

Article

The Impact of Hydrolysis Regime on the Physical and Mechanical Characteristics of Medium-Density Fiberboards Manufactured from Recycled Wood Fibers

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Abstract: Recycling medium-density fiberboards (MDF) presents notable technological challenges, primarily due to the deteriorated properties of the recycled wood fibers obtained from MDF waste. On the other hand, the enhanced valorization of recycled wood in the manufacturing of wood composites represents a viable approach for implementing the principles of a circular bio-economy in the wood-based panel industry and lowering its carbon footprint. This research aimed to investigate and evaluate the impact of the hydrothermal hydrolysis regime on the physical and mechanical properties of recycled MDF panels (rMDF). The hydrolysis temperature was varied from 121 °C (saturated steam pressure 0.2 MPa) to 134 °C (saturated steam pressure 0.3 MPa), and three hydrolysis durations, i.e., 30, 45, and 60 min, were applied. A control MDF panel, manufactured in laboratory conditions from industrial pulp, was used to perform the comparative analyses. It was observed that the degradation of the rMDF panels occurred when the hydrolysis temperature was increased from 121 °C to 134 °C. The research confirmed the deteriorated physical and mechanical properties of rMDF compared to the panels manufactured from natural wood fibers. Markedly, no significant differences were detected between the density profiles of the rMDF panels and the control boards fabricated from industrial pulp. As a result of the study, it was found that the hydrolysis temperature has a more significant effect than the processing time. It was also established that, in the preliminary preparation of the MDF panels into samples with dimensions similar to those of pulp chips, the optimal hydrolysis regime is at a temperature of 121 °C (saturated steam pressure 0.2 MPa) and a time of 30 min.

Keywords: recycling; medium-density fibreboards; thermal hydrolysis; physical and mechanical properties; formaldehyde content



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1. Introduction

Manufacturing wood-based panels is considered a prominent sector within the wood industry. At present, the production of fiberboards, particularly medium-density fiberboard (MDF), is one of the fastest growing wood-based industries worldwide, with an estimated annual market size of 113.09 million m³ in 2023 and a compound annual growth rate of 3.81% for the period 2023–2028 [1]. The increased production of engineered wood products is connected with the growing demand for wood and wood-based products worldwide

and the escalating global deforestation rates. The implementation of circular economy principles in the whole forest-wood value chain, related to the cascading use of wood resources, search for alternative natural feedstocks, and enhanced recycling and upcycling of wood and other lignocellulosic raw materials, is in line with the ongoing digital and green transition of the wood-based sector [2–4]. In addition, introducing sustainable and cost-effective recycling practices will reduce the industry's carbon footprint by eliminating the energy-intensive pulp chip refining process [5,6].

It should be noted that, while the recycling of particleboards is relatively well-developed at an industrial scale [7–9], the recycling of MDF panels is associated with specific technical difficulties, mostly related to the reduced slenderness of the recycled wood fibers [10–16]. The recycling of MDF panels can be carried out with or without removing the resins [17–21]. However, the recycling methods without resin extraction are characterized by an increased formaldehyde emission from the panels produced and the substantial deterioration of their properties [17,18,22,23], i.e., the recycling methods with resin removal are much more promising. This is also supported by the fact that the main type of adhesives used in the production of wood-based panels is the urea-formaldehyde (UF) resin [24–28], which is highly unresistant to hydrolysis [29–35]. The main method used to remove synthetic resins from recycled wood-based panels is hydrolysis [36–44], but there are also some studies on resin extraction by electrolysis [45,46]. The use of electrolysis is often associated with increased processing costs. However, the panels, manufactured from recycled fibers obtained by electrolysis, are characterized by satisfactory physical and mechanical characteristics. Moezzi-pour et al. [45] reported that MDF panels manufactured by electrolysis recycling had mechanical properties that were only about 11% lower than those fabricated from natural fibers. In comparison, those obtained using hydrolysis exhibited approximately 47% worse mechanical properties. However, the increased processing costs resulting from the application of electrolysis are the main drawback of its more comprehensive industrial implementation.

Hydrolysis can be thermochemical (acid) or hydrothermal. Considerable research has been performed on recycling MDF panels through acid hydrolysis [18,24,27]. Lubis et al. [36] obtained MDF panels with properties comparable or superior to those manufactured from natural fibers, with a recycled fiber content of up to 10%. Additionally, a notable decline in the characteristics of MDF panels manufactured only using recycled fibers was reported.

Studies on hydrothermal hydrolysis regimes are relatively limited. In the research by Savov et al. [10], an investigation was conducted to examine the impact of the hydrolysis regime on the characteristics of the recycled fibers obtained. It was found that the recycled fibers were shorter compared to the natural ones, and spherical structures were observed in the pulp from such fibers. In this study, the hydrolysis temperature was varied from 121 to 134 °C, and at a processing time of 30 to 60 min, no changes in the content of the pentosans were observed. With increasing temperatures, an increase in the chemical oxygen demand (COD) values was reported, most likely due to the increased extractives content. Such extracts were also reported in the study by Hagel et al. [42]. Another study [10] reported that, even at a hydrolysis temperature of 121 °C and a hydrolysis time of 30 min, the presence of amino compounds was observed in the pulp, indicating the disintegration of UF resin [47,48]. However, the impact of the hydrolysis regime on the physical and mechanical characteristics of MDF panels fabricated from recycled wood fibers obtained using the thermal hydrolysis of waste MDF panels was investigated in previous studies [10]. Thus, the aim of this research was to investigate and evaluate the impact of the hydrothermal hydrolysis regime on the physical and mechanical properties of MDF panels fabricated from recycled wood fibers (rMDF).

2. Materials and Methods

This study utilized MDF panels produced by Kronospan Bulgaria EOOD, located in Veliko Tarnovo, Bulgaria. The panels were subjected to a hydrolysis recycling process at

121 °C (saturated stem pressure of 0.2 MPa) and 134 °C (saturated stem pressure of 0.3 MPa) hydrolysis temperatures, with processing durations of 30, 45, and 60 min. The temperature and hydrolysis time were determined based on previous investigations [44,49]. Buschalsky et al. [49] reported increased formaldehyde emissions from MDF panels fabricated from recycled wood fibers obtained with hydrothermal hydrolysis at temperatures below 100 °C. Accordingly, in [44], a significant deterioration of the properties of MDF panels was reported after increasing the temperature of hydrothermal hydrolysis from 125 °C to 150 °C. However, in the study [44], the temperature change is significant, suggesting the need for an analysis of the effect of this factor at an intermediate (between 125 °C and 150 °C) hydrolysis temperature. The thermal hydrolysis process was conducted using a TS 14 B+ autoclave (Cixi Tonsor Medical Instrument 146 Co., Ltd., Ningbo, Zhejiang, China). More detailed characterization of the processing parameters of hydrothermal recycling and the properties of the recycled fibers obtained can be found in Savov et al. [10].

In the laboratory, six types of rMDF panels were fabricated from recycled fibers obtained at different regimes of hydrothermal hydrolysis, and a control MDF panel was manufactured from the industrial pulp (Table 1).

Table 1. Manufacturing parameters of rMDF panels fabricated from recycled wood fibers obtained by thermal hydrolysis.

Panel Type	Target Density	Hydrolysis Temperature T, °C	Hydrolysis Time τ , min
A	780	121	30
B	780	121	45
C	780	121	60
D	780	134	30
E	780	134	45
F	780	134	60
REF	780	0	0

The industrial wood fibers used for manufacturing the control MDF panels were produced by the Asplund thermomechanical method using a Defibrator L56 (Valmet, Stockholm, Sweden) in factory conditions at Kronospan Bulgaria EOOD (Veliko Tarnovo, Bulgaria). The pulp was composed of mixed wood raw materials—40% hardwoods (European beech (*Fagus sylvatica*) and Turkish oak (*Quercus cerris*)) and 60% softwoods (Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*)). The industrially produced wood fibers had a moisture content (MC) of approximately 10%. The recycled wood fibers used had the same MC value.

Due to the significant content of hardwoods in the pulp and to increase the compression ratio, the laboratory-fabricated MDF panels had a target density of 780 kg.m^{−3} [24]. The MDF panels, manufactured in laboratory conditions from recycled and natural wood fibers, had dimensions of 400 mm × 400 mm × 6 mm.

The adhesive system used was comprised of 90% urea-formaldehyde (UF) resin and 10% melamine-formaldehyde (MF) resin. The addition of MF resin was aimed mainly at improving the waterproof properties of the panels and partially improving their mechanical properties [24–26]. Both binders were prepared to a solution with a concentration of 50%. The UF resin had a molar ratio 1.0 and a dynamic viscosity of 23.76 ± 0.52 MPa.s. The MF resin had a molar ratio of 1.76 and a dynamic viscosity of 21 ± 0.76 MPa.s. As a hardener, ammonium sulfate ((NH₄)₂SO₄ 20%) was used at 1%, based on the dry resin. The ammonium sulfate was introduced into the adhesive system as a solution with a 30% concentration. As a waterproof substance, wax (paraffin emulsion) was used at a content of 1%, based on the dry fibers. The paraffin emulsion used had a concentration of 50%.

