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Article

Effect of Lignin Modification of Recycled and Fresh Wood Fibers on Physical, Mechanical, and Thermal Properties of Fiberboard

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Abstract: In this study, some physical properties; the thickness swelling, water absorption, surface absorption, formaldehyde emission, and some mechanical properties; internal bond strength, bending strength, bending modulus, and surface soundness of the MDF panels produced using recycled fibers obtained from the waste MDF and fresh wood fibers were investigated. Moreover, the effect of the kraft lignin modification to the recycled fibers and fresh fibers on the bond strength and mechanical properties of the MDF panels was determined. The results were compared with the MDF panels produced using fresh wood fibers. Although replacing fresh fiber with recycled fibers adversely affected the thickness swelling/water absorption (water resistance) and strength properties of fiberboard, the modification of the fibers using the lignin improved the properties of the fiberboard. The internal bond strength of the MDF produced with the 10 wt% recycled fibers modified at the 5 wt% and 7.5 wt% lignin contents was found to be higher than that of the specimens produced with 100 wt% fresh pine fibers. The formaldehyde emission of the MDF increased with increasing recycled fibers content. The lignin modification slightly decreased the formaldehyde emission of the MDF with the recycled fibers. Consequently, it can be said that the utilization of untreated recycled fibers decreased the mechanical properties of the MDF while the modification of these fibers using kraft lignin (5 wt% and 7.5 wt%) improved the mechanical properties, water resistance, and decreased formaldehyde emission of the MDF.

Keywords: fiberboard; kraft lignin; thickness swelling; mechanical properties; formaldehyde emission; urea-formaldehyde resin

Citation: Gürsoy, S.; Ayrilmis, N. Effect of Lignin Modification of Recycled and Fresh Wood Fibers on Physical, Mechanical, and Thermal Properties of Fiberboard. *Forests* **2023**, *14*, 2007. https://doi.org/10.3390/f14102007

Academic Editor: Mathieu Petrissans

Received: 7 September 2023
Revised: 25 September 2023
Accepted: 3 October 2023
Published: 6 October 2023

1. Introduction

MDF is the second most used panel in the furniture industry after particleboard; MDF is also embedded in products such as door skins, moldings, and laminate flooring in buildings. The worldwide MDF production has continuously increased from approximately 23.6 million m^3 in 2001 to nearly 111 million m^3 in 2021 [1]. The global furniture industry generates a huge volume of waste wood and wood-based panels, especially particleboard and MDF. However, there is increasing concern about the disposal of MDF boards following use. Due to the presence of the organic composition, re-use of MDF is very limited and its disposal causes the environmental problems. Generally, most of these wastes are disposed of in landfills or incinerated at the end of its service life [2]. MDF emits free formaldehyde, which is a hazardous chemical that is harmful to human when breathed [3]. Hence, the firing of the waste MDF in an open air in oven has been banned in many countries [4]. Furniture manufacturers and designers are changing consumer behavior because they create a perception on the end users of a fashion product rather than a durable product,

and therefore the lifespan of MDF panels is shorter than in the past. In general, the life span of the general purpose MDF panels is between 15 and 20 years before becoming waste [5].

The recycled fibers obtained from waste MDF offer a new, low-energy, and reliable source of raw materials for MDF manufacturers. Nevertheless, because of the hydrothermal or steam-based defibrillation processes in the MDF production process, the combined effects of some disadvantages, for example fiber shortening, alterations in the chemical composition of the fibers, and the cure resin residues on their surfaces, may cause a deterioration in the strength properties and water resistance of the MDF as compared to the MDF produced with fresh wood fibers [6]. Especially, the interfacial bond strength between the fibers is inferior compared to the MDF panels made from 100% fresh wood fibers [7]. The recycling process causes mechanical changes in the fibers, which can be the cause of the loss of up to 30% of the original strength. Furthermore, it is inevitable that MDF, which has completed its life and is scrapped, will harm the environment if it is placed in the ground or burned. Today, although natural fibers are widely used in biocomposites [8–11], the use of the recycled fibers of waste MDF panels from the furniture industry and defective MDF panels after hot pressing in the MDF process is very limited (only 2%–3%) [12]. One of the best recycling methods is that waste MDF boards can be made into fibers and mixed with fresh wood fibers or used completely in MDF production [7,12,13]. For example, Roffael et al. [12] replaced 33 wt% of fresh fibers with recycled fibers and the internal bond (IB) strength reduced by about 26%, and the higher amount of the recycled fibers did not meet the standard requirements of the MDF panel.

Although the use of bio-based adhesives in the particleboard industry is insufficient, scientific studies in this field are increasing. Currently, with the increasing trend towards sustainable materials, MDF manufacturers are also showing an interest in bio-based adhesives. The raw material of synthetic glues is largely based on oil and natural gas, and their prices are increasing gradually due to the decreasing fossil fuel reserves. Therefore, priority is given to the production of sustainable environmentally friendly bio-based adhesives. The development of open-air and water-resistant adhesives, whose raw materials are renewable resources, is of great importance for the future.

Lignin is the second most abundant natural polymer in nature following cellulose. Its polyphenolic structure has always aroused interest in the preparation of wood adhesives. Lignin, one of the main structural components of wood, is a largely branched three-dimensional biopolymer. Lignin is isolated commercially as a by-product of the pulp and paper industry, mostly as kraft lignin and lignosulfonates [14]. It has a hydrophobic character as compared to cellulose and hemicellulose. Recently, the use of lignin as an adhesive for wood-based panels or the modification chemical in wood has gained scientific attention.

Currently, none of the glues made from pure lignin have been commercialized [15]. However, they have been found to be successful with the addition of synthetic glue [15]. The chemical extraction or processing of lignin causes even greater variation among different lignins [16]. In general, harsher purification conditions have been found to result in more significant changes in the structure. One of the most obvious examples of this is the kraft process for the manufacture of chemical wood pulp. Due to the elevated temperatures and alkali treatment, the structure of lignin changes significantly during the wood pulping processing. The kraft lignin is a resistant material that is less reactive than natural lignin. The utilization of the kraft lignin in the production of wood-based panels has been widely studied [16–19]. In a previous study, it was determined that adding up to 20 wt% of phenolized kraft lignin only slightly reduced the IB strength of the UF resin in particleboard, while significantly reducing the formaldehyde emission of the particleboard [18]. Another pre-treatment method for the application of lignin esterified with maleic anhydride in UF resins was recently studied by Gao et al. [19] for application in plywood and MDF as an additive in the resin. Lignin with 5 wt% maleic anhydride-modified composition was used as a binder in UF resin for the production of plywood. The results showed that the water absorption of the plywood decreased in comparison to the reference UF resin-treated

plywood [19]. The utilization of MDF waste as a potential lignocellulosic raw material in the manufacture of MDF can be one of the best uses instead of burning it or dumping it into the soil. In addition, recycled or waste MDF may partially contribute to the raw material supply problem in MDF production, which is one of the most important bottlenecks of the MDF industry [7,20].

