Effect of Calcite Addition on Technical Properties and Reduction of Formaldehyde Emissions of Medium Density Fiberboard

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Physical, mechanical, and formaldehyde emission properties were studied for medium density fiberboard (MDF) produced with oak (75%) and pine (25%) fibers that had been mechanically refined in the presence of calcite particles. The calcite slurry was prepared at two levels of solids, 1.5% and 3% (10 and 20 kg·m^{-3}). Chips were cooked for 4 min at 185 °C, under 8 bar vapor pressure in an Andritz defibrillator. 1.8% liquid paraffin, 0.72% ammonium sulphate solution, and 11% urea-formaldehyde were added by percentage based on oven-dried wood fibers in the blowline at the exit of the defibrator. The fibers were dried to 11% moisture content. MDF boards (2100 mm × 2800 mm × 18 mm) were created using a continuous hot-press process. The addition of calcite in the course of MDF production resulted in improved physical properties, such as thickness swelling (ThS 24 hours) and water absorption (WA 24 hours). MDF boards prepared with calcite exhibited higher internal bond (IB), modulus of rupture (MOR), and modulus of elasticity (MOE). Resistance to axial withdrawal of screw also was increased by addition of 3% calcite. In addition, the lowest levels of formaldehyde emission were observed for MDF prepared with calcite at the 3% level.

Keywords: MDF; Fibreboard; Calcite filler; Technical properties; Formaldehyde emission

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INTRODUCTION

Medium density fiberboard (MDF) is typically comprised of cellulosic materials, thermoset resins, hardening agents, paraffin, and chemical agents. The use of many types of inorganic minerals are being investigated in an effort to improve the physical and mechanical properties of MDF boards and to explore the potential of scavengers for formaldehyde emissions. Calcite inorganic minerals were used in this study.

Calcite minerals can be used in place of some of the lignocellulosic fibers as a filler in MDF. The calcite minerals may also be used as a formaldehyde scavenger. Güller (2001) explained that inorganic materials can be used at a level of 10 to 70% of the weight of wood chips in composite board products. Akgul and Camlibel (2008) studied the production of MDF from *Rhododendron* (*R. ponticum* L.) biomass. In their investigation, they prepared MDF boards by mixing different tree types at certain mixing ratios and examined the physical and mechanical performances. Boran *et al.* (2011) studied MDF manufactured *via* adding different ratios of some amine compounds to urea-formaldehyde resin, which had a 1:1.17 molar ratio (urea and formaldehyde synthesis ratio). According to EN standard methods, the formaldehyde content, and mechanical and physical properties of MDF were determined. Zahedsheijani *et al.* (2011) studied the potential use of Na^+ montmorillonite (Na^+MMT) nanoclay in MDF production. The objective of the researchers was to evaluate the air permeability and mass diffusivity of the MDF.

Kalaycıoğlu *et al*. (2012) performed some studies on cement composites and wood wool. According to their work, the wood wool cement boards were examined relative to their physical, mechanical, and technological properties. They reported recent development of large wood-wool cement wall elements for building. Candan *et al.* (2012) investigated effects of some production parameters on the layer thickness swelling properties of MDF. He *et al*. (2012) conducted research on formaldehyde emissions using formaldehyde-containing glues in wood-based boards. It was found that the amount of formaldehyde released in the boards was directly proportional to the amount of formaldehyde in the used glue. Salari *et al.* (2012) produced oriented strand board (OSB) by adding adhesive nano-clay-layered silicates (0%, 2%, 4%, 6%, and 8%). They tested the physical and mechanical properties of the resulting OSB

Istek *et al.* (2013) studied combustion properties of MDF coated by a mixture of calcite and various fire retardants. Mao and Kim (2013) studied the formaldehyde emission effect value of wood-based composite board made of methylene ether groups in the structure of low mole urea-formaldehyde resin. According to the results, increasing methyl ether groups in the urea-formaldehyde glue led to an increase of formaldehyde emissions. Yamanaka *et al.* (2014) employed a scalable and template-free production strategy in the synthesis of mesoporous calcium carbonate, and it was observed that the mesoporous calcium carbonate powder adsorbed formaldehyde gas. Taghiyari and Nouri (2015) made MDF by adding nano-wollastonite (NW) at 5, 10, 15, and 20 g/kg dry weight basis of wood fiber. They investigated the physical and mechanical properties of MDF. Based on the results, they suggested the use of NW at levels of 10% and 15% for internal and surface applications of MDF.