The adhesive content was 10%, based on the dry fibers. The glueing was conducted within the controlled environment of a laboratory setting, utilizing a blender equipped with needle-shaped blades. This particular blender was developed as a prototype by the

University of Forestry (Sofia, Bulgaria) and operated at 850 rpm. The adhesive mixture was applied through a 1.5 mm nozzle, which facilitated the injection of the paraffin emulsion.

The hot-pressing process was performed using a laboratory hydraulic press (PMC ST 100, Italy). The hot-pressing temperature applied was 175 °C, and the press factor was 30 s.mm^{−1}. The temperature and press factor used were chosen following previous studies on manufacturing fiberboard panels at a similar MC of the raw material [50–52].

The experimental procedure involved the implementation of a four-stage pressing regime. During the initial stage, the pressure was gradually raised to 4 MPa, which accounted for 15% of the total pressing time. Subsequently, in the second stage, the pressure was reduced to 1.2 MPa, constituting 15% of the total pressing time. In the third stage, the pressure was maintained at 0.8 MPa for 60% of the total pressing time. Finally, the fourth pressing period was conducted at a pressure of 1.5 MPa, encompassing 10% of the total pressing time. In contrast to the production of particleboards, in the production of fiberboard panels, the cohesive bonds between the fibers have a significant role even in the dry-process method. Because of that, in the present study, a final hot-pressing stage with increased pressure is applied, which does not allow the remaining minimal amount of steam to leave the panel, resulting in the formation of additional lignin and hydrogen bonds.

The physical and mechanical characteristics of the MDF panels were assessed by the European standards EN 310, EN 317, EN 319, and EN 323 [53–56]. The mechanical properties were evaluated using a WDW-50E universal testing machine (UTM, HST, Jinan, China). Eight MDF test samples were used to determine each property. The density profile of the panels was determined in the factory laboratory of Kastamonu-Bulgaria AD (Gorno Sahrane, Bulgaria). A GreCon DENSITYPROFILER (Fagus-CreCon, Alfeld, Germany) was used for that purpose. The X-ray voltage used was 32.833 kV at a measurement speed of 0.1 mm.s^{−1}. The quantification of formaldehyde emission was conducted using the perforator method [57], and the findings were reported using a DR 2800 photo-spectrometer (Hach Lange GmbH, Düsseldorf, Germany).

The main statistics, average (mean value), standard deviation, standard error, and probability were determined for each of the physical and mechanical properties of the panels. Hierarchical cluster analysis was also performed using specialized software, IBM SPSS Statistics 18 (2010).

3. Results and Discussion

The results obtained for the density of the laboratory-fabricated MDF panels and the main statistical parameters are presented in Table 2. The data on the density of the MDF panels fabricated from recycled and natural fibers showed a slight variation in this property, with the density being close to the targeted value of 780 kg.m^{−3}. The difference between the panel with the highest density (panel type F) and the lowest (panel type A) is 20 kg.m^{−3}, or only 2.6%. That is, the difference between the MDF densities is significantly below the statistical error of 5%.

Table 2. Density of MDF panels produced in this work.

Panel Type	Average (Mean Value) ρ , kg.m ^{−3}	Standard Deviation S_y , kg.m ^{−3}	Coefficient of Variation V_y , %	Standard Error m_y , kg.m ^{−3}	Probability P_y , %
Type A	777	47.61	6.13	16.83	2.17
Type B	786	51.41	6.54	18.17	2.31
Type C	776	70.68	9.11	24.99	3.22
Type D	780	53.50	6.86	18.91	2.42
Type E	779	64.90	8.33	22.95	2.95
Type F	797	49.99	6.27	17.67	2.22
REF	783	28.32	3.62	10.01	1.28

The ANOVA results for the significance of the panel types on their density values are presented in Table 3. The absence of differences between the densities of the MDF panels was due to the hot pressing method using metal bars to determine the panel thickness. The direct consequence of the panels having practically the same density is that this main property will not affect the other physical and mechanical properties of the MDF panels. Therefore, their variation will be attributed to the hydrolysis regimes used to obtain the recycled wood fibers.

Table 3. ANOVA for the significance of panel type on the density of the fabricated MDF panels.

Source of Variation	SS	df	MS	F	<i>p</i> -Value	Fcrit
Panel type	2630.581	6	438.4301	0.151336	0.987926	2.290432
Error	141,955.8	49	2897.057			
Total	144,586.4	55				

The density profiles of the laboratory-made MDF panels are presented in Figure 1. When analyzing the density profile of the MDF panels fabricated from recycled wood fibers obtained with the different regimes of thermal hydrolysis and natural wood fibers, it was determined that there was no significant difference between the minimum and average density values. This difference was much less than the technologically permissible threshold for a minimum deviation of 15% for all panels produced in this work [24]. For the rMDF panels, the minimum density was from 86% to 97% of the average. There was no significant variation in the density of these types of panels along their cross-section, i.e., the rMDF can be classified as relatively homogeneous panels. The reference MDF panel, fabricated from natural, industrially obtained wood fibers, had a minimal density value, representing 96% of the average value.

The water absorption (WA) of the laboratory-fabricated MDF panels from recycled wood fibers and industrial wood pulp, determined after 24 h of immersion in water, is presented in Figure 2. The WA values of the rMDF panels varied from 50.8% to 66.4%. The lowest WA value was determined for the rMDF panel fabricated with recycled fibers at a hydrolysis temperature of 121 °C and a hydrolysis time of 30 min (panel type A). The highest WA value was recorded for the rMDF panel fabricated with fibers recycled at a hydrolysis temperature of 134 °C and a hydrolysis time of 60 min (panel type F). The difference in the WA between these two types of rMDF was 1.31 times. The control MDF panel, manufactured from industrially produced fibers, exhibited a WA value of 43.5%, or 1.17 times lower than the lowest for the rMDF panels.