According to the results of previous studies, the water resistance and strength properties of the MDF panels produced from waste MDF fibers were lower than those produced entirely from fresh wood. The first objective of the present study was to find industrial uses for the waste MDF panels in the MDF process without reducing the mechanical properties of the panels. For this aim, the recycled and fresh wood fibers were modified with the kraft lignin prior to the MDF production using urea-formaldehyde (UF) resin. The MDF panels were produced by adding different ratios of the recycled wood fibers (10 and 30 wt%) and fresh wood fibers. Secondly, we aimed to understand the overall impact of lignin modification of the recycled and fresh wood fibers on the water resistance, strength properties, formaldehyde emission, and thermal properties of the MDF.

2. Materials and Methods

2.1. Preparation of Raw Materials

Fresh wood fibers were supplied from Kastamonu Integrated Wood Company, Gebze plant, Kocaeli, Turkey. First, the pine chips were pre-heated in a digester silo and then transferred into the digester. The chips were softened at 9 bar, 170–180 °C for 2.5 min in the digester. Paraffin with a solution of 60 wt% based on the oven-dry weight of the wood was purchased from a local market in Turkey. Waste MDF panels without lamination to be used in the study were obtained from Kastamonu Integrated Wood Company, Gebze plant, Turkey. The MDF panels were previously produced using 100% pine fibers. Some MDF panels cannot be used in the furniture industry due to blistering problems during the production of MDF in the factory. The recycling of these panels in MDF production is very limited because the water resistance and strength of the panel is negatively affected by the recycled fibers. These MDF panels were first passed through a chipper and turned into chips again (Figure 1A). The chips obtained from the waste MDF boards were stored in a separate place in the chip storage area so that they do not mix with other chips. The chips obtained from the waste MDF boards were then taken to the chip bunker in the MDF production flow and exposed to steam. Then, they were taken into the cooking vessel and cooked for 2.5 min at 9 bar steam pressure. The wet fibers were dried in an oven until 3% moisture content was reached before resin application (Figure 1B). There was not any special pre-treatment to remove the cured UF resin, paraffin, and hardener from the surface of the recycled MDF fibers.

(**A**) (**B**)

Figure 1. (**A**) The scraps of the waste MDF. (**B**) Recycled fibers obtained from the waste MDF.

The kraft lignin (Lineo™ Prime) in powder form, a complex plant-derived polymer, was supplied from Stora Enso company with an annual kraft lignin capacity of 50,000 tons, Helsinki, Finland (Figure 2) [21]. The kraft lignin was extracted from lignocellullosic material during the pulping process at the Sunila Mill of Stora Enso company, Kotka, Finland.

Figure 2. The kraft lignin sample [21].

The technical properties of the lignin are given in Table 1.

Table 1. Technical properties of lignin solution [21].

Property	Unit	Result
Appearance		Dark brown powder
Solids content	%	60–70
Ash content	%	<1.5
Sulfur	%	<2.5
Waste carbohydrates	%	<2
pH (40% water solution)		2.5–3.5
Moisture content	%	≤4
Density	kg/m^3	550–650
Average molecular weight	M_w	5500–7500

E1 grade urea-formaldehyde (UF) resin with a mole ratio of 1.05 and paraffin emulsion with a solids content of 60 wt% were obtained from the resin plant of Kastamonu Integrated Wood Company in Gebze location, Kocaeli, Turkey [22]. The technical specifications of the UF resin and paraffin were determined at the research and development center given in Table 2. A 25% aqueous solution of the ammonium chloride, according to the weight of the UF resin, was prepared as hardener.

Table 2. Technical properties of UF resin and paraffin [22].

Property	Unit	Result	
		UF Resin	Paraffin
Solids content	%	50.0	60.4
Viscosity	cps	17–50	-
Density	g/cm^3	1.190–1.225	0.95
Gel time	s	40–100	-
pH		7.8–9	9.9
Flow time	s	-	18.7
Melting point	°C	-	62

2.2. Production of MDF Panels

The fresh wood fibers and waste MDF fibers were mixed in a blender according to the raw materials formulations given in Table 3. The mixed fibers were placed in the blender

for the application of the UF resin. First, the 0.5 wt% paraffin emulsion was pulverized to the surface of the fibers using spray gun. Then, the different contents of the lignin solution, 2.5%, 5%, and 7.5% (by weight), were pulverized into the wood fibers using a spray gun. The lignin modification was followed by 10 wt% UF resin and 1 wt% hardener applications on the fiber surface using a spray gun. The amount of UF resin, paraffin, and lignin were calculated according to the oven-dry weight of the wood, while the hardener content was calculated according to the oven-dry weight of UF resin. The blender was run for 5 min so that the homogenization was ensured. The average moisture content of the fibers taken from the blender was 8%.

Table 3. The experimental design of the study.

	Fiber and Lignin Contents in the MDF Panels		
MDF Code	**Fresh Wood Fiber (wt%)**	**Recycled Wood Fiber (wt%)**	**Lignin (wt%)**
A	100	0	0
B	90	10	0
C	90	10	2.5
D	90	10	5
E	90	10	7.5
F	70	30	0
G	70	30	2.5
H	70	30	5
I	70	30	7.5

The production of the 5 mm thick MDF panels was carried out under laboratory conditions. The mat was manually prepared using a forming box with a size of 500 mm × 500 mm. The waxy paper was used between the mat and metal cauls. The mats were pre-pressed without heat and then hot-pressed at 210 °C for 210 s under a pressure of 3.5 N/mm^2. The resulting MDF panels were cooled so that the panel temperature decreased to the environment temperature. Three MDF panels were produced for each type of treatment (Figure 3).

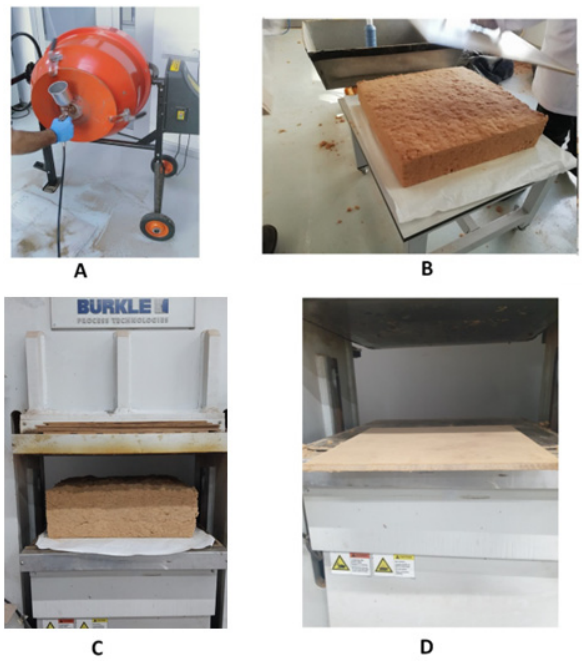

Figure 3. The production of the MDF panels at the laboratory. (**A**) UF resin application to the fibers in the blender. (**B**) The MDF mat. (**C**) The hot pressing of the MDF mat. (**D**) The resulting MDF panel.

