Improved Properties of Particleboards Produced with Urea Formaldehyde Adhesive Containing Nanofibrillated Cellulose and Titanium Dioxide

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Urea-formaldehyde is one of the commonly used resin types in the particleboard industry. In this study, the effect of nanofibrillated cellulose (NFC) and titanium dioxide (TiO_2) addition in the formulation of the urea formaldehyde resin on the physical, mechanical, and morphological properties of particleboard samples was investigated. The NFC (0.5% and 1%) and TiO_2 (0.5%, 1%, and 2%) were added to the 10% adhesive formulation. Two different pressure times, 4 and 8 min, were applied during the production of samples. Subsequently, the water absorption (WA), thickness swelling (TS), internal bonding strength (IB), modulus of rupture (MOR), modulus of elasticity (MOE), scanning electron microscopy (SEM), and statistical analysis of test samples were determined. The thickness swelling values ranged from 19.9% to 34.9% and WA values were from 74.50% to 110.6%. However, the maximum MOR, MOE, and IB values were 22.2 MPa, 2570 MPa, and 1.1 MPa, respectively.

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INTRODUCTION

Wood is a popular raw material commonly used in many structural applications, including buildings, furniture, for decoration purposes, *etc*., from ancient times to the present. Because of the decrease in forest resources, many wood-based panels have been developed and continue to be developed. Particleboard is the most popular of the panel types in the world because of low installation costs. The panels are manufactured by mixing wood particles with a suitable wood adhesive, followed by hot pressing, to provide a bonding mechanism (Owodunni *et al*. 2020). Wood adhesives play a key role in the production of wood-based panels and other structural layered wood composites. Improving the bonding quality and properties of wood-based panels mainly depends on the quality of the adhesives (Cui *et al*. 2015). The most used adhesives in the production of particleboard panels are the synthetic ones such as urea-formaldehyde (UF), phenol-formaldehyde (FF), and melamine formaldehyde (MF) (Lengowski *et al*. 2019). The majority of wood-based panel board production worldwide are produced with the help of UF adhesives. Therefore, studies on UF adhesives have an important place in the wood industry (Khanjanzadeh *et al*. 2019). Although numerous research studies have appeared on UF in the literature, information on nanoparticle reinforced UF resins is limited. Due to the increasing demands of UF resins and developments in production technologies, nanoparticles have recently attracted great attention in both research and industry (Dorieh *et al*. 2022).

Several nano-scaled fillers including organic and inorganic particles are beginning to be used to improve the bonding abilities of the adhesives. This is a reflection of the way that nanotechnology has begun to enter our lives in various fields. The fillers added to the adhesives have been considered to improve the bonding ability of wood particles in the particleboards (Kawalerczyk *et al*. 2020). Nanoparticles are added to wood and wood-based panels to develop new and improved materials with important functions, and physical and chemical properties. The production of lightweight and high-strength composites is the largest commercial application of nano-fillers. Nano-fillers can be applied in different ways, such as adding them to resin in wood-based panels or adding them to surface coatings (Ayrılmış 2021). One type of improvement is the reinforcement of adhesives with nanocellulose. Among the various improvements that nanotechnology offers in the forest products industry, nanocellulose-reinforced resin has been determined to be promising. It has improved the physical and mechanical properties of the boards (Lengowski *et al*. 2021).

In recent years, nanocellulose has been increasingly investigated for its many interesting properties and enormous potential (Aydemir and Gardner 2020 and 2022). Micro- and nano-fibrillated cellulose have recently gained importance as fillers for wood adhesives in particleboards (Kızılkaya *et al*. 2020; Iglesias *et al*. 2021). It was indicated that in the literature, the usage of nanocellulose as a reinforcement in adhesives for the production of wood panel boards has advantages such as improving the mechanical and physical properties of the panels and reducing formaldehyde emissions (Kargarzadeh *et al*. 2017). It was indicated that the addition of cellulose nanofibers (NFCs) to urea-formaldehyde adhesives strengthened cellulose nanofibers (Vineeth *et al*. 2019a). Moreover, the addition of small amounts of nanocellulose (5 and 10 g) resulted in an improvement in properties such as bonding quality, modulus of elasticity, and bending strength (Kawalerczyk *et al*. 2021).