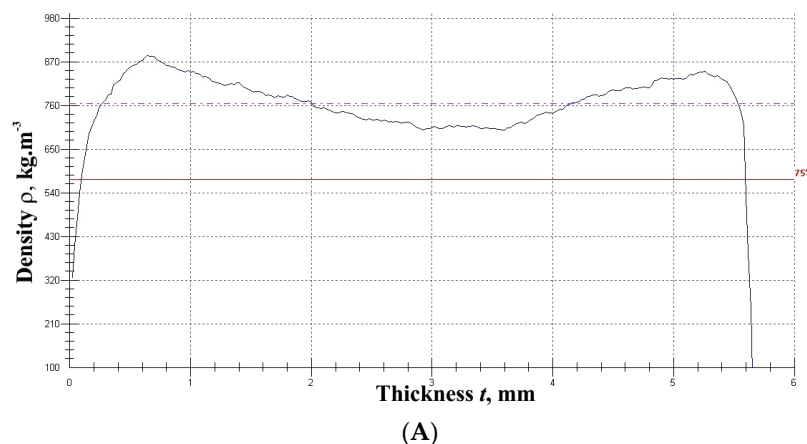


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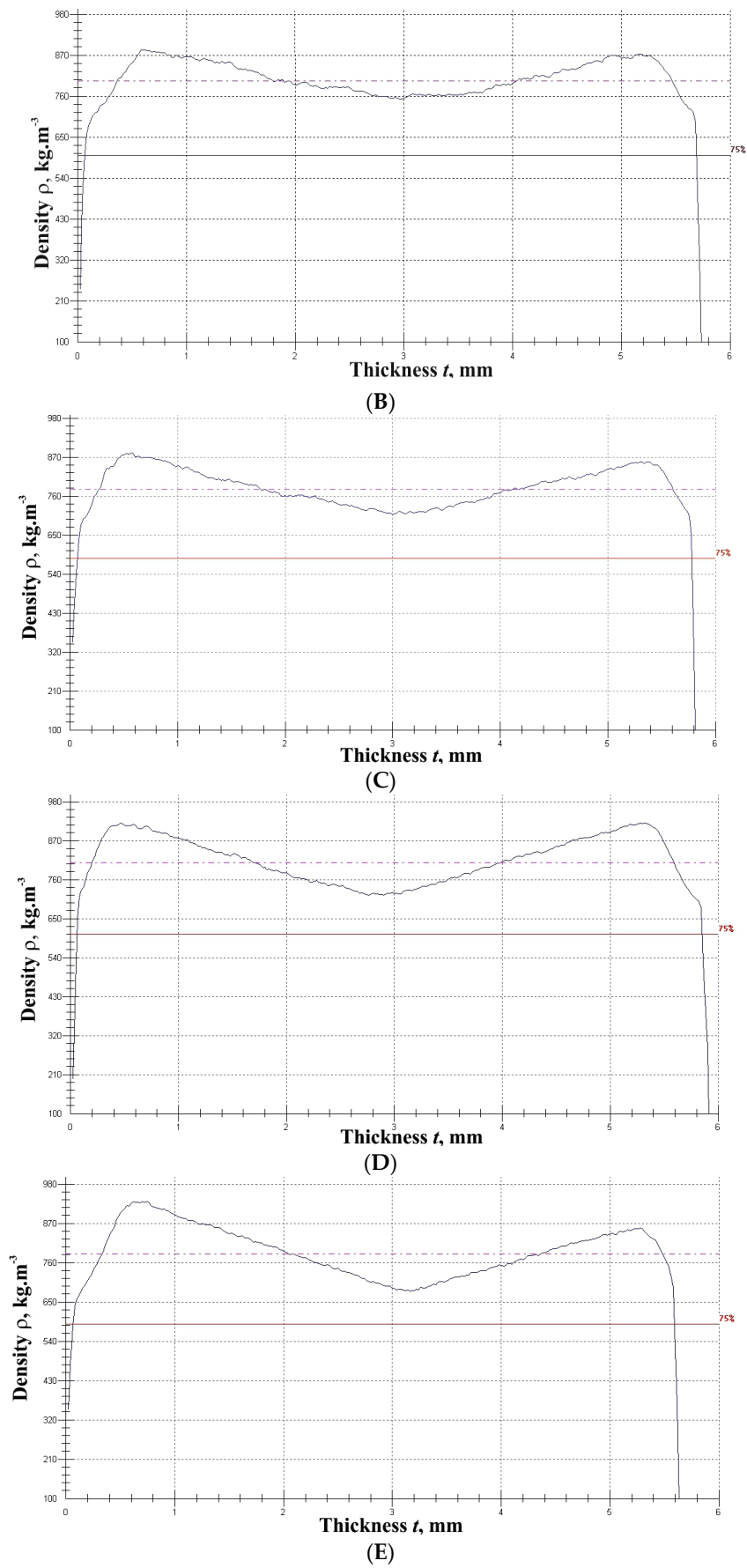


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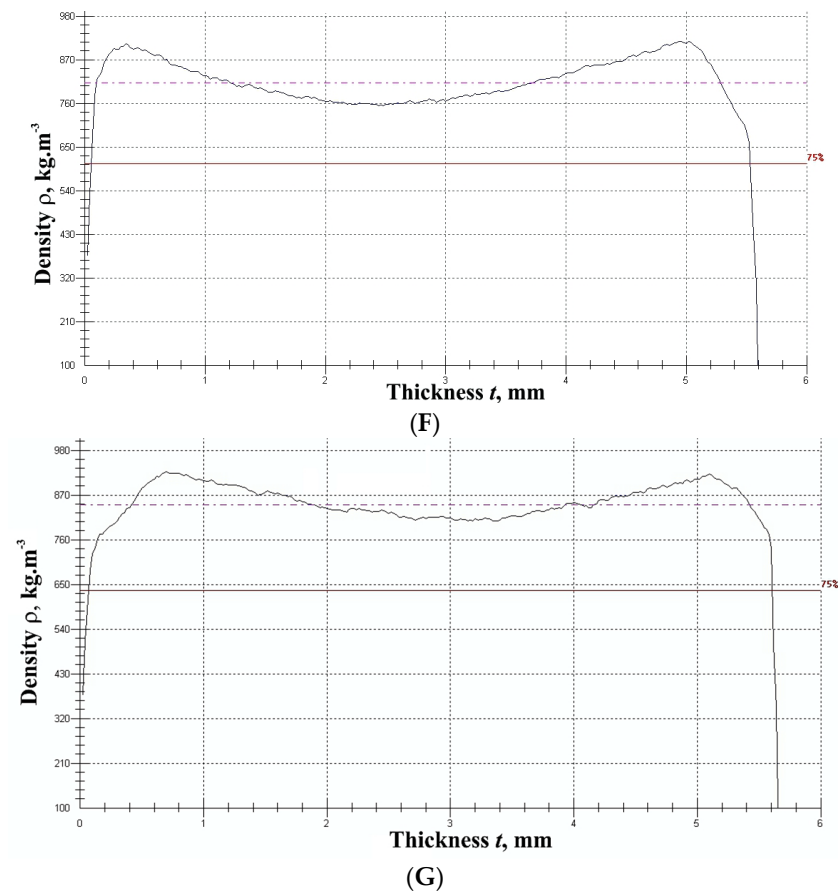


Figure 1. Density profiles of the MDF panels produced: (A) rMDF type A; (B) rMDF type B; (C) rMDF type C; (D) rMDF type D; (E) rMDF type E; (F) rMDF type F; (G) REF MDF. The dotted line shows the average density value.

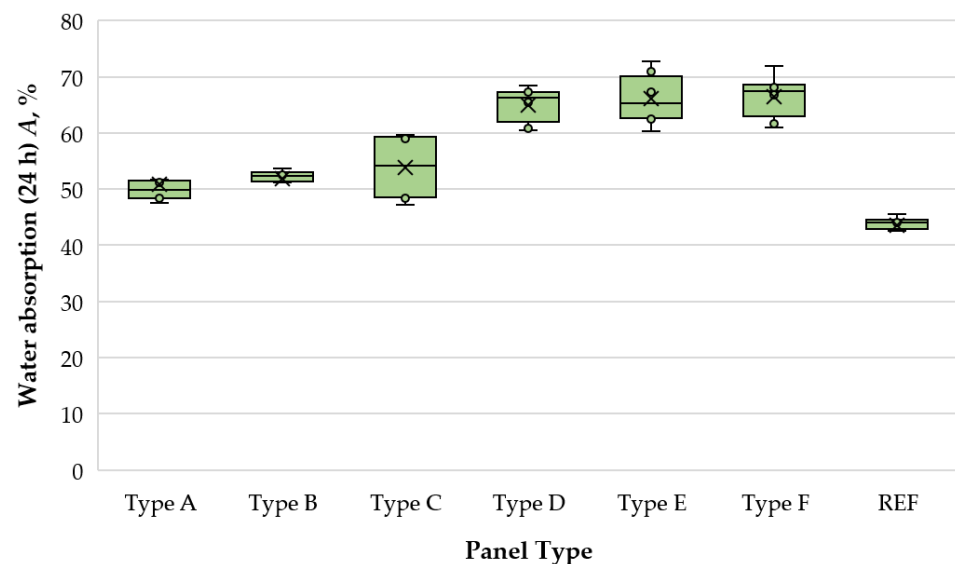


Figure 2. Water absorption (24 h) of the MDF panels produced.

The chemical oxygen demand (COD) was studied as a measurement of wastewater contamination and as an indirect indicator of the changes in the recycled fibers [10]. It should be noted that the hydrolysis temperature also affected the COD values [10]. The deterioration of the WA of the rMDF panels with increasing hydrolysis temperature was

also reported by [45]. It was established that the temperature and time of hydrolysis, in the studied range of variation, did not affect the content of the pentosans in the recycled fibers [10]. In this specific case, the deterioration of the WA at an increased temperature was attributed to the removal of extractives from the fibers or as a result of the excerpt of lignin from the fiber surfaces [45].

Compared to the WA of the reference MDF panels, the deteriorated WA values of the rMDF panels manufactured from natural fibers were consistent with the results reported by [49], where a 1.15 times increase in the WA was observed in the first MDF recycling. An average WA deterioration of 1.3 times was also reported by [36], when the recycled fibers completely replaced the natural ones.

The results obtained for the thickness swelling (TS) of the rMDF panels are presented in Figure 3. For the experimental conditions, the TS of the rMDF panels varied from 23.7% to 32.3%, i.e., an overall difference of 1.36 times was determined. Again, rMDF type A (hydrolysis temperature 121 °C and hydrolysis time of 30 min) had the lowest TS values, and rMDF type F (hydrolysis temperature 134 °C and hydrolysis time of 60 min) had the highest TS value, respectively.

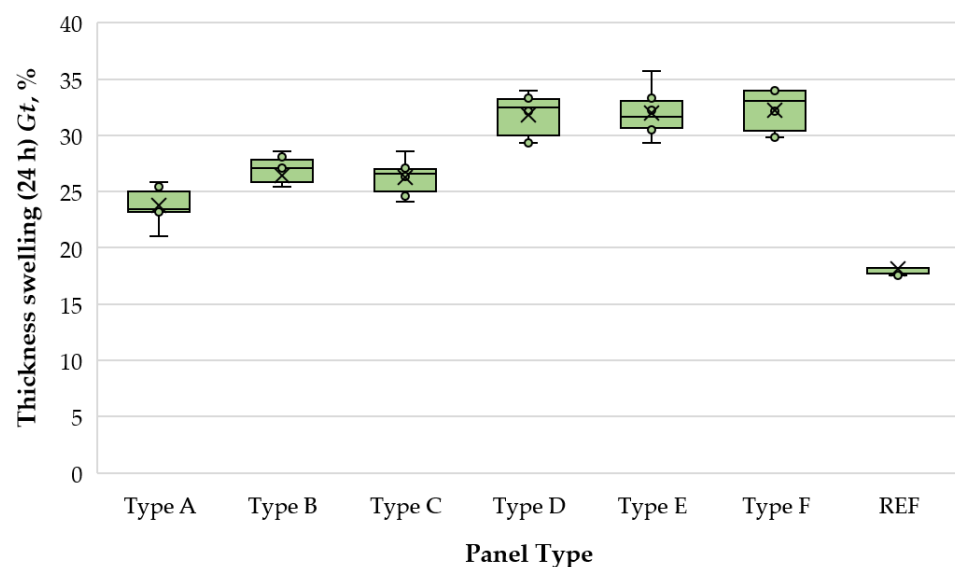


Figure 3. Thickness swelling (24 h) of the MDF panels produced.