All the parameters used in the production of the panels were kept constant in the production of the MDF panels, except for the lignin content and fresh wood/recycled fibers content. The experimental design is given in Table 3.

2.3. Determination of Physical and Mechanical Properties

The test specimens were cut from the experimental panels according to the EN standards. The bending strength (MOR) and bending modulus (MOE) tests were carried out according to the EN 310 standard [23]. The maximum failure load was reached in a minute. Ten specimens with dimensions of 150 mm × 50 mm × 5 mm were used in the bending strength and bending modulus. The IB strength (tensile strength perpendicular to the surface) test was performed according to the EN 319 standard [24]. The surface soundness of the specimens was determined according to the EN 311 standard [25]. Ten specimens with dimensions of 50 mm × 50 mm × 5 mm were used in the IB strength and surface soundness tests. The tests were performed in a universal testing machine (ZwickRoell material testing machine, Ulm city, Germany).

After 24 h of immersion in water, the thickness swelling (TS) and water absorption (WA) of the ten specimens with dimensions of 50 mm × 50 mm × 5 mm were measured according to the EN 317 standard [26]. The TS and WA express the water resistance of the MDF. The formaldehyde emission test of the specimens was performed according to the EN 120 standard [27]. KFD apparatus (Behr Labor Technik GmbH, Düsseldorf, Germany) was used for the extraction of formaldehyde from the MDF specimens. For the formaldehyde test, 105–110 g of the sample was cut from a plate with dimensions of 25 mm × 25 mm × 5 mm. The test specimens were weighed to 0.1 g and put into the round bottom flask. Then, 600 mL of toluene was added. When the toluene boiled, dropped, and started to fall from the cooler above, it was kept for 2 h. After 2 h, the perforator was turned off and cooled on its own for 30–45 min. The formaldehyde passing into the perfator in the volumetric flask was removed and then the exact formaldehyde concentration was determined according to the formula given in the EN 120 standard.

2.4. Thermogravimetric (TGA) Analysis

TGA analysis from 25 °C to 600 °C 10 °C/min quickly with nitrogen (20 mL/min) was carried out with Mettler Toledo equipment. A 70 µL alumina pan was used in the analysis. The unmodified and resin-modified wood fibers were used in the TGA analysis.

2.5. Differential Scanning Calorimetry (DSC) Analysis

DSC analysis from 25 °C to 350 °C 10 °C/min, quickly, with nitrogen (50 mL/min) was carried out with Mettler Toledo equipment. A 100 µL aluminum pan was used for the analysis. The curing time was calculated using the following equation.

$$t_{curing} = \frac{Endset(^{\circ}C) - Onset(^{\circ}C)}{\beta\ (^{\circ}C\ min^{-1})}$$

where

t_{curing}: curing time (min);
Endset: endset temperatures of the cure (°C);
Onset: onset temperatures of the cure (°C);
β: Curing speed (min).
The unmodified and resin-modified wood fibers were used in the TGA analysis.

3. Results and Discussion

3.1. Physical and Mechanical Properties

The TS and WA results of the MDF specimens are presented in Figures 4 and 5, respectively. The water resistance of the specimens improved with increasing the recycled content from 10 to 30 wt%. For example, the TS and WA of the specimens produced from the fresh wood fibers were found to be 31% and 57%, which are almost the same results as

for the specimens containing 30 wt% recycled fibers. The modification of the fibers with lignin considerably decreased the TS and WA values of the specimens. The lowest TS and WA values were found in the specimens containing the 30 wt% recycled fibers and 7.5 wt% lignin, which were 24% and 49%, respectively. Lignin has a hydrophobic structure and its aromatic structure can be explained by its resistance to water molecules. As the amount of recycled fibers increased in the MDF specimens produced with fresh wood fibers, the TS and WA values decreased. This can be explained by the fact that the surface of the recycled fibers still has the previously cured UF glue which has hydrophobic properties, although the waste MDF chips were exposed to the digester process. After that, the fresh wood and recycled wood fibers were modified with kraft lignin and then UF resin was applied. Hence, the recycled fibers may show greater hydrophobic property as compared to the fresh wood fibers due to their previously cured UF resins before the digester. Zeng et al. [28] reported that recycled fibers obtained from the waste MDF had better dimensional stability and water resistance than fresh wood fibers.

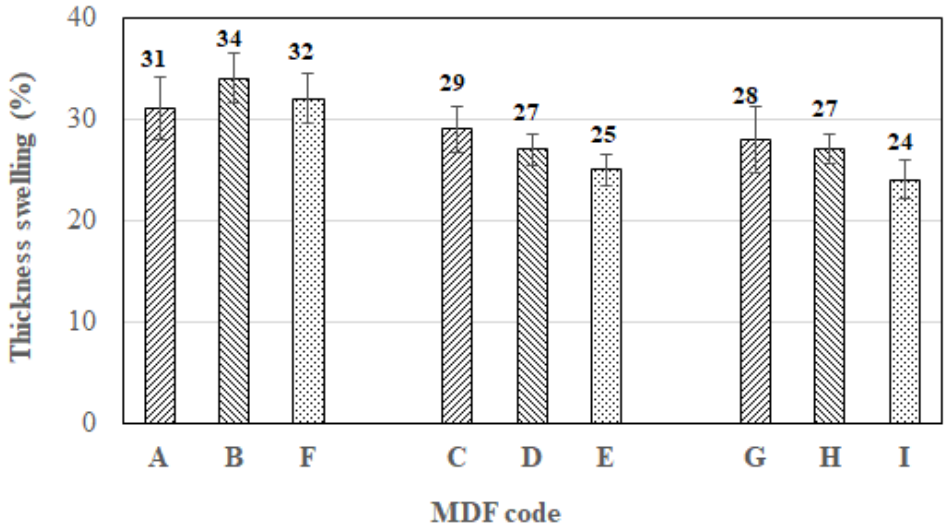

Figure 4. Thickness swelling (TS) of the MDF specimens (see Table 3 for the MDF codes).

