Production of Biodegradable Composite Plates from Cross-Linked Starch and Cellulosic Fibers

Sebahir Ülpki Köselerli,[a] Mehmet Onurhan Gücüş,[b,]* and Mustafa Kemal Uslu [c]

Plastic used in food packaging causes permanent damage to living things. Therefore, biodegradable packaging has gained importance. In this study, biodegradable composite plates made from cross-linked wheat starch and cellulose-based fibers were examined for their physical and mechanical properties. The mechanical and physical properties were significantly altered when the obtained composite plates were examined. According to texture analysis, the plate with the lowest brittleness and with the highest crushing toughness value was produced from 7% carboxymethylcellulose. The densities of the composite plates obtained from cross-linked wheat starch were found to be 0.171 g/cm³, and their densities were found to be lower than the composite plates produced from natural wheat starch. It was determined that the plate with the highest water resistance was produced from 7% carboxymethyl cellulose. Added cellulosic fibers (commercial cellulose, linter fiber, hemp fiber) reduced moisture absorption from the air, reducing the average moisture content to 8.71. All of the plates produced with 7% linter fiber, which has the lowest moisture content, completely disappeared from nature within 40 days.

DOI: 10.15376/biores.18.4.6772-6783

Keywords: Biodegradable; Cross-linked starch; Composite plate; Cellulosic fiber

*Contact information: a: Department of Forest İndustry Engineering, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey; b: Department of Food Engineering, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey; c: Department of Food Engineering, Akdeniz University, 07000 Antalya, Turkey; *Corresponding author: onurgucus@kmu.edu.tr*

INTRODUCTION

The use of polystyrene foam plates in the food packaging sector is growing persistently (Baker 2018). This packing material takes hundreds of years to vanish from nature (Franz and Welle 2003). Increasing the use of packaging made from biodegradable materials as opposed to polystyrene will be essential for achieving sustainability Unfortunately, the mechanical and physical properties of packaging materials derived from natural resources presently are insufficient, thereby limiting their applicability.

Foam plates made from polystyrene have a lower density than biodegradable composite foam plates made from starch. Therefore, it is easier to transport it to the oceans or rivers with the help of wind. This causes irreparable harm to aquatic organisms. To prevent this damage, restrictions have been imposed on its use in many countries (Dauvergne 2018). Starch is an essential component of composite plates produced to solve these problems. The fact that starch is abundant and cheap causes it to be popular. Composite plates made of starch in the desired mold are baked similar to wafer production (Shey *et al.* 2006; Uslu and Polat 2012).

The production of biodegradable composite plates can utilize wheat, maize, potato, and cassava as sources of starch. It has been observed that the disparities in starch structures have an effect on the foam structure of composite plates (Shey *et al*. 2006; Uslu and Polat 2012). It has been observed that the analogous chemical structures of starch and cellulosic fibers have improved the mechanical properties of composite plates (Soykeabkaew *et al*. 2004). In order to increase the water resistance of composite dishes, materials with hydrophobic properties such as hydrophobic wax were used as eggshell coating material as a filler in the suspensions produced by changing starch and fiber types (Chaireh *et al*. 2020; Maocheng *et al*. 2021).

Cross-linking, which is one of the chemical modification methods used to improve the physical properties of starch, is one of the techniques used to increase the water resistance of starch, since it significantly reduces the water holding capacity, swelling power, solubility, and hydrophilic properties of starch. The quantity of water absorption and density of composite plates produced by cross-linking starch with glyoxal diminished (Uslu and Polat 2012).

The addition of fiber reduces the water solubility and water absorption of biodegradable composite dishes, since fibers have greater crystallinity than starch and are less hygroscopic (Kaisangsri *et al.* 2014). For this reason, water resistance of biodegradable composite plates has been increased.

In the study, the physical properties of starch arising from its natural structure were improved by the cross-linking process. Biodegradable composite plates that can replace polystyrene plates have been produced from modified wheat starch. The strength of the plates was increased by adding cellulosic fibers to the composite plate formulations produced.

EXPERIMENTAL

Material

Wheat starch used in the production of biodegradable composite plates was obtained from local markets in Karaman. Wheat starch used in the production of biodegradable composite board was procured from local markets in Karaman. Linter fiber, hemp fiber and commercial cellulose were obtained from Istanbul University Faculty of Forestry. Carboxymethyl cellulose, guar gum, and glyoxal were supplied by the corporation Yapilcan Saglik Gerecleri ve Pazarlama.

Cross-linking of Starch with Glyoxal

Natural wheat starch was weighed (250 g) and placed into a beaker. A suspension was formed by adding 375 mL of distilled water. The total amount of glyoxal added to the suspension was 1% of the total amount. It was stirred for 24 h on a magnetic stirrer to allow the cross-linking reaction between glyoxal and wheat starch to occur. After the reaction was completed, the starch suspension was first filtered with the help of filter paper, and the filtered starch was washed 3 times with approximately 300 mL of distilled water. To dehydrate the cross-linked wheat starch, it was placed in an oven at 40 °C. The powder was sieved with a 250-mesh screen.