The TS value of the reference MDF panel fabricated from the industrial pulp was 18.1% or 1.31 times better (lower) than that of rMDF type A. A similar deterioration of this property due to the characteristics of the fibers obtained by the hydrothermal hydrolysis recycling of the MDF was also reported by [45]; as in the cited study, an increase in the TS by 1.53 times was reported. Lubis et al. [36] also reported a deterioration of the TS values by nearly 1.8 times when completely replacing the natural fibers with the recycled fibers obtained by acid hydrolysis. That trend was also confirmed by [49], where a 1.13 times deterioration of the property was reported for the first generation of recycled fibers.

None of the rMDF panels fabricated from recycled fibers at a hydrolysis temperature of 134 °C fulfilled the requirements of EN-622-5 [58] in terms of the TS (no more than 30%).

The results obtained for the modulus of elasticity (MOE) of the rMDF panels are presented in Figure 4. The MOE values of the MDF panels, manufactured from recycled and natural wood fibers, varied from 3268 to 3680 N.mm⁻², i.e., the total difference was about 12%. The MDF panel fabricated with natural fibers (REF) had the highest MOE value, and the rMDF manufactured with fibers, recycled at 134 °C and for a time of 60 min had the lowest. The rMDF panel type A, i.e., fabricated from recycled wood fibers obtained at a hydrolysis temperature of 121 °C and a processing time of 30 min, exhibited the highest MOE. That panel had a 9.3% lower MOE than the reference MDF (REF 10). The difference

between the MOE values of these two panels was statistically significant, as determined by the *t*-test, where the *p*-value was 0.04.

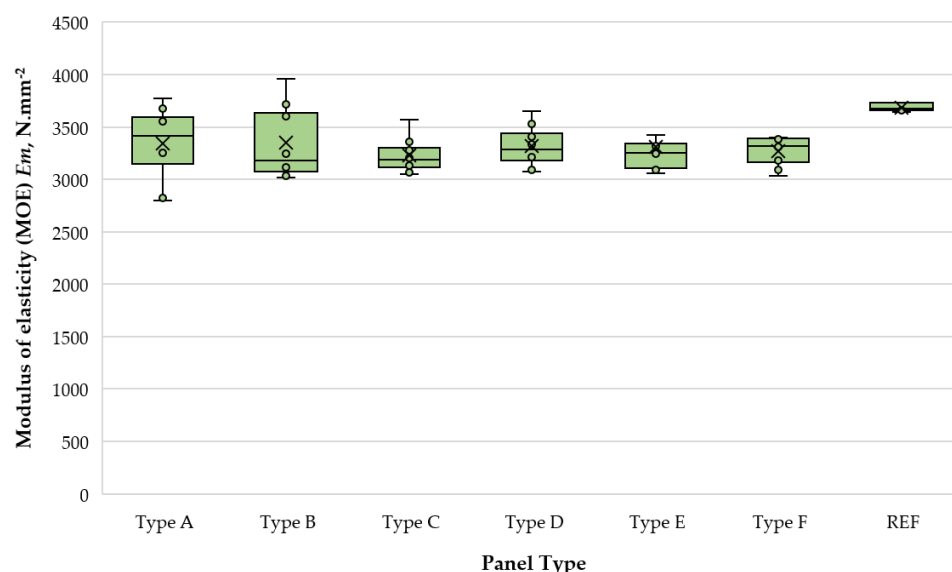


Figure 4. Modulus of elasticity (MOE) of the MDF panels produced.

Previous studies have also found a decrease in the MOE of rMDF panels [36,45,49]. Thus, when MDF recycling was performed with acid hydrolysis [36], a reduction in the MOE was reported, by an average of 1.3 times. Lowering the thermal hydrolysis temperature resulted in a reduction in the MOE values by 1.2 times [49].

That decrease in the MOE may be due to the reduced length of the fibers during recycling and the presence of spherical structures in the pulp from recycled fibers [10].

The results obtained for the bending strength (MOR) of the rMDF panels are presented in Figure 5. The MOR values of the rMDF panels, fabricated from recycled wood fibers obtained at different hydrolysis temperatures and times, ranged from 18.23 to 21.65 N.mm⁻². The control MDF panel, fabricated from natural fibers, exhibited a MOR value of 32.68 N.mm⁻²; i.e., the panels, manufactured from recycled fibers, had a 34% lower MOR than the MDF fabricated from the industrial pulp. Compared to the values reported in other studies, the slightly increased MOR values might be attributed to the use of MF resin in the adhesive system. However, none of the rMDF panels achieved the minimum standard requirement of 23 N.mm⁻² for general-purpose MDF panels for use in dry conditions [58]. This shows that, in terms of the bending strength, it is not appropriate for the MDF panels to be manufactured entirely from recycled fibers. The rMDF panel type A exhibited the highest MOR value (hydrolysis temperature of 121 °C and hydrolysis time of 30 min), and the lowest MOR value was determined for the panel type F (hydrolysis temperature of 134 °C and hydrolysis time of 60 min). The difference between the MOR values of these two rMDFs was 16%.

The data showed that hydrolysis temperature affected MOR, while the hydrolysis time was insignificant.

This also follows the established effect of this factor on the COD values [10]. To note, wastewater contamination during hydrolysis was not due to a change in the content of the pentosans. It was, therefore, due to the increased release of extractives, which negatively affected the MOR values of the rMDF panels fabricated from recycled wood fibers. The minor change in the MOE should be attributed to the significant influence of the raw material stiffness on this property. Even though the MOR is primarily determined by the strength of the bonds between fibers, the hydrolysis mode has a more significant impact. Regarding the MOR, applying hydrothermal hydrolysis temperatures above 121 °C is not recommended.

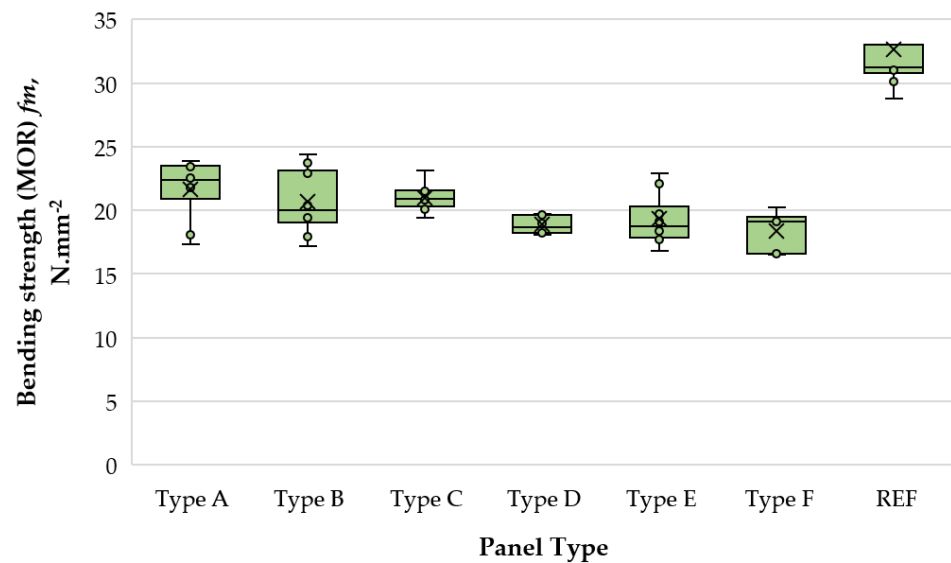


Figure 5. Bending strength (MOR) of the MDF panels produced.

Previous studies [36,45,49] have also reported the decreased MOR values of MDF panels manufactured from recycled fibers. Thus, with acid hydrolysis [36], the reported decrease was nearly three times. In hydrothermal hydrolysis, the established decrease was 1.3 times [45]. Lowering the process temperature resulted in a MOR decrease of 1.13 times [49]. The reduced content of the hemicelluloses can explain the significant decrease in the MOR in chemical hydrolysis.

