ABSTRACT • In this study, the effect of using olive stone residues (OSR) on some properties of particleboard was investigated. For this purpose, particle boards were manufactured from particles of white poplar (Populus Alba L.), which were partially substituted with OSR particles in amounts of 10 %, 20 % and 30 %. In addition, boards containing 30 % OSR, which had previously been chemically modified with NaOH solution, were produced. Phenol formaldehyde adhesive was used in the production of the boards. Chemical properties of wood and OSR particles (pH, alcohol benzene solubility, amount of ash), physico-mechanical properties (density, moisture content thickness swelling, modulus of rupture, modulus of elasticity and internal bond strength) and formaldehyde emission values of boards were determined. Water absorption and thickness swelling values were generally decreased with the increase in the use of OSR. When the effect of OSR usage on bending strength, modulus of elasticity, and perpendicular tensile strength values were examined, a decrease in the values was observed except for the 10 % OSR usage ratio. As a result of the application of alkaline pretreatment, an increase in thickness swelling values was observed, while the values of mechanical properties increased. Scanning electron microscopy (SEM) analysis results showed more spaces between particles with an increasing OSR usage ratio. Formaldehyde emission values decreased with the increasing amount of OSR. Formaldehyde emission values increased slightly with the application of alkali pretreatment. Based on the findings of this study, we can conclude that OSR can be used at particularly low ratio in particleboard production.

KEYWORDS: olive stone residues, particleboard, physical and mechanical properties, formaldehyde emissions

SAŽETAK • U istraživanju je ispitan učinak iskorištenja ostataka koštica masline (OSR) na neka svojstva ploča iverica. Za potrebe eksperimenta izrađene su ploče od iverja drva bijele topole (Populus alba L.) koje je djelomično zamijenjeno korenima masline u količini od 10, 20 i 30 %. Osim toga, izrađene su ploče s 30 % ostataka koštica masline pretvorene otopinom NaOH. Pri izradi ploča upotrijebljeno je fenol-formaldehidno ljepilo. Utvrđena su kemijska svojstva, koštica masline te fizičko-mehanička svojstva (gustoća, debljinsko bubrenje, modul loma, modul elastičnosti i čvrstoća raslojavanja) i vrijednosti emisije formaldehida proizvedenih ploča. Upijanje vode i debljinsko bubrenje u osnovi je smanjeno zbog povećanja udjela ostataka koštica masline. Pri ispitivanju utjecaja udjela

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Particleboards are materials obtained by mixing wood particles with synthetic adhesives and pressing at high temperatures and pressure. Their most important advantages are their low cost, ability to be produced in the desired thickness and size and high mechanical resistance values (Nishimura, 2015).

Particleboards (PB) are composites that have been developed with the increasing demand for wood-based materials and have become the primary raw material for furniture production in a short time. Today, industries such as pulp and thermal energy recovery plants demand the same type of raw materials as low-value logs and round or splitting woods used in wood composite production. This has led to increased competition and the shortage of such wood raw materials caused their prices to skyrocket. The use of lignocellulosic alternative resources in production of PB will be an important way out to reduce competition for the particleboard industry and to avoid problems in the future raw material supply -environmentally friendly and continuous supply at low cost (Trischler, 2016; Borysiuk et al., 2019).

In addition to the studies using recycled wood materials for this purpose (Li et al., 2004; Wang et al., 2008; Azambuja et al., 2018), the following materials were also studied: kenaf (Kalaycioglu and Nemli, 2006), kiwi wastes (Nemli et al., 2003), flax and hemp (Sam-Brew and Smith, 2015), sugarcane bagasse and green coconut (Fiorelli et al., 2019), bamboo (De Almeida et al., 2017), rice husk (Nicolo et al., 2020), pinecones (Buyuksari et al., 2010) and wood composites production with lignocellulosic materials such as wheat and canola straw (Mo et al., 2003; Kord et al., 2016), sunflowers stalks (Tas and KUL, 2020) and walnut shells (Pirayesh et al., 2012). Also, studies were carried out on the evaluation of wood bark (Blanchet et al., 2000; Medved et al., 2019) in particleboard production. In this respect, studies have been increasing due to the necessity of using forest resources more efficiently and lignocellulosic materials being a good alternative for particleboard production.

According to the International Olive Council (IOC) data of 2021, the total olive oil production in the world was 3.1 million tons. European Union countries are leading in the production of olive oil (about 2 million tons). In Turkey, 227500 tons of olive oil is produced annually, and Turkey is third in olive oil production (IOC, 2020).