Wang *et al*. (2016) produced vermiculite-added MDF boards. They investigated the modulus of rupture (MOR), modulus of elasticity (MOE), limiting oxygen index (LOI), and simultaneous thermal analysis (TG-DSC) of MDF boards. Özdemir and Tutus (2016) investigated the effects of coating with calcite together with various fire retardants on the fire properties of particleboard. Taghiyari *et al.* (2016) produced MDF from wollastonite fibers, camel-thorn, and wood fibers. Funk *et al.* (2017) studied diatomaceous earth as an inorganic additive to reduce formaldehyde emissions from particleboards. It was found that particleboard produced with nano-mesoporous diatomaceous earth additive scavenged about 45% of the formaldehyde. On the other hand, the boards showed significantly lower internal bond and bending strength. Özdemir and Ayaz (2017) investigated the effects of ammonium polyphosphate (APP) and boric acid (BA) on the fire resistance of MDF panels as surface coating materials. Akgül *et al.* (2017) produced agri-based lignocellulosic biomass (okra, tobaccos, hazelnut, walnut shell, and pine cone) in MDF production. They investigated the physical and mechanical properties of medium MDF.

Kaya (2018) investigated the physical and mechanical properties of fiber layers produced by using a glass fiber mixture of walnut shells and sunflower stalks in different ratios. Özdemir (2019) produced medium-density fiberboard with three different minerals (sepiolite, dolomite, and perlite) and five different levels (3%, 6%, 9%, 12%, and 15%) according to the oven-dry wood fiber weight. They studied the physical, mechanical, LOI, and thermogravimetric analysis (TGA) properties of boards. Silva *et al.* (2019) produced MDF with urea-formaldehyde resin and melamine-formaldehyde attaching 0.5% and 1.0% of ZnO nanoparticles for the physical properties assessment. The objective of the researchers was to increase resistance and diminish the attack of fungi because of the use of wood-based panels in humid environments. Solt *et al.* (2019) assessed individual adhesive systems based on preferred product process, formaldehyde emission parameters, and technological parameters suitable for particleboard production. Dönmez Çavdar *et al.* (2019) examined fire, mechanical, and morphological properties of thermoplastic composites filled with fire retardant (mono ammonium phosphate, ammonium zeolite, natural zeolite) and microcrystalline cellulose.

Dönmez Çavdar (2020) studied zeolite Y and natural zeolite as filler in medium density fiberboard production with urea formaldehyde and melamine formaldehyde. She produced MDF by using three different zeolite contents within 4%, 8%, and 12% based on dry resin amount. The produced boards were tested for physical, mechanical, limiting oxygen index (LOI), and thermogravimetric properties. Ozyhar *et al*. (2020a) produced MDF with ground calcium carbonate (GCC) filler addition to make 8 mm thickness boards in the laboratory. The MDF was made with 10%, 20%, and 30% of the fibers replaced by using calcium carbonate on a weight basis (dry/dry) and within target densities of 550, 700, and 850 kg m^{-3}, respectively. However it was reported that MDF contains more than 10 wt% of ground calcium carbonate in place of wood fiber, the physical and mechanical properties of the boards are more negatively affected.

The aim of this study was to explore the possible use of calcite as a partial substitute for lignocellulosic raw materials. There are millions of tons of the calcite mineral reserves in Turkey. In the MDF production process, the calcite mineral, which had the mixing ratio of 1.5% or 3%, was produced for boards on an industrial process scale. Formaldehyde gas emissions released from wood-based panel products is desired to be at CARB 1 or CARB 2 levels for indoor living conditions. The California Air Resources Board (CARB 2007) adopted regulations to limit the amount of formaldehyde radiated from composite wood products. These regulations are related to formaldehyde emission levels from composite wood products. In this study, the experimental investigations aimed to realize the technical properties and formaldehyde gas analysis properties of the produced boards that contained calcite mineral in comparison to control specimens prepared without calcite.

EXPERIMENTAL

Raw materials

Oak wood (*Quercus robur* L.) from Kastamonu province forestry (Turkey) and pine (*Pinus sylvestris* L.) from Bolu province (Turkey) were used for the production of MDF.

Resin

Urea formaldehyde was produced by Kastamonu Glue Plant (Kastamonu, Turkey). Properties of the glue were as follows: solid content 62 ± 1%; molar ratio of U:F (urea: formaldehyde) for UF was 1.17; density 1.227 g·cm^{-3} (at 20 °C); viscosity (250 C cps) 20 to 35 s; gel time (100 °C) (20% $(NH_4)_2SO_4$): 20 to 45 s; pH 7 to 8.5; free formaldehyde 0.20% max; methylol groups 12 to 15%; and shelf life of 75 days.

Hardener

The ammonium sulphate was supplied from a private company from Gebze (Turkey), the catalyst used was 20% ammonium sulphate $(NH_4)_2SO_4$ solution (density of 0.95 g/cm^{-3} and pH 6.5).

Paraffin

The liquid paraffin used was dirty white and liquid form. It had a solids content of 60%, the pH was 9 to 10, viscosity was 13 to 23 s, and the density was 0.96 g·cm^{-3}. The liquid paraffin was supplied from Mercan Chemistry in Denizli (Turkey).