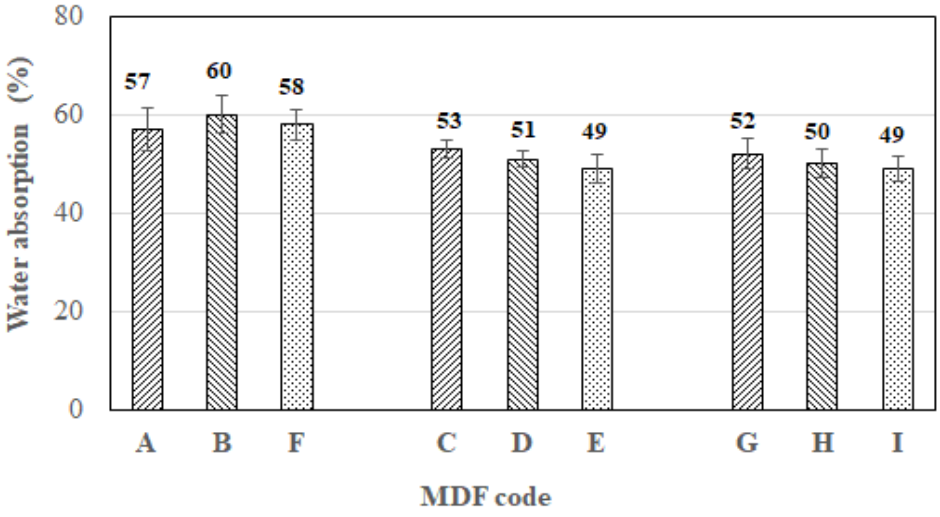

Figure 5. Water absorption (WA) of the MDF specimens.

The surface absorption of the MDF specimens increased with increasing the amount of the recycled fibers, which resulted in shorter absorbance values (Figure 6). The top side of the MDF specimens made from the fresh wood fibers had a surface absorption value of 160 mm, while it was found to be 120 mm and 110 mm for the MDF specimens

with 10 wt% and 30 wt% recycled fibers, respectively. Similar results were observed in the bottom layer of the MDF specimens. However, the modification of the fibers with the kraft lignin decreased the surface absorption of the specimens. For example, when 2.5 wt% lignin was added into the fibers, the surface absorption value of the top layer of the specimens increased from 120 to 160 mm. There was no difference in the absorption values of the 5 and 7.5 wt% lignin additions (170 mm). The absorption of the specimens containing 10 wt% recycled fibers modified with 7.5 wt% lignin was lower than the specimens produced using fresh wood fibers, which gave the best results among all the MDF types. This could be explained by the hydrophobic character of the lignin macromolecules, which may be described as the ability to repel water. The fibers modified with lignin make the surface of the MDF more hydrophobic as compared to the specimens without lignin and reduce the surface absorption [29]. The effectiveness of the lignin modification was more pronounced at the lower content of the recycled fibers. The absorption values of the specimens with 30 wt% recycled fibers was lower than those of the specimens with 10 wt% recycled fibers at all the loading levels of the lignin.

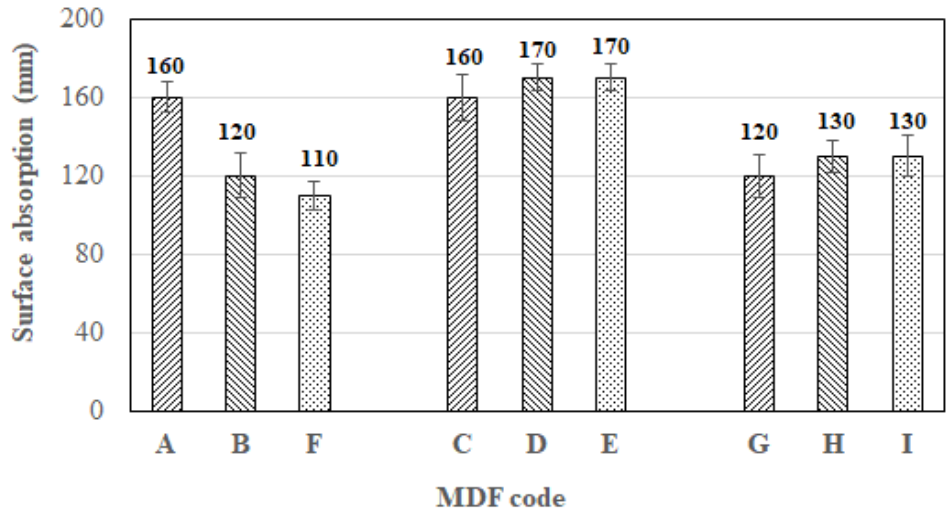

Figure 6. Surface absorption of the MDF specimens.

The formaldehyde emission of the specimens produced from fresh wood fibers was determined as 6.9 (0.6) mg/100 g. It was observed that the free formaldehyde emission increased with the content of recycled fibers without lignin modification in the MDF panels (Figure 7). This may be due to the presence of the UF glue that was previously present in the waste MDF fibers. For example, when the amount of recycled fiber content increased from 10 to 30 wt%, the formaldehyde emission of the specimens increased from 7.9 to 8.3 mg/100 g. However, the modification of the fibers with lignin decreased the formaldehyde emission of the specimens. A similar study was reported by Bütün et al. [30] for the MDF panels produced from recycled fibers of waste MDF. The urea, ammonia, and oligomeric degradation products of the UF resin can react with formaldehyde and act as formaldehyde scavengers. For this reason, several studies reported that the formaldehyde content and emissions of recycled MDF were significantly higher than those of MDF panels produced from fresh wood fibers [5,30,31]. The lignin molecule contains many oxygen derivative functional groups such as hydroxyl, carbonyl, and carboxylic acid attached to the aromatic structure [32]. Since these functional groups have the ability to react with glue and free formaldehyde, they are effective in reducing formaldehyde emission from the board.

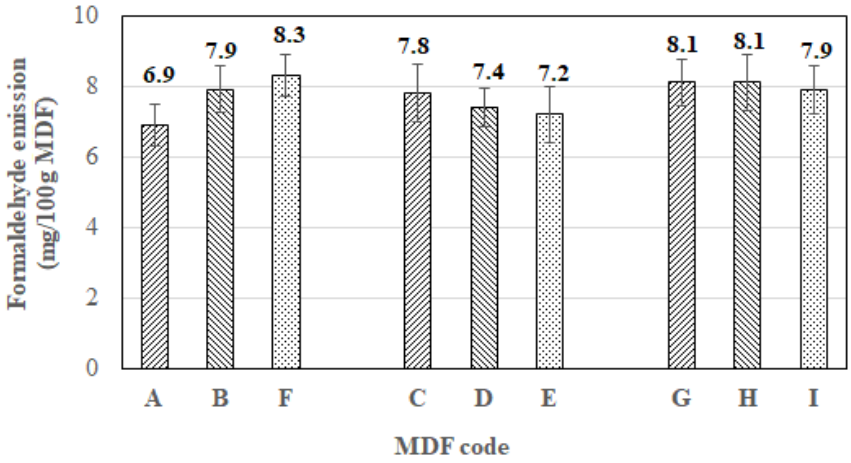

Figure 7. Formaldehyde emission of the MDF specimens.