The results obtained for the internal bond (IB) strength of laboratory MDF panels are presented in Figure 6. The IB values of the rMDF panels varied from 0.50 to 0.59 N.mm⁻², representing a total variation of 18%. Again, two main groups related to hydrolysis temperature stand out in those types of MDF panels. The highest IB value was determined for the rMDF panel type A (hydrolysis temperature of 121 °C and hydrolysis time of 30 min) and the lowest IB value for the rMDF type F (hydrolysis temperature of 134 °C and hydrolysis time of 60 min). In the investigated temperature range, increasing the hydrolysis temperature above 121 °C (saturated steam pressure of 0.2 MPa) is unjustified and undesirable.

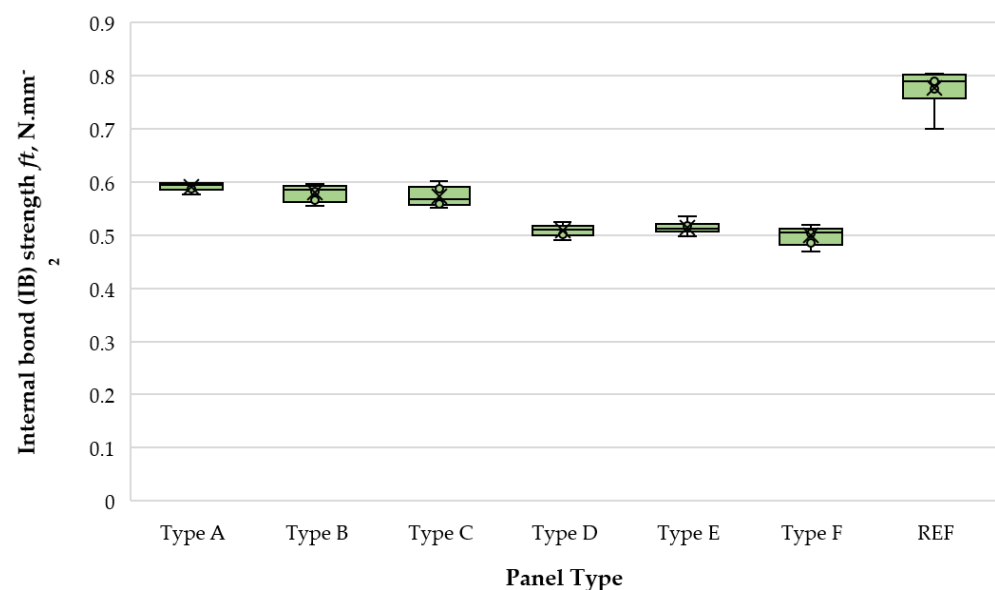


Figure 6. Internal bond (IB) strength of the MDF panels produced.

The reference MDF panel, fabricated from industrial pulp, exhibited an IB strength of 0.78 N.mm^{-2} or 31% higher than the rMDF type A.

None of the rMDF panels fabricated from recycled wood fibers fulfilled the requirements of EN-622-5 [58] in terms of the IB strength (no less than 0.65 N.mm^{-2}).

The IB results obtained align with the findings reported in previous studies on MDF recycling [36,45,49]. Thus, with acid hydrolysis, the decrease in the IB strength was nearly two times [36]. However, no such decrease was reported when hydrothermal hydrolysis was used [45,49], and even a slight improvement in this property was observed. The improvement in the IB strength [45] is explained by the depolymerization of the hemicelluloses (due to the applied elevated time or temperature), the products of which perform an auxiliary binding function. While in the research by [49], rMDFs had a slightly increased density, strongly influencing the IB strength, in the present study, a method was used to fabricate MDF panels with similar densities, and the applied hydrolysis temperature did not lead to changes in the hemicelluloses [10], which is why the effects described above were not observed.

A graphical representation of the formaldehyde content of the laboratory MDF panels, determined by the perforator method, is presented in Figure 7.

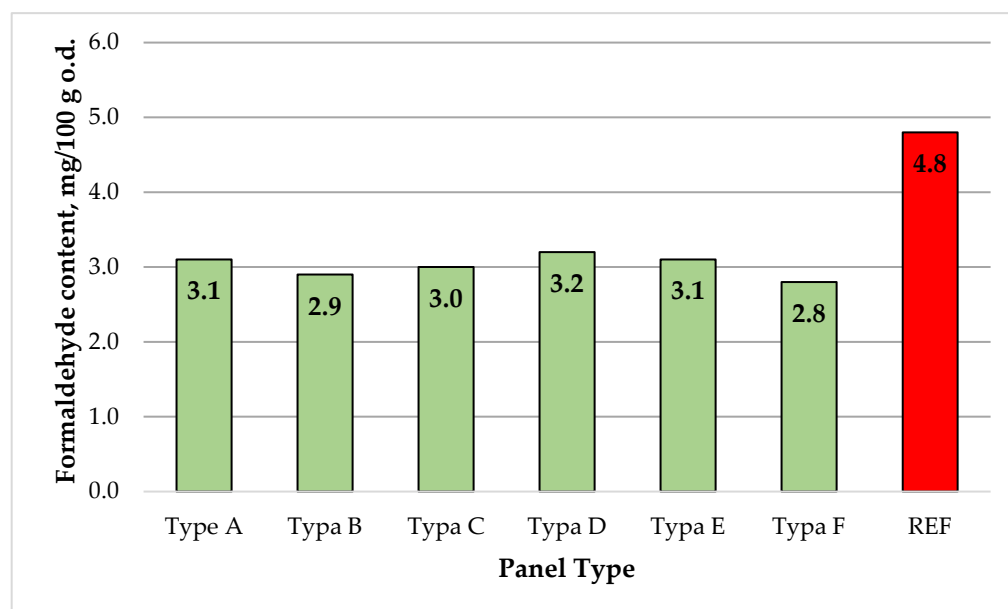


Figure 7. Formaldehyde content of the MDF panels produced.

As seen from the results obtained, there was almost no difference in the formaldehyde content of the rMDF panels. These results demonstrated that even at a hydrolysis temperature of 121°C and a hydrolysis time of 30 min, the UF resin was depolymerized to amino compounds, fulfilling the role of a formaldehyde scavenger. Such amino compounds were found in the study by Savov et al. [10]. The absence of a subsequent decrease in the formaldehyde content with an increase in the temperature and time of hydrolysis indicated that the following changes in the composition of the fibers were not related to the hydrolysis of the resin but to a change in their other components.

The rMDF panels exhibited about a 1.6 times lower formaldehyde content than the reference panel fabricated from the industrial pulp (REF MDF). That is an indirect indicator for the amino compounds formed due to the destruction of UF resin in the recycled fibers.

A decrease in the formaldehyde content ranging from 1.25 to 2.7 times was also reported in the studies [36,45]. In [49], no reduction in the formaldehyde contents was observed, but in that study, the hydrolysis was carried out at temperatures below 100°C .

Markedly, none of the rMDF panels fabricated in the present study fulfilled the requirements of EN 622-5 for TS, MOR, and IB strength [58]. That suggests that it is not

appropriate to fabricate MDF panels entirely from recycled fibers, but a solution should be sought by combining recycled and natural fibers. The cluster analysis based on all the properties measured in the present study demonstrated a distinct grouping of the panels produced with natural fibers (REF) from the six other panels fabricated with recycled fibers (Figure 8). Moreover, the clusters of the six panels produced with recycled fibers were also distinctly arranged, mainly based on the hydrolysis temperature rather than the three different hydrolysis durations (30, 45, and 60 min). That implied a higher impact of the hydrolysis temperature than hydrolysis duration on the overall properties of the panels. However, some similarities might have been observed between the treatments of the two durations when a particular property was considered (for instance, MOE values).

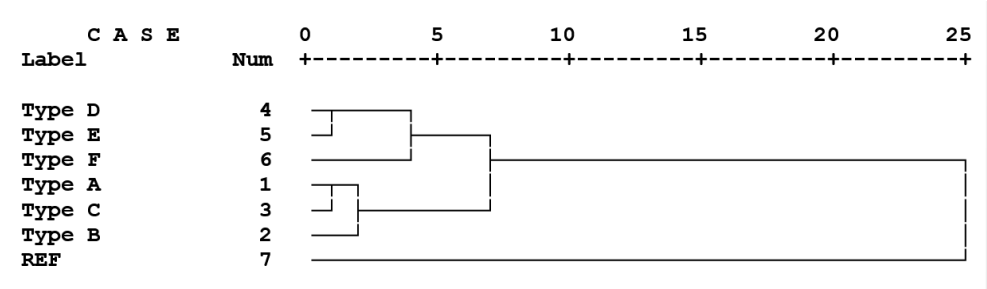


Figure 8. Cluster analysis based on all physical and mechanical properties.