However, particleboards prepared with UF containing 1 wt% NFC showed a reduced thickness swelling, and better internal bond and bending strength than boards produced with pure UF (Veigel *et al*. 2012). Some mechanical properties of particleboard panels produced with nanocellulose increased considerably compared to the unreinforced samples. It was concluded that some physical and mechanical properties of lignocellulosic composites could be improved by changing the nanocellulose ratios (Yildirim and Candan 2021). Meanwhile, research on the reduction of formaldehyde emission in wood adhesives has prompted scientists to conduct research on biomaterial-based binders. In addition, it was shown that the formaldehyde emission of UF resin reinforced with nanocellulose can be reduced by up to 31.25% (Yildirim *et al*. 2021). In this case, nanocellulose (NC) is a material that has reinforcing ability and has natural binding properties (Vineeth *et al*. 2019b).

Cellulose nanomaterials (CNs) are gaining increasing attention due to their attractive natural properties such as biodegradability, high surface area, lightness, and ability to form effective hydrogen bonds along cellulose chains or within other polymeric matrices (Tayeb *et al*. 2018). The feasibility of hardening urea-formaldehyde wood adhesive bonds by adding cellulose nanofibrils was demonstrated. For this purpose, the suitability of the combination of cellulose nanofibrils and urea-formaldehyde resin has been demonstrated (Veigel *et al*. 2011).

Results have shown that the addition of both microfibrillated cellulose (MFC) and nanocrystalline cellulose (NCC) to UF resin make it more viscous, which can delay the gel time (Kawalerczyk *et al*. 2020). A positive effect of 1% and 2% TiO_2 on bonding strength and thermal stability of poly(vinylacetate) PVAc was indicated (Bardak *et al*. 2016). However, the appropriate amount of titanium dioxide and a suitable addition point for the production of E0 type urea-formaldehyde resin (UF) was investigated. The reduction of free formaldehyde from particleboard treated with UF resin was also investigated. It was found that the addition of 1% TiO_2 gave good values for Eco type urea-formaldehyde resin. However, the increase in the added titanium dioxide content caused the mechanical properties to decrease (Park and Lee 2009). TiO_2 was chosen in small sizes to ensure homogeneous heat distribution within the panel. Also, its low price (75 $/kg) is also a factor in this choice.

In this study, it was aimed to strengthen the urea formaldehyde resin by using different ratios of titanium dioxide and cellulose nanofibers, and to improve the load distributions within the polymer matrix with nanofibrillated cellulose (NFC). In addition, the heat transfer was accelerated in the matrix due to the presence of TiO_2, and it was aimed to harden the adhesive at lower resin ratios and in a shorter time. Furthermore, the physical, mechanical, and morphological properties of the obtained board samples were investigated. The fact that there are not many studies investigating the effect of TiO2 and pressing time in NFC based UF resin makes this study original.

The literature reports that if the nanocellulose ratio is more than 1%, it causes agglomeration and generally reduces the mechanical properties of 0.5% and above. Therefore, NFC was used as 1% in this study. However, TiO_2 was used, as it better conducts heat from the press surface and improves mechanical properties.

EXPERIMENTAL

Materials

The red pine wood chip and the urea formaldehyde resin were obtained ready-to-use from a commercially operating particleboard plant (Orma Inc. Isparta, Turkey). Urea formaldehyde (UF) resin was used in the production of experimental boards. Ammonium chloride solution (20%) was used as the hardening agent (Orma Inc. Isparta, Turkey). The adhesive used in the study was urea formaldehyde resin with the following characteristics: solution (%) 65 (± 1), density (g/cm^3) 1.27 to 1.29, pH (25 ºC) 7.5 to 8.5, viscosity, Din/cPs 25º 150 to 200, gelling time (s, 100 ºC) 25 to 30, usage period (days) 60, and viscosity time (s, 25 ºC) 20 to 30. The resin ratios were kept constant compared to the dry chip weight and used as 10% and 8% in the boards produced with 0.625 g/cm^3 densities. The amount of hardener used in urea formaldehyde resin was applied as 10%.