After the olive squeezing process, 50 % liquid and 30 % solid waste remains. Solid wastes include broken olive seeds, squeezed residues, leaves, branches, etc. and the disposal of these wastes other than oil creates environmental problems (Monteiro et al., 2009). Organic waste generated during the processing of agricultural products creates storage problems in factories, and when mixed with water and soil, it causes serious environmental issues and greenhouse gas emissions (Sharma et al., 2019). Evaluation of this waste is necessary economically and to eliminate its harmful effects on the environment. It has been determined that OSRs used in various polymer-based composite studies show good physical and mechanical properties (Ayrilmis and Buyuksari, 2010; Banat and Fares, 2015; Kaya et al., 2018). Elbir et al. (2012) determined that the use of OSR increased the resistance to fungal rot in particleboards. It has been determined that OSRs are especially suitable for particleboards to be used indoors where they provide the necessary strength properties (Farag et al., 2020).

Alkaline treatment is one of the most frequently used methods for modifying the fiber and particle surface and increases the amount of reactive OH groups in the material (Ndazi et al., 2007a). The hydroxyl groups increase, and better bonding occurs between lignocellulosic fibers and particles with the alkali pretreatment process. (Lopattananon et al., 2008). For this purpose, alkali pretreatment was applied to OSRs in this study.

In producing wood-based composites, formaldehyde-based glues are mostly used due to their various advantages and ease of use. However, during and after production, formaldehyde decomposition, which is a problem in terms of environment and health, occurs in the produced plates and this process can last for years. Formaldehyde, depending on the amount to which humans are exposed (>0.1ppm), causes allergic diseases such as tearing, irritation of the respiratory system and mucous membranes, skin disorders, cough, exhaustion, rash, and it can also lead to cancer. For this reason, reducing the amount of free formaldehyde amount
is an important criterion, especially for the panels used indoors (Salthammer et al., 2010; Kim et al., 2011; Song et al., 2015). This study investigated the possibilities of using OSRs as substitutes for the production of particleboards.

2 MATERIALS AND METHODS
2.1 Production of boards

White Poplar (*Populus alba* L.) logs with a diameter of 16 cm were used in the production of trial boards. The OSR used in this study was supplied from the Pirina A.Ş. privately owned company in Turkey, Aydin. Phenol formaldehyde (PF) resin (solid content: 40 %) is a product of Polisan Chemical Factory in Kocaeli, Turkey. The PF adhesive was used based on the oven-dried chip weight. The white poplar logs were at first debarked. In the rough chipping process, a laboratory type, two-blade coarse hacker from Vecoplan-hacker (Germany) was used. It was then passed through a Robert Hildebrand (Germany) ring type flaker machine with six hammers and sixteen knives with a blade ring. Algemaier (Germany) branded four-stage shaker sieve was used to sift the resulted particles. Those that pass through a 3 mm sieve and remain on a 1.5 mm sieve are in the middle layer, and those that pass through a 1.5 mm mesh sieve and remain on a 0.5 mm sieve are sieved to be used in the production of the outer layer. The sieved particles were dried in an OSR laboratory type drying oven at 100 °C to 1 % moisture content. In the gluing process, the glue was sprayed on the particles with an air gun and the particles were regularly mixed by hand to achieve a homogeneous gluing. A total of ten boards were produced with two replications, with dimensions of 550 mm × 550 mm × 12 mm. On the other hand, OSR was used in the middle layer with and without pre-treatment (NaOH). The OSR to be pretreated was subjected to 1 % NaOH extraction for 24 hours. Then the particleboards were conditioned at a temperature of (20±2) °C and (65±5) % relative air humidity. The specifications for all board types produced are shown in Tables 1 and 2.

2.2 Chemical properties of wood and OSR particles

The preparation of the particles for chemical analysis was carried out in accordance with the TAPPI T 257 cm-02 (TAPPI, 2002) standard. Wood samples were ground in a laboratory-type Willey mill. Then, they were sieved in a vibrating laboratory type sieve with 40 mesh (425 μ) and 60 mesh (250 μ) sieves. The fraction that passed through the 40 mesh sieve and remained on the 60 mesh sieve was used in the analyses. Finally, the moisture content of the prepared wood samples was determined. Alcohol-benzene solubility and ash content tests of the samples were performed using the standards TAPPI 204-97 (TAPPI, 2007) and TAPPI 211 om-02 (TAPPI, 2002), respectively. The pH values were measured in an extract solution made by 5 g wood flour added to 150-ml distilled water and boiled for 24 h. The pH values of the filtered solutions were determined by means of a pH meter (Kalaycıoğlu et al., 2005; Colak et al., 2007).