The IB strength values of the MDF panels are displayed in Figure 8. The increase in the amount of waste MDF fibers in the MDF decreased the IB strength. The IB strength of the specimens produced from fresh wood fibers was found to be 0.68 N/mm^2. The addition of the 10 wt% recycled fibers made using fresh wood fibers into the MDF caused a slight decrease in the IB strength (0.62 N/mm^2), but further increment in the recycled fibers (30 wt%) considerably decreased the IB strength of the fresh MDF panel (0.59 N/mm^2). The IB strength of the specimens containing the recycled fibers modified with the three loading levels of the lignin was higher than that of the MDF specimens containing the recycled fibers without lignin. The results showed that the increase in the lignin content on the fiber surfaces further improved the interfacial bond between the fibers, in addition to the UF resin. Particularly, the IB strength values of the specimens produced with the 10 wt% recycled fibers modified with the 5 wt% and 7.5 wt% lignin contents were found to be higher than that of the specimens produced with 100 wt% fresh pine fibers. A similar trend was observed for the 30 wt% recycled fibers content in the MDF specimens. This revealed that the recycled fibers modified with kraft lignin gave better bond performance than the traditional MDF panels produced from fresh wood fibers. The reactivity of the kraft lignin increased with increasing carboxylic acid groups. The improvement of the mechanical properties as the lignin ratio increased in the modified fibers can be explained by the presence of carboxylic acid groups [32]. Kraft lignin contains an increased amount of free phenolic hydroxyl groups compared to native lignin and other technical lignin. In addition, kraft lignin also contains an increased amount of carboxyl groups and condensed structures such as biphenyl, quinine, and catechol structures [33].

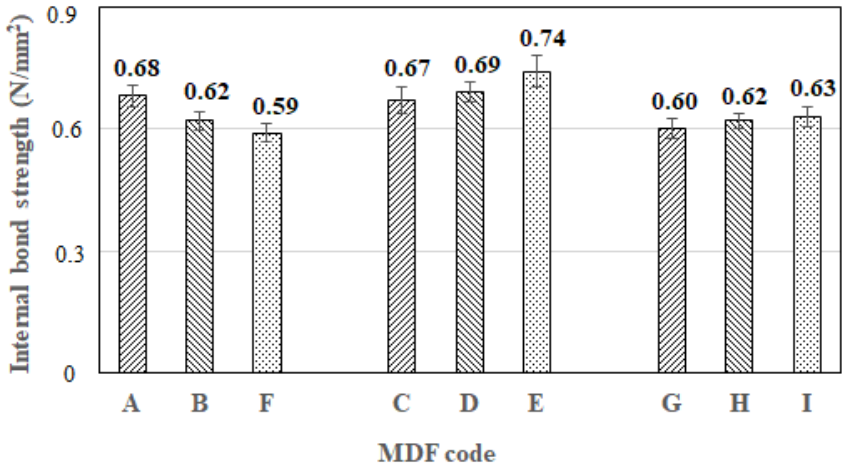

Figure 8. Internal bond (IB) strength of the MDF specimens.

The IB strength directly affects the bending properties of the MDF panels. The improvement in the IB strength increased the MOR and MOE of the specimens. The results of the bending properties showed a similar trend to the IB strength. Although the MOR and MOE of the specimens containing the 10 wt% recycled fibers was lower than the MDF produced from the fresh wood fibers, the lignin modification of the recycled fibers at the 10 wt% level resulted in better properties (Figures 9 and 10). However, this was not determined in the specimens produced with 30 wt% recycled fibers modified with the lignin. The MOR and MOE of the MDF specimens modified with lignin were considerably higher than the specimens without lignin. This was more pronounced at a lower recycled fiber content. It can be said that the lignin modification was more effective on the bending properties of the specimens at lower recycled fibers content. For example, at the 7.5 wt% lignin content, the MOR and of MOE of the specimens containing 10 wt% recycled fibers were 50.4 N/mm^2 and 3990 N/mm^2, while they were found to be 40.1 N/mm^2 and 3015 N/mm^2 for the specimens containing 30 wt% recycled fibers. Similar results were found in the results of the surface soundness test (Figure 11). This test provides information about the delamination performance between the middle layer and the surface layers. The IB strength, MOR, and MOE of the specimens met the minimum requirements of the MDF panels used indoors as specified in the EN 622-5 standard. It was determined that the modification of the fiber surfaces with lignin linearly increased the IB strength. The surface soundness of MDF is generally directly proportional to tensile strength, MOR, and MOE properties.

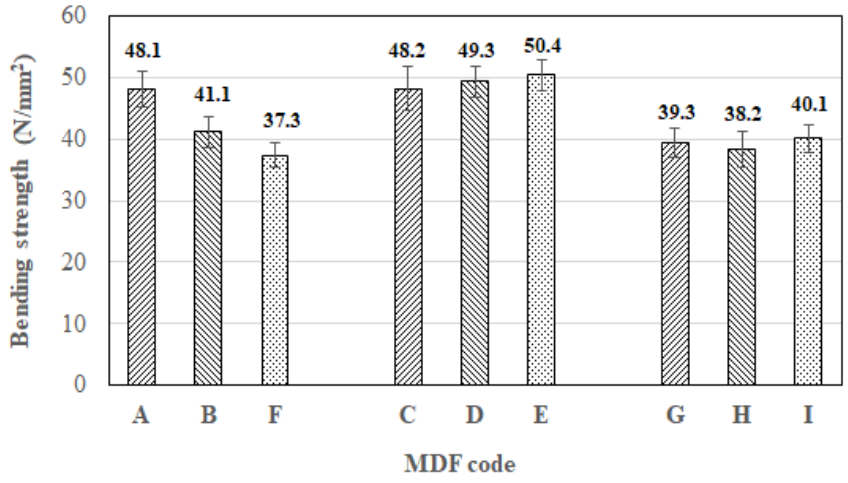

Figure 9. Bending strength of the MDF specimens.

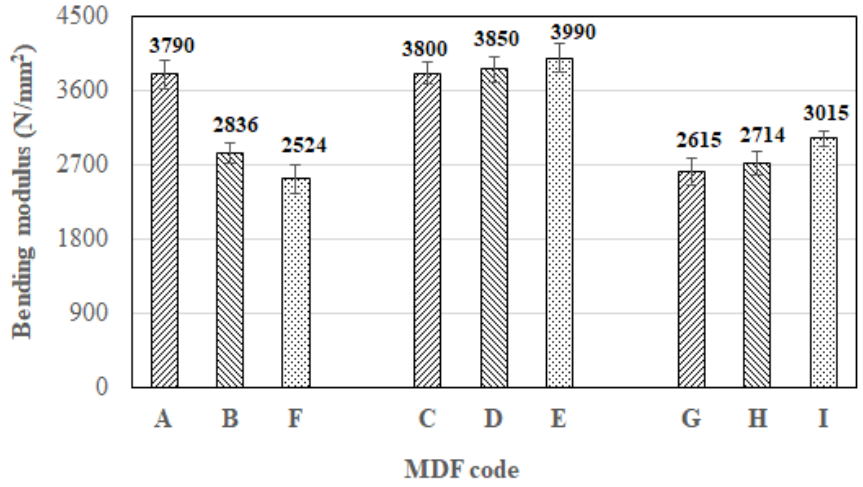

Figure 10. Bending modulus of the MDF specimens.