Titanium dioxide (TiO_2) used in this study was obtained from MKnano Inc. (Ontario, Canada). TiO_2 has a hydrophilic and amorphous structure. The purity and size of TiO_2 were 99.5% and 40 to 50 nm. The specific surface area of TiO_2 was 150 m^2/g. Nanofibrillated cellulose (NFC or CNF), the other filler used as reinforcing agent, was provided by the University of Maine (Orono, ME, USA). The NFC was produced by mechanically refining from bleached softwood flour and the purity of NFC was 98%. Mean particle size and surface charge (zeta potential) of NFC were 5 to 200 nm in width and 130 to 225 μm in length and – 48 to – 5 mV, respectively. The nanocelluloses were supplied in dry form. The material was dried at 103(±2)°C before usage.

Although nanocellulose and TiO_2 are relatively expensive, costs are predicted to be lower when used on an industrial scale. On the other hand, since much higher (up to 40% increase) mechanical properties will be obtained and the amount of urea formaldehyde will be reduced, more ecofriendly sheets can be obtained.

Methods

Production of particleboards with urea formaldehyde-nanofiller resins

The NFC (0.5% and 1%) and TiO_2 (0.5%, 1% and 2%) were mixed with distilled water in an ultrasonic bath for 30 min and the water-filler suspensions were added to the urea formaldehyde resin and mixed with mechanical mixer at 1500 rpm for 30 min, followed by 30 min in the ultrasonic bath until a homogenous mixture occurred. Figure 1 shows the production of particleboard used NFC, TiO_2, and wood chips as raw materials which were incorporated with the of UF resin. It was generally provided the homogeneity in resin, but as mentioned in the literature, more agglomeration was observed in the SEM-mapping analysis, especially at high loading ratios in both nanocellulose and TiO_2 (Artner *et al.* 2021). The resin formulation was applied to wood particles in a blender using a spray gun.

Fig. 1. Raw materials used in particleboard production

All formulations were individually prepared in similar ways, and finally all blends were degassed for 30 min under vacuum. Particleboards were produced in 400 × 400×10 mm^3 dimensions under 15 to 20 N/mm^2 pressure. Pressing temperature was kept at 140 to 160 °C, and press time was determined as 4 min and 8 min. Different pressing times were chosen to examine the effect of TiO_2 on hardening. Table 1 shows the percentage of urea formaldehyde, cellulose nanofiber, titanium dioxide, and duration time of the samples under hot pressure according to the codes of samples. Besides, nanocellulose-free boards were not produced since examined the effect of TiO_2 on the hardening time of nanocellulose-containing resin.

Table 1. Production Conditions of Board Samples

Samples	NFC (%)	TiO_2 (%)	Pressure Time (min)	Samples	NFC (%)	TiO_2 (%)	Pressure Time (min)
0.5NFC-0.5TiO_2-4	0,5	0,5	4	0.5NFC-0.5TiO_2-8	0,5	0,5	8
0.5NFC-1TiO_2-4	0,5	1	4	0.5NFC-1TiO_2-8	0,5	1	8
0.5NFC-2TiO_2-4	0,5	2	4	0.5NFC-2TiO_2-8	0,5	2	8
1NFC-0.5TiO_2-4	1	0,5	4	1NFC-0.5TiO_2-8	1	0,5	8
1NFC-1TiO_2-4	1	1	4	1NFC-1TiO_2-8	1	1	8
1NFC-2TiO_2-4	1	2	4	1NFC-2TiO_2-8	1	2	8
0.5NFC-4	0,5	0	4	0.5NFC-8	0,5	0	8
1NFC-4	1	0	4	1NFC-8	1	0	8
Control	0	0	4	Control	0	0	8

Physical and mechanical properties

The test samples and their dimensions were prepared in accordance with TS EN 325 (1999) and TS EN 326-1 (1999). In addition, ten samples were prepared for each test. After cutting, each test sample was conditioned at 20 ± 2 °C and 65 ± 5% relative humidity for 2 weeks before testing. Water absorption (WA), thickness swelling (TS), modulus of rupture (MOR), and modulus of elasticity in bending (MOE) were determined using TS EN 317 (1999), TS EN 319 (1999), and TS EN 310 (1999), respectively. Panel density profile measurements were taken measuring the dimensions and weights of the samples.

