeolite modified MDF boards are reported by Camlibel (2020). Rashidi et al. (2019) evaluated the effect of synthesized cupric oxide and clinoptilolite zeolite on the removal of the formaldehyde from an air stream, and stated that use of this synthesis is effective for achieving the removal issue. Therefore, utilization of Zeolite in MDF production not only contributes on reduction of gas emission but also provide relatively safe and healthy board materials.

Table 8

Statistics for Formaldehyde gas emission properties of boards

Boards		Average	Standard Deviation	Standard Error of the Mean	t (95% CI)	df	p
EN 717-2 Gas analysis (mg/m^2h)	**R**	4.478	0.091	0.041	49.783	8	0.000
	Z	2.224	0.042	.0019			

CONCLUSION

Utilization of Zeolite in MDF production reduces the ability of making bonds between fibers. Reduction in bonding ability may be the reason for the setbacks in the WA and TS values. Modification of the MDF using Zeolite did not cause significant variations in thickness, density and MC properties. However, thickness swelling and particularly water absorption properties of the MDF boards were significantly increased with using of Zeolite. Furthermore, more importantly, Formaldehyde emission was decreased by the adding 1.5 wt.% Zeolite in MDF production. Therefore, as a natural mineral, utilization of Zeolite in MDF production provides relatively healthy wood-based board material for the community with low emission.

Consequently, zeolite mineral seems to have the ability of absorbing the formaldehyde and therefore reduces the gas release. Zeolite could be a promising additive for reducing formaldehyde emission in order to comply the fiberboards with international regulations but future work should be done to evaluate the optimum rate of zeolite in the particleboards and fiberboards manufacturing.

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