Calcite

Calcite was provided from Niğde province (Nigpaş Calcite Mining Company, Nigde, Turkey). The calcite consisted of 90% $CaCO_3$ containing limestone with Mohs hardness 3 and the specific gravity of 2.5 to 2.7 g·cm^{-3}. Natural micronized calcite was supplied by Nigpaş Calcite Mining Company in Nigde, Turkey.

Methods

Product parameters

The wood fiber contained 75% hardwood and 25% softwood fibers in this study. According to Table 1, the R defines the consumed wood fibers for 1 m^3 board, X defines the consumed 1.5% calcite minerals for 1 m^3 board, and Y defines the consumed 3% calcite minerals for 1 m^3 board. The raw materials formulation for the experimental MDF boards are presented in Table 1. This table shows the addition of calcite suspension and other chemicals to lignocellulosic biomass. Xing *et al*. (2006) showed that wood acidity has a direct effect on the gel time and curing behavior of the UF resins. In this study, the amount of calcite had no significant effect on the curing of the glue.

Table 1. Experimental Design

Board	Product	Biomass (F)	Added Calcite Filler (C)	Resin (UF)	Hardener (AS)	Paraffin (P)
Type	Type	Industrial Fibers (%)	(%)	(%)	(%)	(%)
R	MDF	100	0	11	0.72	1.8
RX	MDF	98.5	1.5	11	0.72	1.8
RY	MDF	97	3	11	0.72	1.8

R: Fiber content; MDF: medium-density fibreboard; F: lignocellulosic; UF: urea formaldehyde; AS: ammonium sulphate; C: calcite; P: paraffin

Boards Manufacturing

The hardwood and softwood species were from the Western Black Sea forests (Turkey). In the production of MDF, the oak and pine fibers were used as raw material, and then these species were chopped and stored one-by-one in silos according to the production parameters listed in Table 1. The calcite minerals were prepared in individual containers to obtain calcite to be used in place of lignocellulosic fibers. After that, calcite fillers were prepared in percentages of 1.5% and 3% in two different tanks. The calcite fillers were mixed in with the chips. Chips were cooked for 4 min at 185 °C, under 8 bar vapor pressure in the Andritz Defibrator (2008 model; Andritz AG, Graz, Austria). The resins and other chemicals were prepared in the glue plant. After that, these chemicals were sent to production resin tanks. Then chemicals were sent to the blowline. The adhesive (urea formaldehyde) was used with 11 wt% based on oven-dried wood fibers. Ammonium sulphate as hardener was used with 0.72 wt% based on UF resins. The paraffin was added as 1.8 wt% based on each adhesive to raise the water-resistance of the MDF panels during the production. The fibers were dried to 12% moisture content. Continuous hot pressing was applied. Experimental MDF boards were manufactured (hot press 2008 model; Siempelkamp ContiRoll, Krefeld, Germany). The hot press was applied at 210 to 220 °C and pressure of 32 to 34 kg·cm^{-2}, press speed of 350 mm·sec^{-1}, 160 s pressing time, and press factor of 8.50 mm·s^{-1} during pressing time. The dimensions of the boards were cut to 2100 mm × 2800 mm ×18 mm. Then, the boards were left to rest in pre-storage for 5 days. The panels were acclimatized. The moisture level was adjusted to 4.5%. After this process, the top and bottom surfaces of panels were sanded with 40, 80, and 120 grit size sandpaper.