Scanning electron microscopy (SEM) analysis

The surfaces of the samples under nitrogen were observed with an environmental scanning electron microscope (ESEM) (TESCAN; MAIA3 XMU, Brno – Kohoutovice, Czech Republic) with an accelerating voltage of 5 kV. The panel surfaces were sputter-coated with palladium-gold mixture using a Denton (Denton Vacuum, Moorestown, NJ, USA) sputter coater for enhanced conductivity.

Statistical analysis

One-way analysis of variance (ANOVA) and Duncan Test were conducted at the 95% confidence level using SPSS 16 (IBM Corp., Armonk, NY, USA) software. The differences between formulation and groups were determined.

RESULTS AND DISCUSSION

Physical Properties

The water absorption (WA, %) and thickness swelling (TS, %) values of boards immersed in water for 24 h are shown in Table 2. The water absorption values were slightly increased with the addition of nano scale cellulose to the structure, because of the hydrophilic feature of nanocellulose (Khanjanzadeh *et al*. 2019). Likewise, the hydrolysis sensitivity of the linkage between the carbon of the methylene bridge and the urea nitrogen explains the low resistance of urea formaldehyde resins against the influence of water and humidity (Baharoğlu *et al*. 2012; Dorieh *et al*. 2022). Moisture content (MC%) for all samples changed from 8.3% to 9.5%.

The thickness swelling values ranged from 19.9% to 34.9%, as shown in Table 2. Furthermore, the range for WA varied from 74.50% to 110.6%. Generally, The TS values of boards did not meet minimum requirement of TS after 24-h of submersion for general purposes. The increase in thickness swelling can be explained by the presence of many hydroxyl groups on the surface of NFC, which increases the swelling kinetics of the material (Cui *et al*. 2015).

Proper bonding between the fibers is necessary to provide good strength, and this is not possible unless the resin is spread homogeneously on the fibers. The weak bond between the fibers increases the water uptake of the boards (Khanjanzadeh *et al*. 2019). In contrast, it appeared that the presence of nanofibrillated cellulose did not considerably effect the water resistance of the board samples.