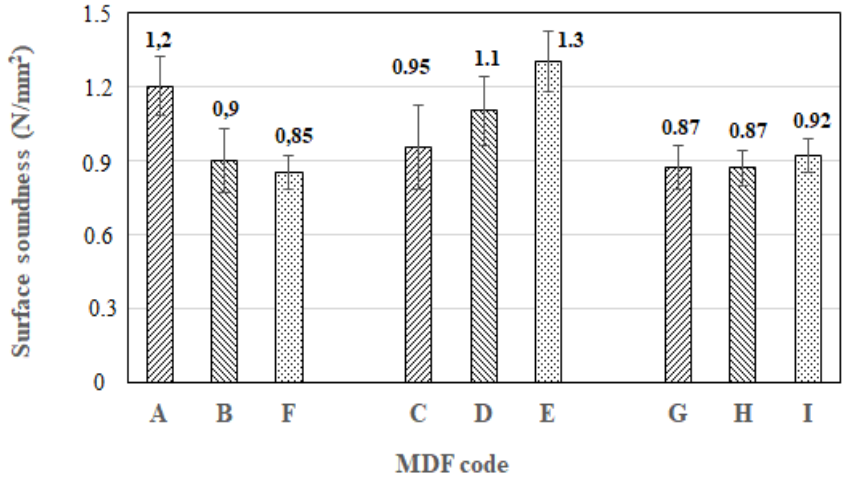

Figure 11. Surface soundness of the MDF specimens.

The role of lignin in enhancing the bond performance could be explained by various factors. The ammonium chloride as a crosslinking catalyst is used for reducing the hot-pressing time [34]. An acidic catalyst that decreases the pH of the environment could promote lignin condensation during hot pressing, thereby making the acidic curing condition in lignin self-crosslinking easier and hereby providing better adhesion performance [34]. The occurrence of lignin self-crosslinking could be confirmed with the increased presence of C–C linkages in hot-pressed lignin. The improvement in the mechanical properties could also be explained by the filling of vessels (pores) with softened lignin and the interfacial crosslinking of lignin and the cell wall [34].

The fiber length directly affects the mechanical properties of the fiberboard. In a previous study, it was reported that the length of the fiber of the recycled fibers was approximately 12% shorter than fresh fibers, the percentage of shorter fibers ($\leq$0.68 mm) was higher in the former than in the latter, and the rate of broken ends was also increased [28]. The proportion of the recycled fibers was 17% higher than fresh fibers. In that study, SEM and XPS characterizations confirmed the presence of some cured UF resin on the surface of the recycled fibers. The cured UF particles on the recycled fibers is responsible for the lower bond performance and mechanical properties because the number of functional groups (hydroxyl groups) in the fibers is lower than in fresh wood fibers. UF resins contain amino groups that can form hydrogen bonds with the hydroxyl groups of the wood [35]. The decrease in the functional groups in the recycled fibers is one of the reasons for the lower mechanical properties of the MDF panels.

The IB strength, MOR, MOE, and IB values of the MDF specimens containing recycled fibers were found to be 11%, 10%, and 5% lower than those of the MDF specimens produced with the fresh wood fibers, respectively. However, the water resistance improved with the increasing content of recycled fibers. A similar result was observed by Hwang et al. [13]. They examined the effects of the recycled and fresh wood fibers on the properties of fiberboard. Replacing fresh fiber with recycled fibers negatively affected the mechanical properties of fiberboard. According to their results, all the panels with over 40 wt% recycled fibers contents failed to meet any commercial requirements for water resistance and strength properties. The decrease in the length of the fiber in the recycled fibers is one of the reasons for the lower bond strength between the wood fibers, due to the reduction in the overlap length between the fibers. In MDF production, the fibers need to be strongly bonded to each other with glue. In the process of re-chipping, softening, and subsequent fibering of waste MDFs, the formed fibers of irregular sizes and shapes are as are randomly broken from the adhesion lines. This may be one of the reasons for the decrease in mechanical properties with the increase in the use of waste MDF fiber.

3.2. Thermal Analysis

3.2.1. DSC Analysis

The DSC thermograms of the fresh wood fibers and recycled wood fibers are presented in Figure 12. When the waste MDF fiber was added to standard pine fiber, an increase in the curing onset temperatures of approximately 10 °C was observed according to the results of the DSC analysis (Table 4). The breakpoint in the DSC thermograms of Figures 12–15 show that the moisture contained in the wood fibers begins to evaporate at a temperature of approximately 100 °C. When the 10 wt% recycled fibers were added, the curing temperature did not change, while an increase of 4 °C in the curing temperature (peak) was observed with the increase in the content of the recycled fibers. The main reason for these increases may be the negative effect of curing or thermal degradation of the already cured adhesives in waste MDF. With the addition of the lignin at different rates to the MDF specimens containing 10% waste MDF fibers, a decrease was observed in the curing start and curing temperatures. The main reason for this decrease may be the positive contribution of lignin to the curing.