2.3 Physical and mechanical properties of particleboards

Moisture (MC) EN 322 (1993), density (D) EN 323 (1993), thickness swelling (TS) EN 317 (1993), modulus of rupture (MOR) and modulus of elasticity (MOE) EN 310 (1993) and internal bond strength (IB) EN 319 (1993) for particleboard samples were determined. The results were evaluated according to EN 312 (2010) and twenty test samples were prepared for each test.

<table>
<thead>
<tr>
<th>Board types</th>
<th><em>Populus Alba</em> particle, %</th>
<th>Olive stone reduce, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>C</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>D</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>E</td>
<td>70</td>
<td>30 (treatment)</td>
</tr>
</tbody>
</table>
2.4 Formaldehyde emission
2.4. Emisija formaldehida

The perforator method (ISO 12460-5, 2015) was used to determine the formaldehyde emission values (FE). In this method, free formaldehyde in the board is determined by extraction. The formaldehyde emission amounts of the samples were determined by using the measured absorbance values. The absorbance values of these solutions were measured photometrically at 412 nm in a UV Spectrometer device.

2.5 Statistical analysis
2.5. Statistička analiza

SPSS 20 package program was used for the statistical analysis. One-Way ANOVA (analysis of variance) was used to evaluate the data obtained from the experiments. If the effect was significant with the Newman-Keuls test, the mean values were compared.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Chemical properties
3.1. Kemijska svojstva

Chemical analysis of the samples used are given in Table 3. According to the results of statistical analysis, the difference between the pH and alcohol-benzene solubility of the wood samples was found to be statistically significant (p<0.001). The pH value also increased with the pretreatment of OSRs with basic NaOH. The pH of the tree species should be between 4 – 5.5 for good adhesion (Cao et al., 2017). The pH value of the pretreated OSRs was high for production (6.59). According to the results, it was determined that the amount of extractive substance of OSRs was much higher. The results obtained in similar studies show that olive stones contain high phenolic compounds (3.56-11.32 mg/g DM) (Erbil et al., 2012). It has been determined that the pretreatment application greatly reduces the amount of extractive material.

Alkali treatment applications remove some extractives, especially oil and wax compounds, from the lignocellulosic material (Troedec et al., 2008; Carvalho et al., 2010). Previous studies also stated that it can decompose lignin and hemicelluloses under room temperature conditions with alkali treatment (Ndazi et al., 2007b). It was determined that 1 % NaOH pretreatment did not affect the ash content values, while the difference in ash content between poplar wood and olive waste was found to be statistically significant. The ash content of OSRs was higher than that of white poplar particles.

3.2 Physical and mechanical properties
3.2. Fizička i mehanička svojstva

Average values of physical properties and results of Newman-Keus analysis are given in Figure 1. It was determined that MC values varied between 7.71 % and 8.18 %. The M values of the boards comply with the values specified in the standard. In addition, it was determined that the use of OSR had no effect on the density of the boards and values close to the targeted density were obtained.

The amount of thickness swelling (TS) increased depending on the soaking time of the boards. The lowest TS values of boards were obtained from the board groups using 30 % OSR after 2 hours and 24 hours of water soaking, while the highest values of boards were determined in the control groups. With the use of OSR rate of 30 %, there was a 31 % decrease in swelling rates compared to the control group. Extractives (phenol, tannin, etc.) found in wood reduce the rate of water absorption as they show water repellent properties (Cameron and Pizzi, 1986; Baharoglu et al., 2013). In addition, oils and waxy compounds in wood form a thin film layer and provide resistance to water (Nasser, 2012).

Swelling the crystalline structure in cellulose during alkali treatment can facilitate water penetration into the boards (Gwon et al., 2010). The TS values increased in the alkali pre-treated OSR boards. The thickness swelling values of the boards were higher than the standards specified in EN 312 (2010).

Average values of mechanical properties and results of Newman-keus analysis are given in Figure 2. It was determined that 20 % and 30 % OSR negatively affected MOR, MOE and IB values. There was no significant decrease in mechanical properties at 10 % usage rate. According to the EN 312 (2010) standard, the re-

![Table 3 Chemical properties of wood and OSR particles](image_url)
Required MOR value for general purpose and interior equipment such as furniture is 12.5 N/mm² and 13 N/mm², respectively, while the MOE value is 1800 N/mm². Except for the board group using 30% OSR without pre-treatment, all boards meet these requirements. According to the EN 312 (EN 2010) standard, the required IB value for general purpose and interior equipment such as furniture is 0.28 N/mm² and 0.40 N/mm², respectively. In general, all board groups meet the required IB resistance values. The adhesive properties are negatively affected by the increase of extractives in the raw material used, resulting in lower strength properties. The increase in the amount of OSRs used in wood composites may adversely affect the mechanical properties due to the increase of gaps in the board structure (Aras et al., 2022).