Table 2. Physical Properties of the Samples

Samples	MC (%)	Density (g/cm^3)	Water Absorption (%)	Thickness Swelling (%)
0.5NFC-0.5TiO$_2$-4	8.5 ± 1.2^{a}	0.788 ± 0.1^{a}	91.4 ± 11.4^{a}	34.9 ± 8.2^{a}
0.5NFC-1TiO$_2$-4	8.9 ± 0.8^{ab}	0.703 ± 0.1^{ab}	92.7 ± 13.5^{ab}	21.8 ± 2.7^{b}
0.5NFC-2TiO$_2$-4	8.9 ± 0.4^{ab}	0.877 ± 0.1^{abc}	81.6 ± 11.6^{abc}	29.5 ± 4.5^{bc}
1NFC-0.5TiO$_2$-4	9.2 ± 0.5^{abc}	0.825 ± 0.1^{abcd}	77.7 ± 9.9^{abcd}	30.9 ± 4.9^{bcd}
1NFC-1TiO$_2$-4	9.6 ± 0.6^{abc}	0.744 ± 0.2^{abcde}	82.2 ± 10.3^{abcd}	26.5 ± 3.4^{bcd}
1NFC-2TiO$_2$-4	9.3 ± 0.2^{abcd}	0.657 ± 0.1^{abcdef}	101.4 ± 6.4^{abcd}	24.3 ± 4.2^{bcd}
0.5NFC-4	9.2 ± 0.3^{abcd}	0.687 ± 0.2^{bcdef}	93.4 ± 13.7^{abcd}	27.8 ± 1.5^{cde}
1NFC-4	9.4 ± 0.4^{bcde}	0.798 ± 0.1^{bcdef}	81.5 ± 5.4^{abcde}	28.6 ± 1.8^{cdef}
Control-4	9.5 ± 0.3^{bcdef}	0.709 ± 0.2^{cdefg}	95.7 ± 6.9^{abcde}	19.9 ± 2.2^{defg}
0.5NFC-0.5TiO$_2$-8	8.9 ± 1.1^{cdefg}	0.839 ± 0.2^{defgh}	80.4 ± 9.2^{bcdef}	22.9 ± 3.4^{defgh}
0.5NFC-1TiO$_2$-8	8.3 ± 0.3^{cdefg}	0.839 ± 0.1^{efghi}	78.9 ± 6.7^{cdefg}	25.7 ± 2.2^{defgh}
0.5NFC-2TiO$_2$-8	8.6 ± 0.2^{cdefg}	0.839 ± 0.2^{fghi}	86.4 ± 8.9^{defg}	22.7 ± 3^{efghi}
1NFC-0.5TiO$_2$-8	8.9 ± 0.2^{cdefg}	0.724 ± 0.1^{ghi}	103.7 ± 8.1^{defg}	20.7 ± 3.3^{efghi}
1NFC-1TiO$_2$-8	9.5 ± 0.2^{cdefg}	0.786 ± 0.1^{hi}	83.6 ± 6.9^{efg}	30.6 ± 4.3^{fghi}
1NFC-2TiO$_2$-8	9.1 ± 0.2^{defg}	0.635 ± 0.1^{hi}	110.6 ± 9.5^{efg}	20.9 ± 1.7^{ghi}
0.5NFC-8	9.5 ± 0.7^{efg}	0.721 ± 0.2^{hi}	90.4 ± 8.5^{fgh}	25.9 ± 3.6^{hi}
1NFC-8	9.4 ± 0.4^{fg}	0.846 ± 0.1^{hi}	74.5 ± 9.4^{gh}	29.1 ± 1.8^{i}
Control-8	9.5 ± 0.5^{g}	0.717 ± 0.1^{i}	96.1 ± 14^{h}	24.9 ± 3.2^{j}

*The letters including A, B, C, *etc.* indicate the statistical differences among the samples according to the one-way variance analysis (ANOVA) and Duncan's test; (±) shows the standard deviation

Mechanical Properties

The IB, MOR, and MOE values of the boards produced from red pine wood particle and NFC-based urea formaldehyde adhesive reinforced with TiO$_2$ are shown in Table 3.

Table 3. Mechanical Strength Values of the Samples

Samples	MOE (MPa)	MOR (MPa)	IB (MPa)
0.5NFC-0.5TiO$_2$-4	1788.62^{bcde}	12.24^{bcd}	0.7^{ab}
0.5NFC-1TiO$_2$-4	2271.46^{ef}	15.77^{defg}	$0.\ 8^{cd}$
0.5NFC-2TiO$_2$-4	2255.56^{ef}	18.86^{gh}	0.9^{d}
1NFC-0.5TiO$_2$-4	2573.26^{f}	22.22^{h}	1.1^{e}
1NFC-1TiO$_2$-4	1343.567^{ab}	13.069^{bcde}	0.8^{bcd}
1NFC-2TiO$_2$-4	1379.199^{abc}	10.272^{ab}	0.7^{abc}
0.5NFC-4	1127.923^{a}	10.368^{ab}	0.7^{abc}
1NFC-4	1509.092^{abcd}	13.476^{bcdef}	0.8^{cd}
Control-4	1969.811^{cde}	13.198^{bcde}	0.9^{d}
0.5NFC-0.5TiO$_2$-8	1321.05^{ab}	8.175^{a}	0.6^{a}
0.5NFC-1TiO$_2$-8	1326.225^{ab}	11.225^{abc}	0.8^{cd}
0.5NFC-2TiO$_2$-8	1321.65^{ab}	9.85525^{ab}	0.7^{abc}
1NFC-0.5TiO$_2$-8	1636.325^{abcd}	10.05^{ab}	0.7^{abc}
1NFC-1TiO$_2$-8	1838.3^{bcde}	16.575^{efg}	1.1^{e}
1NFC-2TiO$_2$-8	1691.9^{abcde}	13.787^{bcdef}	0.8^{cd}
0.5NFC-8	1654.35^{abcd}	17.215^{fg}	1.1^{e}
1NFC-8	1816.75^{bcde}	14.85^{cdef}	1.0^{e}
Control-8	2077.95^{def}	17.35^{fg}	1.1^{e}