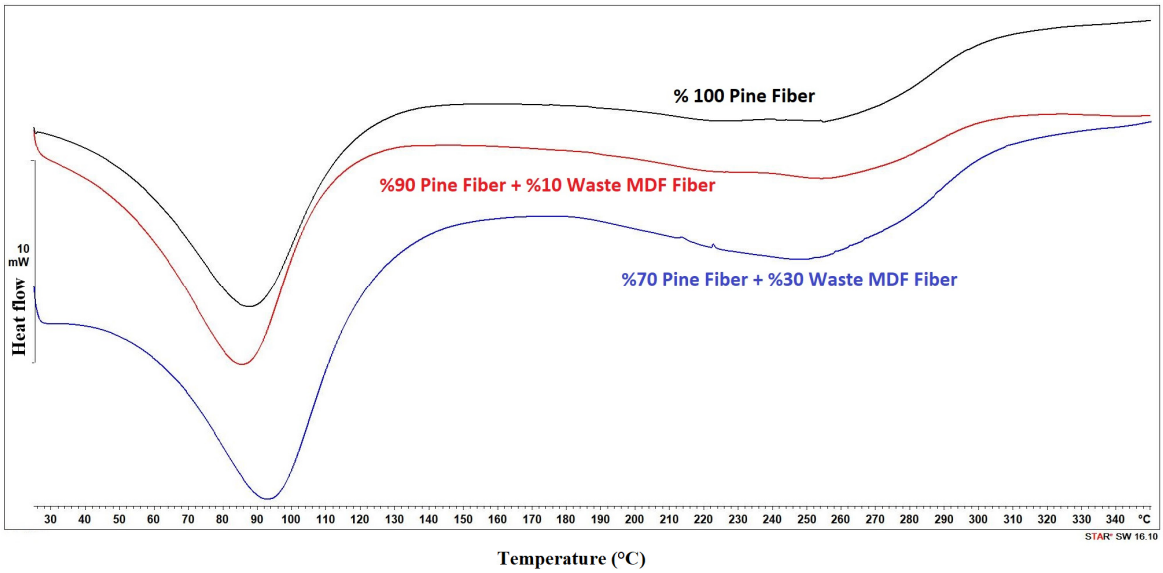

Figure 12. Effect of fresh wood fibers and recycled MDF fibers on the DSC thermograms of MDF.

Table 4. The onset, peak, and endset temperatures of the MDF specimens according to the DSC thermogram.

Lignocellulosic Material Composition in MDF (% Weight)	*Onset* (°C)	Peak (°C)	*Endset* (°C)	t_{curing} (°C/min)
100 pine fiber	266.5	303.6	348.2	8.2
90 pine + %10 recycled fiber	276.6	303.4	344.2	6.8
90 pine + %10 recycled fiber + 2.5 lignin	272.4	308.0	348.1	7.6
90 pine + %10 recycled fiber + 5 lignin	270.5	304.5	349.6	7.9
90 pine + %10 recycled fiber + 7.5 lignin	267.1	305.9	344.5	7.7
70 pine + %30 recycled fiber	272.5	308.0	350.4	7.8
70 pine + %30 recycled fiber + 2.5 lignin	260.6	305.4	349.5	8.9
70 pine + %30 recycled fiber + 5 lignin	271.5	304.5	328.9	5.7
70 pine + %30 recycled fiber + 7.5 lignin	277.0	305.9	349.3	7.3

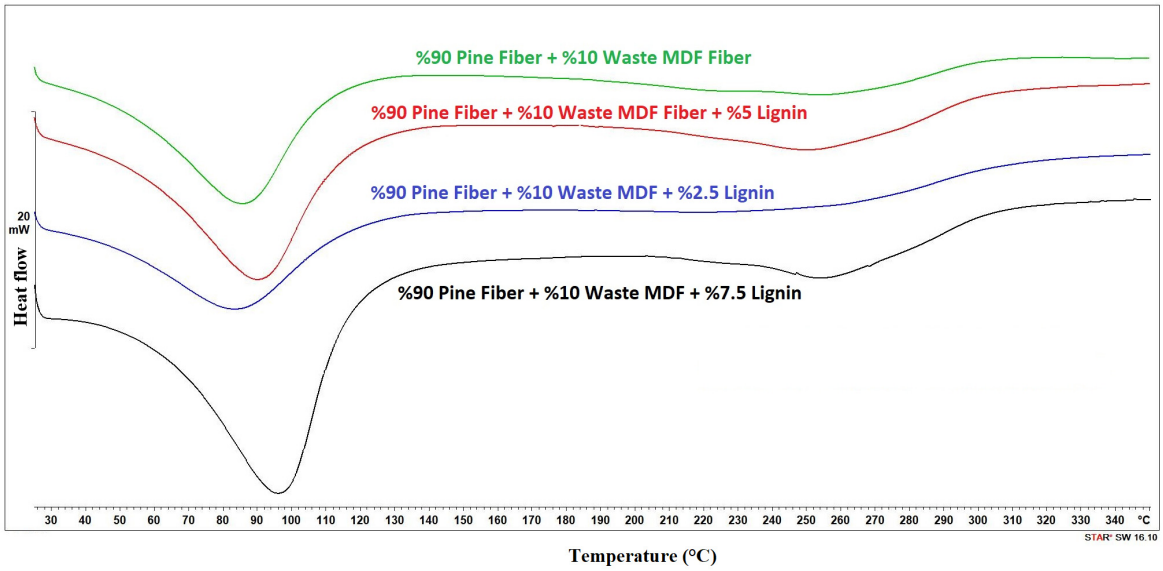

Figure 13. Effect of lignin modification on DSC thermograms of MDF made using 90 wt% fresh wood and 10 wt% waste MDF fibers.

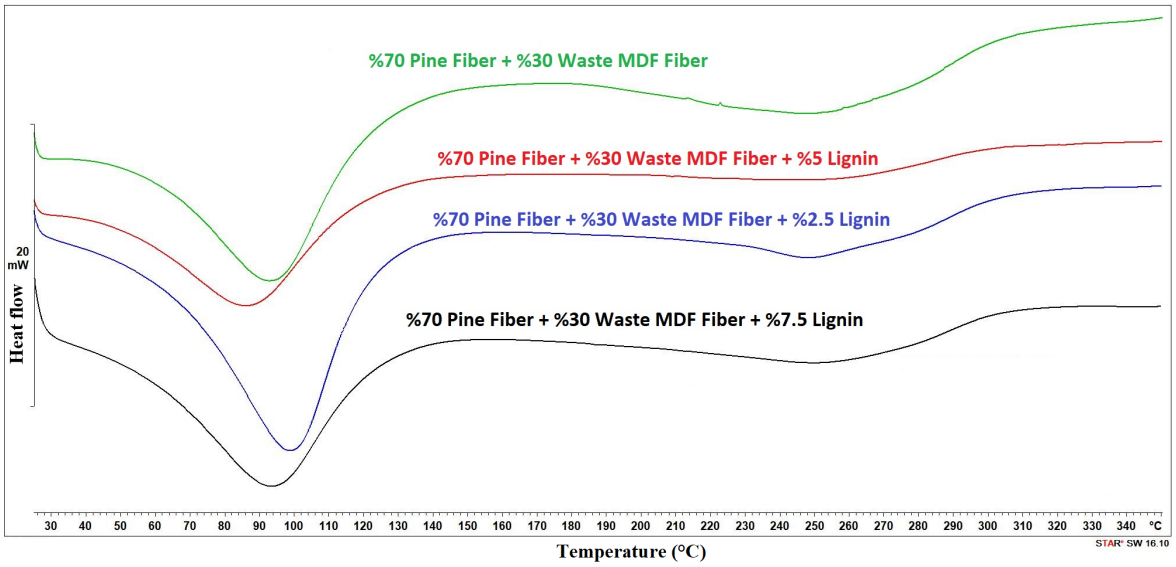

Figure 14. Effect of lignin modification on DSC thermograms of MDF made using 70 wt% fresh wood and 30 wt% waste MDF fibers.