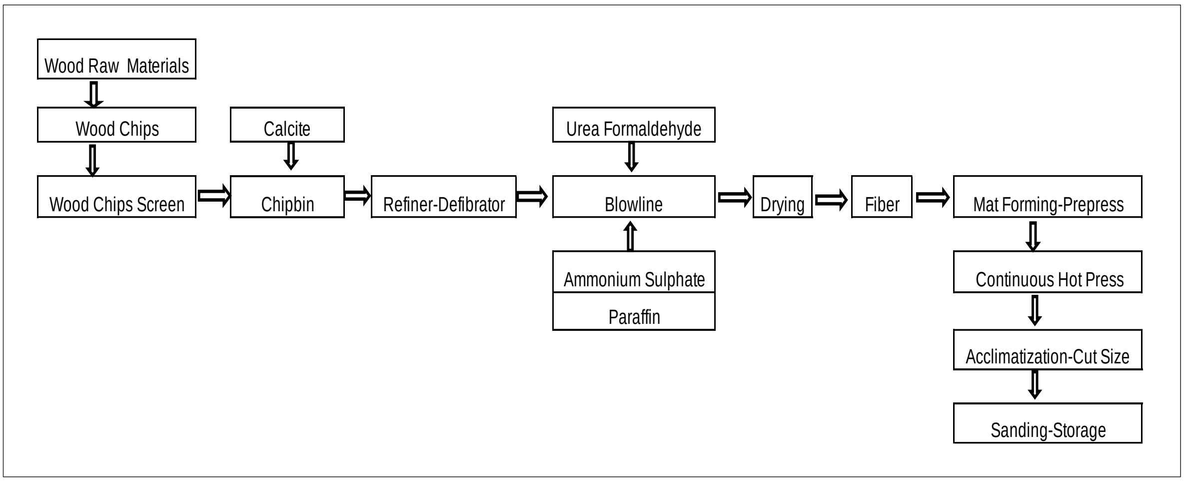

Fig. 1. Product process flow

The MDF boards were created in the MDF production line by Kastamonu Integrated Wood Inc. (Kastamonu, Turkey). Then, all boards were conditioned at 20 ± 2 °C and 65 ± 5% relative humidity according to ISO 554 (1976). The MDF boards manufacturing process flowsheet is shown in Fig. 1.

Physical Testing

Physical properties were tested according to EN 622-5 (2006), and the density of MDF sheets was tested according to EN 323 (1999). The moisture contents of boards were tested according to the EN ISO 287 (2017) standard. The thickness swelling (ThS, 24 hours) and water absorbtion (WA, 24 hours) properties were investigated according to the EN 317 (1999) standard. Thickness and length of sample specimens were measured using a digital micrometer and caliber with 0.01-mm graduations.

Mechanical Testing

The cutting and sizing were performed according to EN 325 (1999) and EN 326-1 (1999) standards and was performed to specify the properties of MDF boards with calcite. These tests were bending strength as per EN 310 (1999), modulus elasticity as per EN 310 (1999), internal bond as per EN 319 (1999), surface soundness of medium-density fibreboard as per BS EN 311(1992), and resistance to axial withdrawal of screw of board as per BS EN 320 (2011). A universal tester (model IB700; Imal Mobiltemp shc 22, San Damaso, Italy) was used to assess both mechanical and physical properties.

Formaldehyde Gas Analysis

Formaldehyde gas analysis of MDF with calcite added formaldehyde was tested according to BS EN 120 (1992), which specifies determination of formaldehyde content in wood-based panels by the perforator method.

Statistical Analysis

One-way analysis of variance (ANOVA) was performed to the test for differences among different board types R, RX, and RY in mean values of all the measured variables. Linear regression ($p < 0.05$) was applied to research the relationship among pyhsical tests, mechanical tests, formaldehyde emission, and the calcite fillers' content of the tested boards R, RX, and RY. As an assesment of these tests, Duncan results were evaluated by the statistical program SPSS 22 (SPSS Software, IBM Corporation, Armonk, NY, USA)

RESULTS AND DISCUSSION

Physical Properties

The results of ANOVA and Duncan's mean separation test for board thickness (mm), density (kg·m^{-3}), board moisture content (%), thickness swelling (TS, 24 h), and water absorption (WA, 24 h) of the fiberboards made from calcite-added fiber and the control fiberboards are shown in Table 2.

Table 2. Control and Calcite Added MDF Board Physical Tests (Board Thickness, Density, Moisture Content, TS 24 h, and WA 24 h)

Samples Calcite		Avg.^{x}	Std. Deviation	Board Calcite		Avg.^{x}	Std. Deviation
Board Thickness (mm)	R	18.64^a	0.12	TS 24 h (%)	R	7.02^a	0.23
	RX	18.60^a	0.08		RX	9.40^b	0.03
	RY	18.70^a	0.04		RY	9.35^b	0.02
Density (kg · m^{-3})	R	725.2^a	1.79	WA 24 h (%)	R	27.89^a	0.03
	RX	729.4^b	1.67		RX	33.83^b	0.05
	RY	726.2^a	1.48		RY	33.47^c	0.05
Moisture Content (%)	R	4.91^a	0.03				
	RX	5.36^b	0.02				
	RY	5.08^c	0.02				

x: Average value of the samples, 95% confidence interval for the average ANOVA; a, b, and c: values with the same letter are not significantly different (Duncan's test); the label "R" means MDF made with just wood fibers. "RX" is with 1.5% calcite, and "RY" is with 3% calcite.

Board thickness

There were no significant differences between R, RX, and RY according to the percentage of board thickness test. The results are shown in Table 2. The ratio for this test decreased 0.27% for RX relative to R. Similarly, the ratio increased by 0.28% for RY relative to R. Therefore, the percentage of board thickness appeared to decrease for RX but appeared to increase for RY. The apparent changes were not significant at a 95% level of confidence.

Board density

The conclusions are shown in Table 2. There was a significant difference in densities for calcite-added panels R, RY, and RX according to this statistical analysis results. The results of MDF densities stayed in the range 0.65 < MDF < 0.80 g·cm^{-3} according to the TS EN 622-5 (2006) standard. Thus, according to Table 2, there was a significant difference in the results. The efficiency of process parameters and the applied continuous hot-press parameters in MDF production affected the optimum homogenous density of the fiberboard. The addition of calcite minerals resulted in no change of gel time and the fixed density of MDF.