*The letters including A, B, C, *etc.* indicate the statistical differences among the samples according to the one-way ANOVA and Duncan's test; (±) shows the standard deviation

The highest IB value was found as 1.1 MPa in four samples of boards; first was the unmodified control sample that stayed under pressure for 8 min, second was 0.5NFC-8 coded sample, which was 0.5% NFC added sample, third was 1NFC-1TiO_2-8 coded sample, which was 1% NFC and 1% TiO_2 added samples to the urea formaldehyde, and lastly was 1NFC-0.5TiO_2-4 named sample, which was 1% NFC and 0.5% TiO_2 stayed under pressure for 4 min. However, the lowest value was seen as 0.6 MPa in the 0.5NFC-0.5TiO_2-8 coded sample. The MOR values ranged from 8.18 to 22.2 MPa. However, the EN 312 (2012) requirement for general-purpose particleboards is a MOR value of 12.5 MPa. Moreover, the highest MOE value was 2570 MPa in the 1NFC-0.5TiO_2-4 and the lowest was seen as 1130 MPa in the 0.5NFC-4 type boards. It was shown that the MOE values met the standard requirement of 1600 MPa for the mechanical properties. Hence, the boards produced with NFC-based resin enhanced the mechanical locking among the fibers and the board's properties met the standard requirements.

The elastic modulus and bending strength values of the boards produced with varying pressing times and adhesive additives are given in Table 3. It was noteworthy that the addition of nanofibrillated cellulose to the adhesive resulted in a noticeable improvement in the bending strength values.