High and statistically significant correlation values were found between the physical and mechanical properties (including the density, WA, TS, MOR, MOE, and IB) (Figure 9A–C). This demonstrated that using recycled fibers had similar deteriorating effects on nearly all the properties. However, the formaldehyde values showed a lower correlation with most of the abovementioned properties. This lower correlation can be considered as corroborating evidence of the effect of the formation of amino compounds, indicating that the amino compounds acted as formaldehyde scavengers (as discussed above) and had an outstanding impact on formaldehyde emission. Still, they had little effect on other measured properties (Figure 10A). This lower correlation can also be observed in the discrepancy in the center of the contour and surface plots (Figure 10B,C).

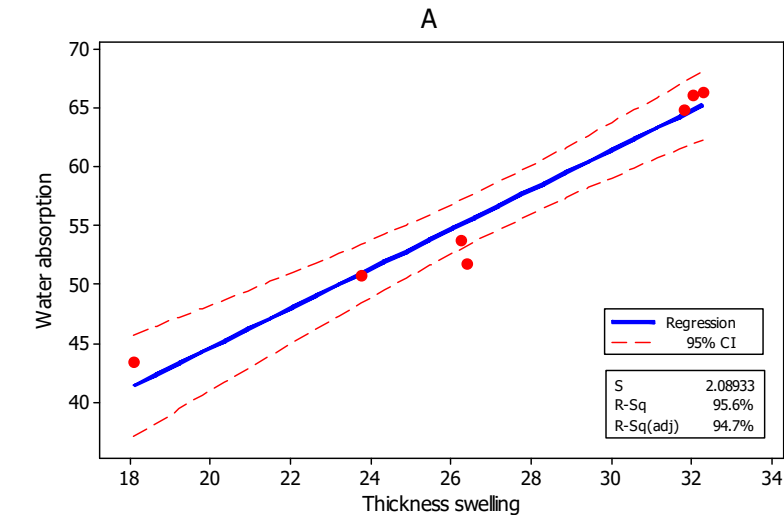


Figure 9. Cont.

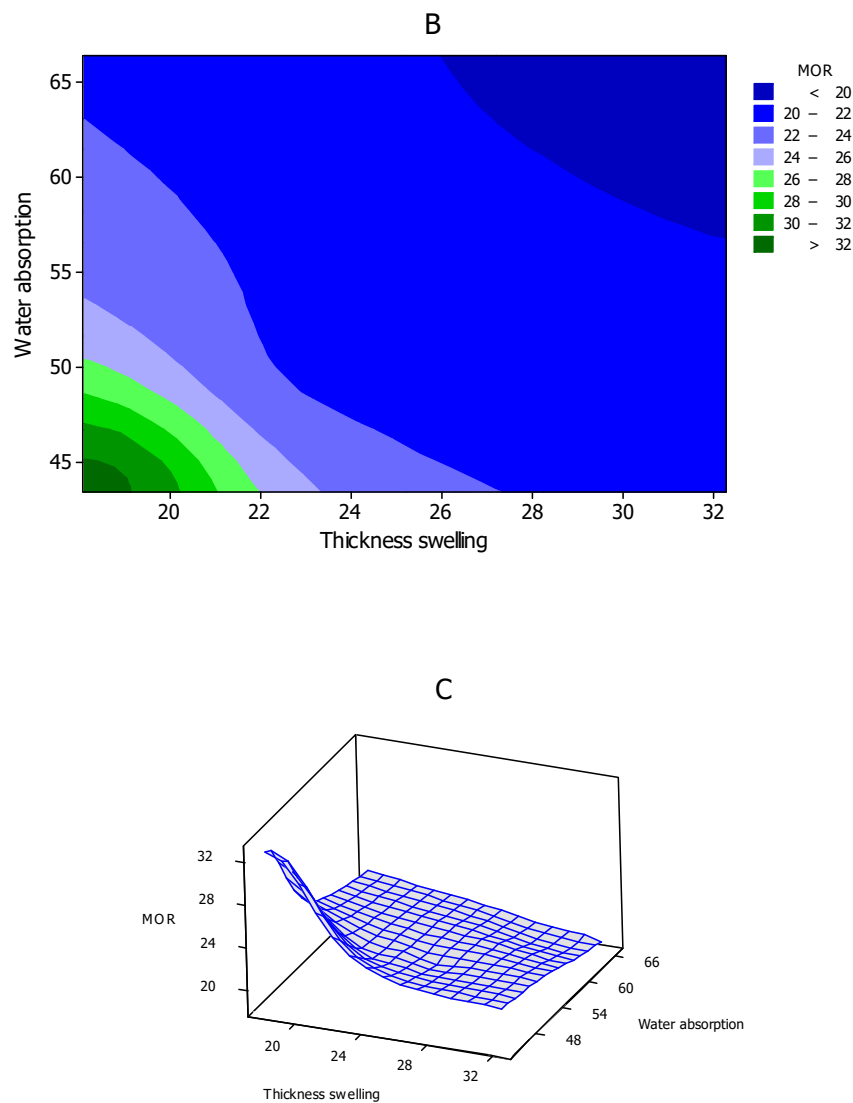


Figure 9. Fitted line (A), contour (B), and surface (C) plots between physical and mechanical properties.

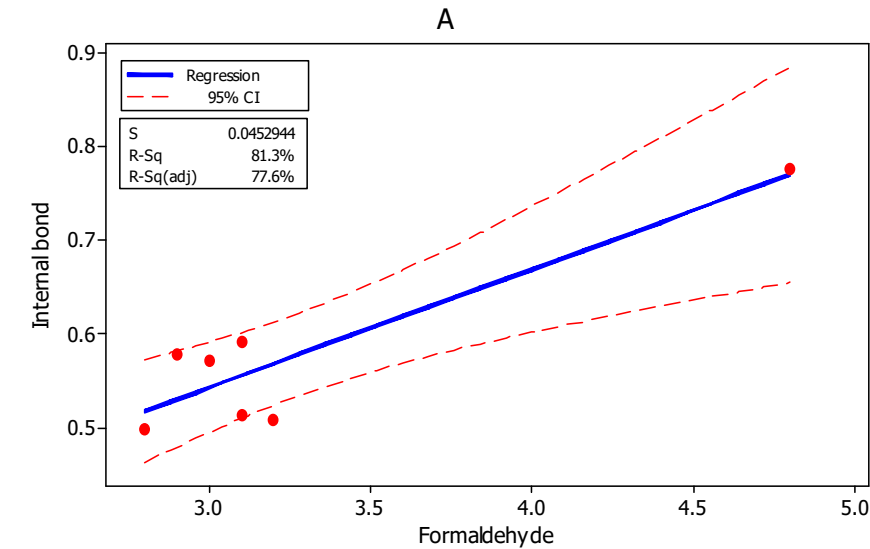


Figure 10. Cont.

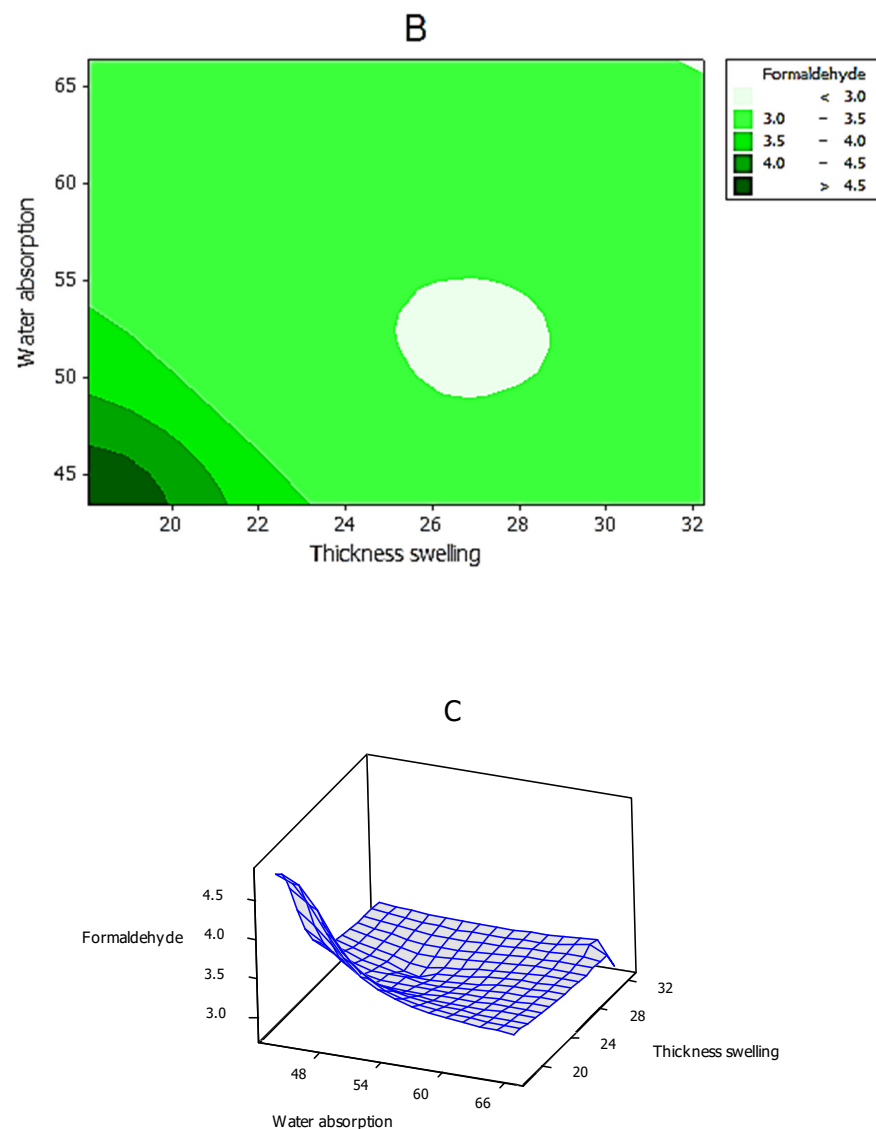


Figure 10. Fitted line (A), contour (B), and surface (C) plots between formaldehyde and other properties.