Hashim et al. (2010) determined that particle geometry is effective in bending and internal bond strength. With the use of particles with a long and thin geometry and a uniform structure, the particles provide a better bonding contact and more homogeneous structure (Cosereanu et al., 2015). Due to the different geometry and blunt chip shape of OSR, less adhesion surface may be provided and internal bonding may decrease.

The high extractive substance content of OSRs, especially layering oils and waxes, can prevent adequate glue penetration during gluing. The alkaline pre-treatment is carried out to cause the removal of the oil and wax layer on the surface, making the surfaces rough and hydrophilic. The bond strength is affected by the covalent bonding between the hydroxyl groups of the wood material and the polar groups of the glue, as well as the adhesion of the glue by penetrating the material on the surface (Mo et al., 2001). In addition, it can be said that the fact that the pH values of OSRs are higher than the appropriate pH (4-5) for adhesion negatively affects the board properties.

Scanning electron microscopy (SEM) analysis was carried out to determine the internal microstructure of the boards and the analysis results are given in...
Figure 3 SEM images of cross-sectional surface of boards: a) control boards, b) particleboard with 10 % OSR, c) particleboard with 20 % OSR, d) particleboard with 30 % OSR, e) particleboard with 30 % OSR-treatment

Slika 3. SEM slike poprečnog presjeka ploča: a) kontrolne ploče, b) ploča iverica s 10 % OSR-a, c) ploča iverica s 20 % OSR-a, d) ploča iverica s 30 % OSR-a, e) ploča iverica s 30 % tretiranog OSR-a
Figure 4 The effect of OSR amount on formaldehyde emission of boards
Slika 4. Utičaj količine ostataka koštica masline na emisiju formaldehida ploča

Figure 3. The white arrows in the Figures show the gaps formed in the boards, while the black arrows show the OSRs. It seems that with the increase in the use of OSR, the space ratio in the board increases and the adhesive bonding decreases. Also, there was less bonding between particle and lignocellulosic material in board groups using OSR.

3.3 Formaldehyde emission
3.3. Emisija formaldehida

The effect of using OSR on the FE of the boards is given in Figure 4. The produced boards have E1 FE class values (≤ 8 mg / 100 g) (ISO 12460-5 2015). The lowest FE values were obtained from the untreated board group using 30 % OSR. Hydrolysation-resistant flavonoid methylene bonds are formed after the pressing process of the boards because of the high content of phenolic compounds in the extractives. Thus, due to the increase in the reactivity of the extractive material, the FE values are significantly reduced (Pizzi, 1983; Pizzi and Mittal, 2017). For this reason, if the extractives and adhesives are treated at appropriate rates, it is possible to get emission values close to the E0 and super E0 formaldehyde classes (Stefani et al., 2008; Navarrete et al., 2012). In other words, OSR high phenolic compound content acts as a formaldehyde scavenger. Similar results were obtained in various studies (Pirayesh et al., 2013; Bekhta et al., 2019). On the other hand, FE values increased in boards produced using pre-treated OSR. This may be because of the removal of the extractives, as well as the spectrometric detection of aldehydes formed due to alkaline pretreatment.

4 CONCLUSIONS
4. ZAKLJUČAK

This study aimed to create an alternative raw material source by evaluating OSRs, which have a significant waste potential in particleboard production. It was determined that the obtained results are suitable for producing particleboards with PF. With the increase in OSR addition to the boards, dimensional stability increased while formaldehyde emission decreased. However, increasing the amount of OSR affected the mechanical properties negatively. There was no significant change in mechanical properties when using 10 % OSR. The results showed that OSR could be used as an alternative raw material in particleboard production. The use of such lignocellulosic materials may be necessary as an alternative to declining forest resources. Also, using these waste materials with no industrial value can contribute to environmental development.

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Corresponding address:

UĞUR ARAS
Karadeniz Technical University, Arsin Vocational Junior College, Materials and Materials Machining Technologies, Furniture and Decoration, Arsin, Trabzon, TURKEY, e-mail: ugararas.86@gmail.com