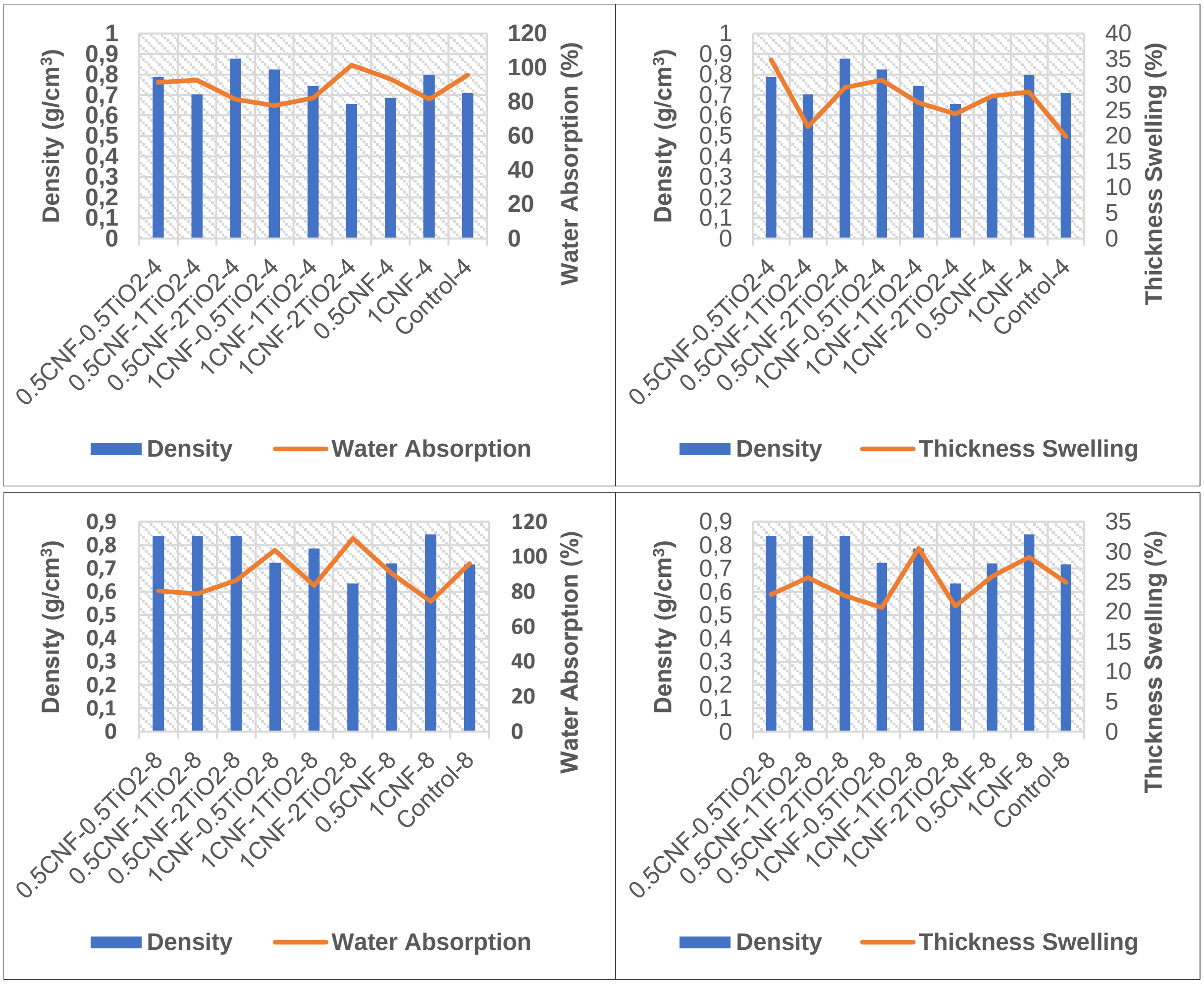

Fig. 2. Changing values of WA and TS related to sample density

It can be seen from Table 3 that 1% of NFC and the 0.5% TiO_2 gave the best modulus of elasticity of 2570 MPa. Another increase in NFC content led to a slight decrease in the performance of the resin. The effects of NFC and TiO_2 addition to urea formaldehyde resin on panel strength were investigated. As a result, it has been shown that the addition of NFC and TiO_2 improved the mechanical strength values to a certain extent. It was observed that the addition of 1% NFC + 0.5% TiO_2 NFC + 1% TiO_2 (8 min) and 0.5% NFC (8 min) to the resin gave the highest internal bond strength value (1.1 MPa).

The relationship between density and water absorption/thickness swelling properties is shown in Fig. 2. In general, thickness swelling increased with increasing densities of the panels, while an adverse effect on water absorption was observed. This depended on the packing density of the panel structures. As the density of the panels increased, the structure became fuller. Therefore, the number of pores through which water molecules diffused decreased, resulting in reduced water absorption. For this reason, the water absorption decreased with the increase of the density of the panels. However, thickness swelling increased as the density increased, as the number of particles and binders swelling in the fixed volume of the panel increased as the density increased (Amini *et al*. 2017). Figure 3 shows the SEM images, SEM-EDX, and SEM mapping in the cross-sections of the particleboards prepared with UF-TiO_2 and NFCs. SEM was made to look at the distribution of resin on the particles. However, the distribution of TiO_2 on the wood particles was examined by SEM mapping.