4. Conclusions

As a result of the study, it was found that, with the applied hydrothermal hydrolysis regimes, none of the rMDFs met the European standard requirements regarding the TS, MOR, and IB strength values. Moreover, all the physical and mechanical properties of the rMDF panels, produced in the laboratory from recycled wood fibers, were inferior compared to those of the MDF panels fabricated from industrial pulp. It was established that, to the highest degree, the rMDFs retained their MOE, as the most significant deterioration was observed in the IB strength. The considerable decrease in the IB strength was due to the reduced slenderness of the recycled fibers and the formation of spherical structures in the pulp. This, in turn, led to a reduction in both the adhesive and cohesive bonds in the panels. However, the rMDF exhibited a significantly lower formaldehyde content than the reference MDF panel fabricated from industrially produced pulp, due to the presence of amino compounds resulting from the depolymerization of the UF resin. No subsequent decrease in the formaldehyde content with increasing hydrolysis temperature or time was observed. This demonstrates that the disintegration of the resin and formation of amino compounds can be achieved at a hydrolysis temperature of 121 °C and a process time of 30 min.

The hydrolysis temperature significantly affected the physical and mechanical properties of the rMDF panels. Increasing the hydrothermal temperature from 121 °C to 134 °C resulted in deteriorated rMDF properties.

Based on the results obtained, it can be concluded that the optimal hydrolysis regime was determined at a hydrolysis temperature of 121 °C and a time of 30 min. It is particularly encouraging that no significant difference was reported in the density profiles of the rMDF and MDF panels fabricated from the industrial pulp. However, manufacturing fiberboard panels entirely from recycled fibers is not recommended due to the substantial deterioration of their physical and mechanical properties. Future studies should optimize the hot-pressing regimes and the ratio between the recycled and natural wood fibers to achieve the optimal performance and compliance of panels' characteristics with the standard requirements.

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References

1. Medium-Density Fiberboard (MDF) Market Size & Share Analysis—Growth Trends & Forecasts (2023–2028). Available online: <https://www.mordorintelligence.com/industry-reports/medium-density-fiberboard-mdf-market> (accessed on 15 September 2023).
2. Neykov, N.; Antov, P.; Savov, V. Circular Economy Opportunities for Economic Efficiency Implement in Wood-Based Panel Industry. In Proceedings of the 11th International Scientific Conference “Business and Management 2020”, Vilnius, Lithuania, 7–8 May 2020; pp. 8–17, ISBN 978-609-476-231-4. [CrossRef]
3. Garcia, C.A.; Hora, G. State-of-the-art of waste wood supply chain in Germany and selected European countries. *Waste Manag.* **2017**, *70*, 189–197. [CrossRef] [PubMed]
4. Besserer, A.; Troilo, S.; Girods, P.; Rogaume, Y.; Brosse, N. Cascading Recycling of Wood Waste: A Review. *Polymers* **2021**, *13*, 1752. [CrossRef] [PubMed]
5. Kim, M.H.; Song, H.B. Analysis of the Global Warming Potential for Wood Waste Recycling Systems. *J. Clean. Prod.* **2014**, *69*, 199–207. [CrossRef]
6. Hellström, L.M.; Carlberg, T.; Engstrand, P.; Gradin, P.A.; Gregersen, Ø.W. Evaluation of collimated chipping technology for reducing energy consumption in mechanical pulping. *J. Sci. Technol. Forest Prod. Process.* **2012**, *2*, 6–9.
7. Lykidis, C.; Grigoriou, A. Hydrothermal recycling of waste and performance of the recycled wooden particleboards. *Waste Manag.* **2008**, *28*, 57–63. [CrossRef] [PubMed]
8. Iždinský, J.; Vidholdová, Z.; Reinprecht, L. Particleboards from Recycled Wood. *Forests* **2020**, *11*, 1166. [CrossRef]
9. Zhang, Y.; He, Z.B.; Xue, L.; Chu, D.M.; Mu, J. Influence of a Urea–Formaldehyde Resin Adhesive on Pyrolysis Characteristics and Volatiles Emission of Poplar Particleboard. *RSC Adv.* **2016**, *6*, 12850–12861. [CrossRef]