Board moisture content

There was a significant difference between R, RX, and RY with respect to the percentage of board moisture content. The results are shown in Table 2. The ratio for this test was 9.07% for RX relative to R. Similarly, the ratio was 3.29% for RY according to R. Therefore, the percentage of board moisture content increased for both RX and RY.

Board swelling in water for 24 h test (TS)

There was a significant difference between R, RX, and RY relative to the percentage of board swelling in water for 24 h. The results are listed in Table 2. The ratio for this test was 34.4% for RX relative to R. Similarly, the ratio was 33.7% for RY relative to R. This means that the percentage of board swelling increased for both RX and RY. This increase in the both thickness swelling and water absorption properties of the boards can be attributed to the material properties of the mineral materials such as hydrophilic properties (Özdemir 2019).

Water absorption for 24 h test (WA)

There was a significant difference between R, RX, and RY according to the percentage of the board water absorption during 24 h. The results are shown in Table 2. The ratio for this test was 21.3% for RX relative to R. Similarly, the ratio was 20.0% for RY relative to R. These findings are supported by other work. For instance, it was found that as the resin content increased, moisture content increased, and also the continuous press speed increased, both the TS values and water absorption of MDF panels decreased (Candan *et al.* 2012). In other work the thickness swelling and water absorption (WA) properties of the test panels increased as the amount of mineral filler was increased (Özdemir 2019).

The increase in WA and TS was attributed to the fact that some parts of hydrophilic wood fibers were exchanged by the inorganic mineral. Due to the increase in the amount of calcite filling between wood fibers, the bonding of wood fibers with each other decreased. The physical properties of the fiber boards were determined according to the raw material source, quantity, and type of additives, resin ratio, and press conditions in MDF boards (Kaya 2018).

With the addition of 1.5% and 3% of calcite minerals, used for 1.17 mole urea-formaldehyde resin board production, it was found that the results were similar for board density, board thickness, and board moisture content. The amount of added calcite filler had a significant effect on the physical properties such as thickness swelling (24 h), water absorption (24 h), and bonding quality of calcite in the mix of fibers of manufactured MDF.

Mechanical Properties

The results of ANOVA and Duncan's mean separation test for internal bond, bending strength, modulus elasticity, resistance to axial withdrawal of screw of board, and surface soundness of the fiberboards made from calcite-added fiber and of the control fiberboards are shown in Table 3.

Internal bond (IB) test

There was a significant difference between R, RX, RX, and RY according to the percentage of internal bond (IB) test. The results are shown in Table 3. The ratio for this test was 2.87% for RX relative to R. Similarly, the ratio was 2.3% for RY relative to R. Therefore, the percentage of the internal bond increased for RX and decreased for RY.

Table 3. Mechanical Properties of the Calcite-added Fiberboards and Control Fibreboard

Samples Calcite		Avg.^{x}	Std. Deviation	Board Calcite		Avg.^{x}	Std. Deviation
Internal Bond (IB) (N· mm^{-2})	R	0.696^{ab}	0.02	Resistance to Axial Withdrawal of Screw (N)	R	904.4^a	1.14
	RX	0.716^b	0.03		RX	853.1^b	3.16
	RY	0.68^a	0.02		RY	882.2^c	1.92
Bending Strength (MOR) (N· mm^{-2})	R	27.29^a	0.23	Surface Soundness (N mm^{-2})	R	1.37^a	0.02
	RX	26.52^b	0.24		RX	1.24^b	0.03
	RY	25.22^c	0.13		RY	1.15^c	0.02
Modulus Elasticity (MOE) (N· mm^{-2})	R	2902.2^a	7.66				
	RX	2926.1^b	3.81				
	RY	2872.8^c	2.39				

x - The average value of the samples; 95% confidence interval for the average ANOVA; a, b, and c values with the same letter are not significantly different (Duncan's test)

Mineral filler type and usage rate had a negative effect on internal bond (IB) values (Özdemir 2019). In this study, as the use rate for calcite minerals increased, the mechanical results in the IB values decreased. Ozyhar *et al.* (2020a) performed a study of GCC filler addition on MDF production in which the data of the 550 and 700 density boards showed that the IB properties decreased as the minerals amount increased. Calcite added RX boards provided better results of mechanical properties (internal bond modulus elasticity) compared to R control boards. Camlibel and Akgül (2020) explained that as the calcite usage rate increases in MDF production the internal bond value in MDF boards decreases. However, in the present study, MDF boards with 1.5% calcite added exhibited higher internal bond values higher than the values of the control boards.