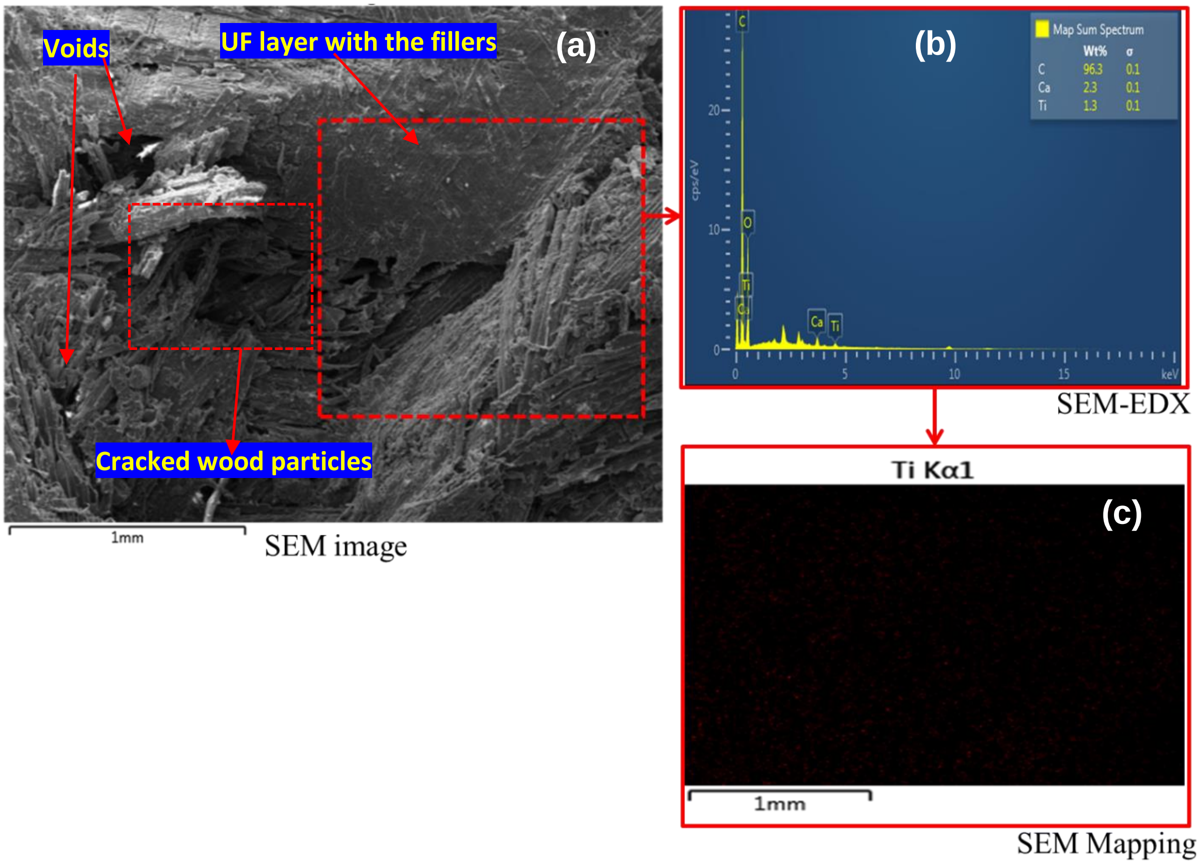

Fig. 3. SEM images (a), SEM-EDX (b), and SEM mapping (c) in the cross-section of the particleboards prepared with UF-TiO_2 and NFCs

It is shown in Fig. 3a that there were cracks in the wood chips that may have formed during pressing. This may be because the chips were over-dried or cracked due to excessive load during pressure. In addition, various cavities were observed in the chips. It was seen in Fig. 3b that the inorganic TiO_2 was determined as a result of SEM-EDX on the board cross-section. However, NFC could not be detected because it is organic. The distribution of TiO_2 as a result of EDX is shown in Fig. 3c. According to the SEM image, TiO_2 shows a homogeneous distribution, and in contrast, it is seen that there was a grouping in very few regions.

CONCLUSIONS

1. This study investigated the effect of nanofibrillated cellulose (NFC) and TiO_2 in the formulation of the urea formaldehyde resin. For this purpose, the physical, mechanical, and morphological properties of particleboard samples were evaluated. The results showed that the TS values of the boards did not meet minimum requirement for general purposes because of hydrophilic structure of the fillers including NFC and TiO_2. Moreover, a small reduction in WA values was found compared to the control samples.
2. The results exhibited that the MOE values met the standard requirement of 1600 MPa for the mechanical properties incorporating with network structure of cellulose nanofibrils. However, the MOR values met the requirement for general-purpose particleboards in some level.
3. The SEM images showed that morphological properties of the panels produced with nano-filled UF were better than the control panels. Both EDX and SEM mapping exhibited the homogeneous distribution and presence in the matrix of TiO_2, respectively.
4. The incorporation of nanocellulose and TiO_2 can provide high-performance properties to UF resin for applications in industrial fields. Besides, it has been possible to produce adhesives that emit low formaldehyde in order to produce environmentally friendly products. However, further research is needed to develop effective methods from laboratory scale to industrial size.

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