10. Savov, V.; Antov, P.; Panchev, C.; Lubis, M.A.R.; Lee, S.H.; Taghiyari, H.R.; Todorova, M.; Petrin, S. Effect of Hydrolysis Regime on the Properties of Fibers Obtained from Recycling Medium-Density Fiberboards. *Fibers* **2023**, *11*, 64. [CrossRef]
11. Wan, H.; Wang, X.-M.; Barry, A.; Shen, J. Recycling wood composite panels: Characterizing recycled materials. *Bioresources* **2014**, *9*, 7554–7565. [CrossRef]
12. Michanicki, A. Recovery of fibers and particles from wood-based products. In Proceedings of the Forest Products Society Conference on Use of Recycled Wood and Paper in Building Applications, Madison, WI, USA, 9–11 September 1997.
13. Kharazipour, A.; Kües, U. Recycling of wood composites and solid wood products. In *Wood Production, Wood Technology, and Biotechnological Impacts*; Universitätsverlag Göttingen: Göttingen, Germany, 2007; pp. 509–533.
14. Mitchell, A.; Stevens, G. *A Life Cycle Assessment of Closed Loop MDF Recycling Using the Microrelease Process to Produce Recycled Wood Fiber from MDF Waste*; Final Report of WRAP Project MDD005; The Old Academy: Banbury, UK, 2009; ISBN 1-84405-417-9.
15. Zimmer, A.; Bachmann, S.A.L. Challenges for recycling medium-density fiberboard (MDF). *Results Eng.* **2023**, *19*, 101277. [CrossRef]
16. Hwang, C.Y.; Hse, C.Y.; Shupe, T.F. Effects of recycled fiber on the properties of fiberboard panels. *Forest Prod. J.* **2005**, *55*, 61–64.
17. Panchev, C.; Savov, V. Recycling of Medium Density Fibreboards—A Review. *Innov. Woodwork. Ind. Eng. Des.* **2022**, *1*, 39–46.
18. Antov, P.; Savov, V. Possibilities for Manufacturing Eco-friendly Medium Density Fiberboards from Recycled Fibers—A Review. In Proceedings of the 30th International Conference on Wood Science and Technology—ICWST 2019 “IMPLEMENTATION OF WOOD SCIENCE IN WOODWORKING SECTOR” & 70th Anniversary of Drvna industrija Journal, Zagreb, Croatia, 12–13 December 2019; pp. 18–24.
19. Irle, M.; Privat, F.; Couret, L.; Belloncle, C.; Déroubaix, G.; Bonnin, E.; Cathala, B. Advanced recycling of post-consumer solid wood and MDF. *Wood Mat. Sci. Eng.* **2018**, *11*, 19–23. [CrossRef]
20. Roffael, E.; Athanassiadou, E.; Mantanis, G. Recycling of particle and fiberboards using the extruder technique. In Proceedings of the Umweltschutz in der Holzwerkstoffindustrie; Georg-August Universität Göttingen: Göttingen, Germany, 2002; pp. 56–65.
21. Mantanis, G.I.; Athanassiadou, E.; Nakos, P.; Coutinho, A. A New Process for Recycling Waste Fiberboards. In Proceedings of the 38th International Wood Composites Symposium, Pullman, WA, USA, 5–8 April 2004; pp. 119–122.
22. Franke, R.; Roffael, E. Zum recycling von span-und MDFplatten. *Holz Roh-Werkstoff* **1998**, *56*, 79–82. [CrossRef]
23. Nuryawan, A.; Risnasari, I.; Pohan, A.P.; Husna, A.U.; Nasution, T.I.; Banurea, R.; Hartini, K.S. Properties of fiberboard (F.B.s) and recycle fiberboard (rFBs) and analysis of their wastage after recycling. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *935*, 012060. [CrossRef]
24. Irle, M.; Barbu, M.C. Wood-based panels technology. In *Wood-Based Panels: An Introduction for Specialists*; Thoemen, H., Irle, M., Šernek, M., Eds.; Brunel University Press: London, UK, 2010. Available online: <http://www.cost.eu/media/publications/10-35-Wood-Based-Panels-An-Introductionfor-Specialists> (accessed on 15 September 2023).
25. Pizzi, A.; Papadopoulos, A.N.; Policardi, F. Wood composites and their polymer binders. *Polymers* **2020**, *12*, 1115. [CrossRef] [PubMed]
26. Mantanis, G.I.; Athanassiadou, E.T.; Barbu, M.C.; Wijnendaele, K. Adhesive systems used in the European particleboard, MDF and OSB industries. *Wood Mater. Sci. Eng.* **2018**, *13*, 104–116. [CrossRef]
27. Roffael, E.; Behn, C.; Schneider, T.; Krug, D. Bonding of recycled fibers with urea-formaldehyde resins. *Int. Wood Prod. J.* **2016**, *7*, 36–45. [CrossRef]
28. Kristak, L.; Antov, P.; Bekhta, P.; Lubis, M.A.R.; Iswanto, A.H.; Reh, R.; Sedliacik, J.; Savov, V.; Taghiyari, H.; Papadopoulos, A.N.; et al. Recent Progress in Ultra-Low Formaldehyde Emitting Adhesive Systems and Formaldehyde Scavengers in Wood-Based Panels: A Review. *Wood Mater. Sci. Eng.* **2023**, *18*, 763–782. [CrossRef]
29. Dunky, M. Urea-formaldehyde (UF) adhesive resins for wood. *Int. J. Adhes. Adhes.* **1998**, *18*, 95–107. [CrossRef]
30. Chuang, I.; Maciel, E. NMR Study of the Stabilities of Urea-Formaldehyde Resin Components Toward Hydrolytic Treatments. *J. App. Pol. Sci.* **1994**, *52*, 1637–1651. [CrossRef]
31. Abdullah, Z.A.; Park, B.D. Hydrolytic Stability of Cured UF Resins Modified by Additives. *J. App. Pol. Sci.* **2009**, *114*, 1011–1017. [CrossRef]
32. Girods, P.; Dufour, A.; Rogaume, Y.; Rogaume, C.; Zoulalian, A. Pyrolysis of Wood Waste Containing Urea-Formaldehyde and Melamine-Formaldehyde Resins. *J. Anal. Appl. Pyrolysis* **2008**, *81*, 113–120. [CrossRef]
33. Grigsby, W.J.; Carpenter, J.E.P.; Sargent, R. Investigating the extent of urea formaldehyde resin cure in medium density fiberboard: Resin extractability and fiber effects. *J. Wood Chem. Technol.* **2014**, *34*, 225–238. [CrossRef]
34. Grigsby, W.J.; Thumm, A.; Carpenter, J.E.P.; Hati, N. Investigating the extent of urea formaldehyde resin cure in medium density fiberboard: Characterization of extractable resin components. *Int. J. Adhes. Adhes.* **2014**, *50*, 50–56. [CrossRef]
35. Lubis, M.A.R.; Park, B.D. Analysis of the hydrolysates from cured and uncured urea-formaldehyde (UF) resins with two F/U mole ratios. *Holzforschung* **2018**, *72*, 759–768. [CrossRef]
36. Lubis, M.A.R.; Hong, M.K.; Park, B.D.; Lee, S.M. Effects of recycled fiber content on the properties of medium density fiberboard. *Eur. J. Wood Wood Prod.* **2018**, *76*, 1515–1526. [CrossRef]
37. Liu, M.; Wang, Y.; Wu, Y.; Wan, H. Hydrolysis and recycling of urea formaldehyde resin residues. *J. Hazard. Mater.* **2018**, *355*, 96–103. [CrossRef]
38. Bütün, F.Y.; Sauerbier, P.; Miltz, H.; Mai, C. The effect of fiberboard (MDF) disintegration technique on wood polymer composites (WPC) produced with recovered wood particles. *Compos. Part A Appl. Sci. Manuf.* **2019**, *118*, 312–316. [CrossRef]

39. Bütün, F.Y.; Mayer, A.K.; Ostendorf, K.; Gröne, O.-E.Z.; Krause, K.C.; Schöpfer, C.; Mertens, O.; Krause, A.; Mai, C. Recovering fibers from fiberboards for wood polymer composites production. *Int. Wood Prod. J.* **2018**, *9*, 42–49. [[CrossRef](#)]
40. Lubis, M.A.R.; Hong, M.K.; Park, B.D. Hydrolytic Removal of Cured Urea–Formaldehyde Resins in Medium-Density Fiberboard for Recycling. *J. Wood Chem. Technol.* **2018**, *38*, 1–14. [[CrossRef](#)]
41. Hagel, S.; Joy, J.; Cicala, G.; Saake, B. Recycling of Waste MDF by Steam Refining: Evaluation of Fiber and Paper Strength Properties. *Waste Biomass Valorization* **2021**, *2*, 5701–5713. [[CrossRef](#)]
42. Hagel, S.; Saake, B. Fractionation of Waste MDF by Steam Refining. *Molecules* **2020**, *25*, 2165. [[CrossRef](#)] [[PubMed](#)]
43. Ormondroyd, G.A.; Elias, R.M.; Curling, S.F. MDF Recovery: Recycled MDF technologies for routed and laminated applications. In Proceedings of the Conference: COST action FP1303, Sofia, Bulgaria, 28 February–1 March 2017.
44. Moezzi-pour, B.; Ahmadi, M.; Abdolkhani, A.; Doosthoseini, K. Chemical changes of wood fibers after hydrothermal recycling of MDF waste. *J. Ind. Acad. Wood Sci.* **2017**, *14*, 133–138. [[CrossRef](#)]
45. Moezzi-pour, B.; Abdolkhani, A.; Doost-hoseini, K.; Ramazani, S.A.A.; Tarmian, A.S. Practical properties and formaldehyde emission of medium density fiberboards (MDFs) recycled by electrical method. *Eur. J. Wood Wood Prod.* **2018**, *76*, 1287–1294. [[CrossRef](#)]
46. Ahmadi, M.; Moezzi-pour, B. Thermal Stability of Wood Fibers Produced from Recycled Medium Density Fiberboards. *Drvna Ind.* **2019**, *70*, 149–155. [[CrossRef](#)]
47. Cowling, E.B.; Merrill, W. Nitrogen in wood and its role in wood deterioration. *Can. J. Bot.* **2011**, *44*, 1539–1554. [[CrossRef](#)]
48. Dazmiri, M.K.; Kiamahalleh, M.V.; Kiamahalleh, M.V.; Mansouri, H.R.; Moazami, V. Revealing the Impacts of Recycled Urea–Formaldehyde Wastes on the Physical–Mechanical Properties of MDF. *Eur. J. Wood Wood Prod.* **2018**, *77*, 293–299. [[CrossRef](#)]
49. Bütün Buschalsky, F.Y.; Mai, C. Repeated thermo-hydrolytic disintegration of medium density fiberboards (MDF) for the production of new MDF. *Eur. J. Wood Prod.* **2021**, *79*, 1451–1459. [[CrossRef](#)]
50. Carvalho, L.; Costa, C. A global model for the hot-pressing of MDF. *J. Wood Sci Technol.* **2003**, *37*, 241–258. [[CrossRef](#)]
51. Gul, W.; Khan, A.; Shakoor, A. Impact of Hot Pressing Temperature on Medium Density Fiberboard (MDF). *Perform. Adv. Mater. Sci. Eng.* **2017**, *2017*, 4056360. [[CrossRef](#)]
52. Savov, V. Engineering of Selected Properties of Light Medium Density Fibreboards Produced from Hardwood Tree Species. *Innov. Woodwork. Ind. Eng. Des.* **2020**, *1*, 53–59.
53. EN 310:1999; Wood-Based Panels—Determination of Modulus of Elasticity in Bending and of Bending Strength. European Committee for Standardization (CEN): Brussels, Belgium, 1999.
54. EN 317:1998; Particleboards and Fibreboards—Determination of Swelling in Thickness after Immersion in Water. European Committee for Standardization (CEN): Brussels, Belgium, 1998.
55. EN 319:1993; Particleboards and Fibreboards; Determination of Tensile Strength Perpendicular to the Plane of the Board. European Committee for Standardization (CEN): Brussels, Belgium, 2001.
56. EN 323:2001; Wood-Based Panels—Determination of Density. European Committee for Standardization (CEN): Brussels, Belgium, 2001.
57. EN ISO 12460-5:2015; Wood-Based Panels-Determination of Formaldehyde Release—Part 5. Extraction Method (Called the Perforator Method). European Committee for Standardization: Brussels, Belgium, 2015.
58. EN 622-5:2010; Fibreboards—Specifications—Part 5: Requirements for Dry Process Boards (MDF). European Committee for Standardization (CEN): Brussels, Belgium, 2010.

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