Bending strength test (MOR)

There was a significant difference between R, RX, and RY according to the percentage of bending strength test. The results are shown in Table 3. The ratio for this test was 2.82% for RX relative to R. Similarly, the ratio was 7.59% for RY relative to R. Therefore, the percentage of bending strength decreased for both RX and RY.

The increase in the mineral filler content reduced the effect of interconnection among the fibers, causing MOR and MOE resistance to be adversely affected (Özdemir 2019). In the study of GCC filler addition on MDF production (Ozyhar *et al.* 2020a), the data of the 550, 700, and 850 kg·m^{-3} density boards showed that the bending strength (MOR) properties decreased as the filling amount increased.

MOE test

There was a significant difference between R, RX, and RY according to the percentage of modulus elasticity test. The results are shown in Table 3. The ratio for this test was 0.82% for RX relative to R. Similarly, the ratio was 1.01% for RY relative to R.

Mineral fillers increased the contact surface between the fibers and the glue and also created a barrier effect. The intermolecular force and the sliding rubbing force between the constituents of the MDF was reduced rapidly, resulting in a reduced MOR and MOE (Wang *et al*. 2016). In this study, as the calcite minerals increased, RX MOE properties increased but RY MOE properties were reduced. According to the results of Camlibel and Akgül (2020), as calcite minerals usage percentage increases in MDF production there was a negative effect on physical and mechanical properties. Calcite minerals usage ratios (3% and 6%) were recommended for MDF production.

Resistance to axial withdrawal of screw test.

There was a significant difference between R, RX, and RY according to the percentage of the resistance to axial withdrawal of screw test. The results are given in Table 3. The ratio for this test was 5.68% for RX relative to R. Therefore, the percentage of the resistance to axial withdrawal of screw board decreased for RX. Similarly, the ratio was 2.45% for RY according to R. Therefore, the percentage of the resistance to axial withdrawal of screw of board decreased for RY.

Surface soundness test.

There was a significant difference between R, RX, and RY according to the percentage of surface soundness test. The results are listed in Table 3. The ratio for this test was 9.34% for RX relative to R. Therefore, the percentage of surface soundness decreased for RX. Similarly, the ratio was 15.47% for RY relative to R. Therefore, the percentage of surface soundness decreased for RY. With an increase of calcite mineral interfering with wood fibers and a reduction in the surface soundness for creating an adhesive bond with the wood fibers, an impairment in the created fiber-to-fiber glue bonds was expected. In this study, it was seen that surface soundness test results decreased.

The amount of added calcite filler had a significant effect on the mechanical properties such as IB, MOR, MOE, resistance to axial withdrawal of screw of board, surface soundness, and bonding quality of calcite in the mixed fibers of manufactured MDF. Consequently, introduction of 1.5% and 3% calcite minerals caused a minor deterioration of MDF mechanical properties.

According to inter-fiber bonding quality, the IB, MOR, MOE, resistance to axial withdrawal of screw of board, and surface soundness depended on the amount the filler.

Özdemir (2019) explained that the minerals (sepiolite, dolomite, and perlite) usage ratio increase in MDF manufacture led to a negative effect on physical and mechanical properties results.

A calcite mineral usage ratio of 1.5% in boards had the best effect on physical and mechanical properties results.

Formaldehyde Gas Analysis

The results of the ANOVA and Duncan's mean separation test for formaldehyde gas analysis made from calcite-added board and control fiberboards are shown in Table 4. There was a significant difference between R and both RX and RY according to the percentage of formaldehyde gas analysis. The results are explained in Table 4. The ratio for this test decreased 26.6% for RX relative to R. Similarly, the ratio decreased 27% for RY relative to R. Therefore, the percentage of the formaldehyde gas analysis decreased for both RX and RY.

Formaldehyde gas analysis was performed according to BS EN 120 (1992). According to Table 4, the results were important, resulting in a reduction in formaldehyde gas analysis (21%) due to the increased calcite minerals. Therefore, the calcite mineral was effective as a scavenger for formaldehyde in MDF production. For 3% calcite minerals, formaldehyde emission showed the best alaysis property results and gave the lowest free formaldehyde content (21.2%). Calcite minerals usage ratio 3% in boards had the best effect on formaldehyde gas emission results.

Table 4. Formaldehyde Gas Analysis of the Calcite-added Fiberboards and Control Fibreboard

Samples	Type	Avg.x	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Formaldehyde Content (mg $100gr^{-1}$)	R	25.29[a]	0.03	0.01	25.26	25.32	25.26	25.33
	RX	19.98[b]	0.26	0.12	19.66	20.31	19.55	20.26
	RY	19.92[b]	0.12	0.05	19.78	20.07	19.83	20.10

x: The average value of the samples; 95% confidence interval for the average ANOVA; a, b values with the same letter are not significantly different (Duncan's test)

Calcite added MDF boards properties are shown as a graph in Fig. 2. The parameters R (consumed wood fibers for 1 m^3 board), RX (consumed 1.5% calcite minerals for 1 m^3 board), RY (consumed 3% calcite minerals for 1 m^3 board), and S (standard values according to reference EN , ISO, EN ISO and BS EN) are shown in the figure.