The effects of the lignin modification on the DSC thermograms of the MDF panels containing 10 and 30 wt% recycled wood fibers are presented in Figures 13 and 14. The decrease in the curing initial temperatures with the increasing lignin content was an indication that lignin content triggers curing at lower temperatures. In this case, curing that starts at low temperatures can also increase press speeds. As for the MDF specimens containing 30% recycled fibers, it was observed that the lignin followed an inverse trend compared to 10 wt% recycled fibers. The increase in the content of the recycled fibers reduced the efficiency of lignin and shifted the curing temperatures to higher temperatures.

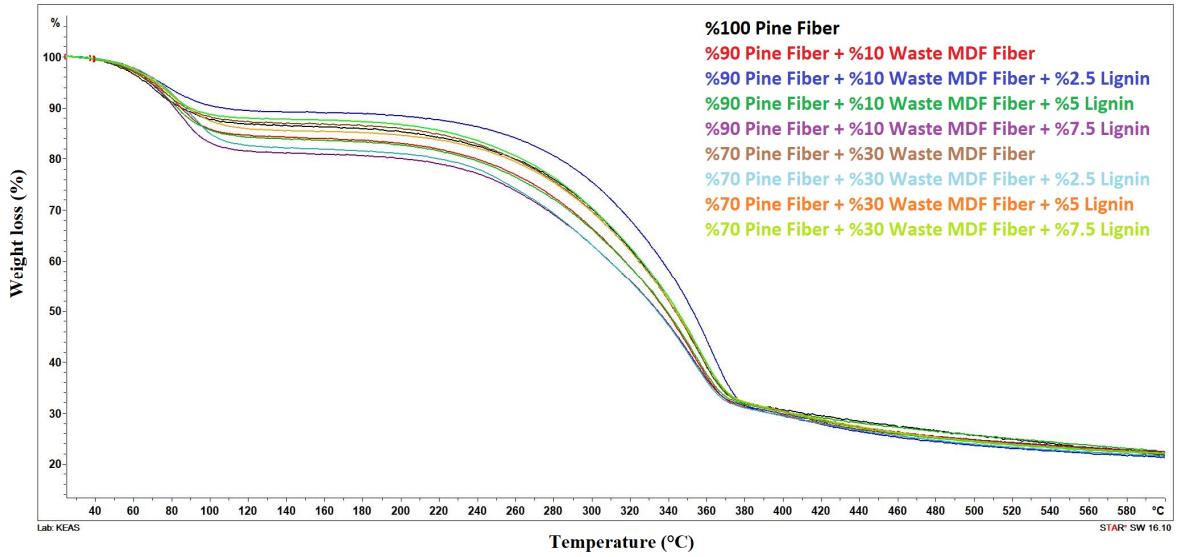

Figure 15. TGA thermograms of the MDF specimens.

3.2.2. TGA Analysis

The thermal degradation temperatures (onset, peak) and mass loss obtained from the TGA thermogram are given in Table 5. No significant change in thermal degradation temperatures was observed with the addition of waste MDF fiber in the TGA thermograms of the samples (Figure 15). As shown in the TGA thermogram, the moisture evaporation from the wood fibers started at about 100 °C. Very little thermal degredation (the breakdown of the chemical bonds via dehydration and the production of volatile gases) occurred at about 200 °C, and the whole thermal degredation of the wood fibers started at about 250 °C. Rowell and LeVan-Green [36] reported that the majority of the degredation of carbohydrate polymers occurred between about 300–375 °C and only lignin remained.

Table 5. Degradation temperatures (onset, peak) and mass loss of the MDF specimens according to the TGA thermogram.

Lignocellulosic Material Composition in MDF (% Weight)	Moisture (%)	*Onset* (°C)	Peak (°C)	Mass Loss (%)	Residual Mass (%)
100 pine fiber	13	274.8	351.0	56	31
90 pine + %10	16	269.3	349.7	54	30
90 pine + %10 recycled fiber + 2.5 lignin	11	296.1	359.0	60	29
90 pine + %10 recycled fiber + 5 lignin	16	275.6	350.3	56	28
90 pine + %10 recycled fiber + 7.5 lignin	19	266.3	349.5	51	30
70 pine + %30 recycled fiber	13	278.5	350.7	56	31
70 pine + %30 recycled fiber + 2.5 lignin	18	270.3	349.2	53	29
70 pine + %30 recycled fiber + 5 lignin	15	265.4	352.0	55	30
70 pine + %30 recycled fiber + 7.5 lignin	12	275.0	352.2	58	30

The increase in the content of the recycled fibers did not affect the thermal stability. No significant change was detected in the loss and residual mass ratios. No trend was observed between the additive ratio and thermal degradation in lignin addition. On the other hand, in the samples containing 10% recycled fibers and 2.5% lignin, the thermal resistance increased by about 10 degrees. However, the mass loss was slightly higher than the other samples. In summary, it was determined that lignin and recycled fiber additions did not contribute to the thermal properties of the samples and did not change their thermal resistance. The DSC thermograms and cure start temperature (initial), cure temperature (peak), and cure end temperature (finish) obtained from these analyzes are given in Table 5.

4. Conclusions

The results of the present study show that the recycled fibers obtained from MDF waste could be successfully mixed with the fresh wood fibers in MDF production after lignin modification. Although the utilization of the recycled MDF fibers without lignin in a new product tended to diminish the strength of the MDF panel, the lignin modification of the fibers gave better mechanical properties and water resistance. A linear increase in the tensile strength perpendicular to the surface was found with the modification of the surface of the fibers with lignin. The increase in the content of the recycled fibers and lignin did not improve or affect the thermal stability of the MDF. Furthermore, no significant change was detected in the residual mass ratios of the MDF with recycled fibers modified with lignin. The formaldehyde emission of the MDF specimens increased with increasing the content of the recycled fibers because the surface of the recycled fibers had already cured the UF resin. However, the lignin modification and its increasing loading level slightly decreased the formaldehyde emission of all types of MDF specimens. Considerable savings in wood raw materials can be achieved by using lignin-modified recycled fibers in MDF production. Furthermore, the use of the modified recycled wood contributes to reducing the environmental pollution caused by waste MDFs. According to the results, the MDFs produced with 5 wt% and 7.5 wt% lignin modification of recycled MDF fibers at a rate of up to 10% can a give better quality of MDF than that made from fresh wood.

Author Contributions: Conceptualization, N.A. and S.G.; methodology, N.A. and S.G.; software, S.G.; validation, S.G. and N.A.; investigation, S.G. and N.A.; resources, S.G.; writing—original draft preparation, N.A.; writing—review and editing, N.A. and S.G.; visualization, N.A. and S.G.; supervision, N.A. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank Istanbul University-Cerrahpasa for the laboratory equipment used in this study.

Data Availability Statement: The data included in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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