Wang and Zang (2020) explained that surface roughness plays a significant role in the wettability and floatability of calcite particles. According to Wenzel's (1936) principle, the rough nature of the surface of calcite will tend to increase the wettability of its surface if it is hydrophilic, while it will enhance the hydrophobicity of the mineral if it is hydrophobic. For instance, it might be rendered hydrophobic by being covered with a monolayer of extractive compounds from the wood. A good correlation has been found between the wettability and surface energy of various roughness surfaces .

Obviously the co-refining of the calcite in the presence of wood defibration exposes the calcite to wood extractives. One might propose that the carboxylic acids (fatty acids and resin acids) would be interacting to some extent with the calcium sites at the mineral surfaces. This would render the calcite somewhat hydrophobic.

Camlibel and Akgul (2020) reported the addition of calcite at levels of 3%, 6%, and 9% substitution of wood fibers in MDF production. As the amount of calcite was increased, the physical properties of the board deteriorated. However, according to the test results, the mechanical properties of boards with 6% calcite content showed better performance than the control boards.

Calcite usage rates (3%, 6%) were recommended for MDF production by the researchers. Fimbel and Siffert (1986) studied the mutual effect between cellulose fibers and calcium carbonate particles. The quantity retained by the fibers was 1.4 g/g of dry cellulose. They reported that calcite minerals were deposited on the cellulose surface; increased deposition was observed with increasing addition of ions. Subramanian *et al.* (2005) investigated composites of precipitated calcium carbonate and pulp manufactured by co-precipitating calcium carbonate in pulp. It was found that well distributed precipitated calcium carbonate particles and a higher fraction of optically active cellulose surfaces contributed to an increased optical performance of papers with composite fillers.

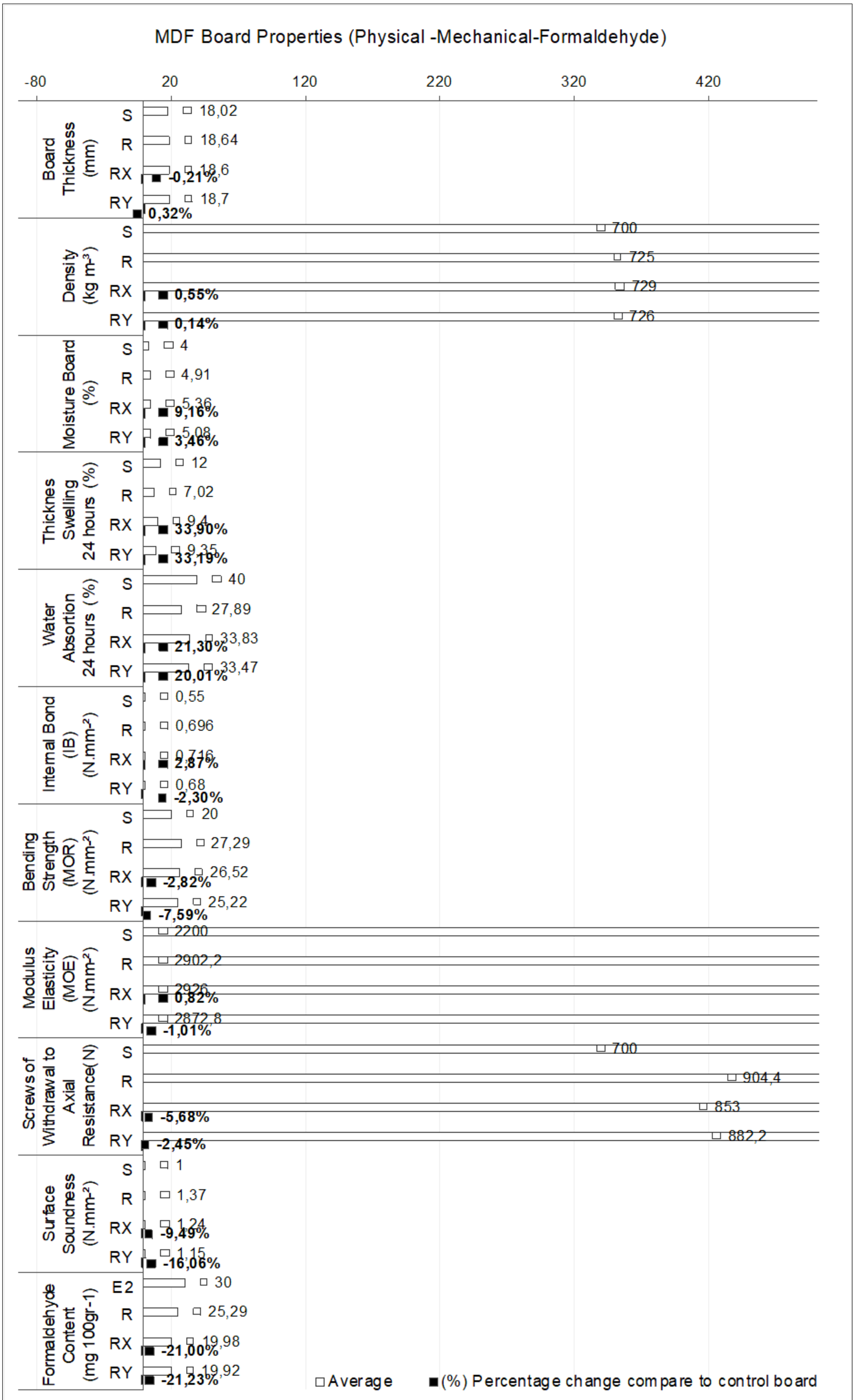

Fig. 2. The results of the test properties (physical, mechanical, and formaldehyde) of calcite addition boards and standard values according to reference

Ozyhar *et al.* (2020a) produced fiberboards with 10%, 20%, and 30% fibers replaced by calcite weight basis (dry/dry) and three different target densities (550, 700, and 850), respectively. According to results, the addition of mineral filler to fiberboards up to grades of 10 wt% had little effect, if at all, on the fiberboards properties. According to the author's description, calcite had no effect on the strength development in the curing of the resin and thickness swelling. In addition, formaldehyde and volatile organic compound emissions of the product were not affected by filler additive grades of up to 10 wt%. Although resins without formaldehyde are used in particleboard production or natural wood products, a certain amount of formaldehyde gas was released as a result of formaldehyde gas measurement (Solt *et al*. 2019). Ozyhar *et al.* (2020b) investigated the use of alkenyl succinic anhydride and surface-treated calcite (10 wt%, 20 wt%, and 30 wt%) in properties of wood fiber-reinforced polylactic acid composite board. According to study results, calcite minerals additive provided both better control of fluidity during processing and significant economic advantages because of taking the place of polylactic acid in the composite. Huuhilo *et al.* (2010) tested for wood-plastic composites with addition calcium carbonate, soapstone, talc, and two different types of wollastonite. The mineral addition improved the tensile strength and hardness of the wood-plastic composites. However, the acicular shape of wollastonite became crushed during the manufacturing process.

The mechanical, physical, and formaldehyde properties are shown graphically in Fig. 2, to allow a better understanding of differences between groups. The figure makes it possible to calculate percentage differences of control MDF board relative to MDF with calcite added. The test results for 1.5% and 3% calcite added boards samples are shown relative to the control and standard reference values. According to this study, boards prepared with 3% calcite showed the best performance of physical properties and formaldehyde scavenger emission. Boards with 1.5% calcite added exhibited the best performance of mechanical properties. A calcite mineral level of 3% in boards provided the best effect on formaldehyde gas emission results. In this study, all test results showed a positive performance compared to the control and standard reference values.

CONCLUSIONS

1. Introducing calcite mineral as a partial replacement for lignocellulosic fibers as a filler into the medium density fibreboard (MDF) had a significant effect on the physical, mechanical, and formaldehyde emission properties of the fillers.
2. Regarding the 24-h thickness swelling (ThS) and water absorption, it was observed that the addition of 1.5% of calcite minerals presented the best results, indicating the improvement in the performance of the panels in contact with calcite. However, an addition of 3% calcite minerals gave less favorable results.
3. According to the results on internal bond (IB) and modulus of elasticity (MOE), the samples with addition of 1.5% calcite minerals presented better results than the control samples. The addition of 3% calcite minerals (RY) indicated that the results decreased in the board for IB, MOR, and MOE, resistance to axial withdrawal of screw of board, and surface soundness. The highest MOE was measured on the boards with 1.5% calcite (RX).
4. Regarding the formaldehyde emission according to the BS EN 120 (1992) standard, it was observed that the addition of 3% calcite minerals (RY) presented the best results, indicating an improvement in the performance of the panels in contact with calcite

minerals. The results indicated that for formaldehyde gas emission, as the amount of calcite increased in board production, the lowest level was present in the RY boards. Due to the increasingly restrictive regulations on the emission of harmful formaldehyde (CARB-2), it was beneficial to reduce its content in MDFs manufactured with the use of calcite minerals. The free formaldehyde emission was significantly lowered in all variants containing calcite minerals. The maximum reduction was 21.2% compared to control samples.

5 Calcite minerals may be used as a formaldehyde scavenger for UF resins in MDF production.

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