Foam Plate Production

Wheat starch containing 1% by volume glyoxal and distilled water was used to form

35% suspensions. Biodegradable composite plates were produced by adding 5%, 7%, and 10% cellulosic fiber types (linter fiber, hemp fiber, and commercial cellulose) and carboxymethyl cellulose into the suspensions. To prevent the starch in the suspension from precipitating, 0.5% guar gum was added. Suspensions in various formulations were homogenized in a homogenizer at 5000 rpm for 5 minutes. Samples were homogenized under high pressure. It can operate at high circular speeds with small diameter rotators. (Ultraturrax T-25, IKA Labortechnik, Staufen, Germany). The suspension prepared in the variable mold foam plate production machine was added to the lower mold and cooked as a result of automatically combining the upper mold with the lower mold.

Density

The bottoms of the composite plates were cut to specific proportions. A micrometer was used to measure the thickness of the pieces. Density calculations were performed by dividing the pieces' weights by their volumes.

$$d = m/v \tag{1}$$

Analysis of Water Percentage

Materials from the composite plate samples were 4 g thick. Specimens were allowed to dry for 24 h in an oven at 105 °C, then placed in a desiccator until it reached room temperature. Using the initial weight and the final weight, the quantity of moisture was computed.

$$w(\%) = \frac{m_1 - m_2}{m_1} \times 100 \tag{2}$$

Analysis of Percent Water Absorption Amount

To determine the quantity of water absorbed by the composite plate samples, they were placed in 1000 mL of distilled water at 25 °C for 1 min after being weighed. Utilizing the initial and final weights of the composite plates, which were weighed again after 9 min, the water absorption amounts were calculated (Uslu and Polat 2012).

$$water\ absorption(\%) = \frac{m_2 - m_1}{m_1} \times 100 \tag{3}$$

Texture Analysis

Mechanical properties were determined according to TS 985 EN ISO 178: 2011 + A1 Texture analyzer with the 2005 standard method (TA-XT plus, Stable Micro Systems, Surrey, England) and three-point bending apparatus (HDP/3PB). First, 100 mm x 25 mm samples were obtained from the undersides of the composite plate examples. The test specimen was placed on two supports, 60 mm apart, symmetrically, and a force was applied to the middle with the load application tip. The force was applied until the test specimen broke. The results were calculated according to the first peaks in the graphics using the device's software (Texture Exponent 32). (Uslu and Polat 2012). Hardness, brittleness, and fracture toughness values of biodegradable composite plates were determined.

Images from a Scanning Electron Microscope

From the composite plate samples, approximately 0.2 cm^2 sections were extracted and coated with 150 Å gold-palladium alloy. The coated samples were examined under the SEM scanning electron microscope.

Biodegradability

Composite plate samples obtained by adding cross-linked wheat starch and auxiliary substances in different proportions were cut into pieces of approximately 4 cm^2 and buried in the soil in the autumn season in an open field environment with mild climate conditions. Plate samples were taken from the soil at ten-day intervals for 40 days and their photographs were taken.

Statistical Analysis

To examine all the findings, plate production was made in 2 replications and analyzes were made in 2 parallels. Analysis of variance was used and changes between groups were concluded with the Tukey Multiple Addition test.

RESULTS AND DISCUSSION

Density

The results obtained as a result of the study are shown in Fig. 1. The average density of composite sheets produced from carboxymethyl cellulose was found to be 0.198 g/cm^3, the density of composite sheets produced from commercial cellulose was 0.150 g/cm^3, and the density of composite sheets produced from linter fiber was 0.150 g/cm^3. The density of the composite boards was 0.158 g/cm^3 and 0.158 g/cm^3. The hemp fiber was 0.181 g/cm^3. As can be seen in Fig. 1, as the amount of auxiliary material in composite plate formulations increased, the density increased due to the gelation that occurred in the structure.

One of the most important factors in determining food prices is packaging prices. When the average density of polystyrene foam boards used in daily life is between 0.06 and 0.08 g/cm^3, packaging costs are significantly reduced. In the food packaging industry, expanded polystyrene sheets have a wide range of applications. Densities of biodegradable composite sheets that can be used instead of polystyrene sheets range between 0.1 and 0.48 g/cm^3. As the amount of fiber added as an auxiliary substance in composite plaque formulations increases, the density increases proportionally as the gelation occurring in the structure increases. (Gleen *et al.* 2001; Preechawong *et al.* 2004; Salgado *et al.* 2008; Uslu *et al.* 2012; Kisac *et al.* 2022).

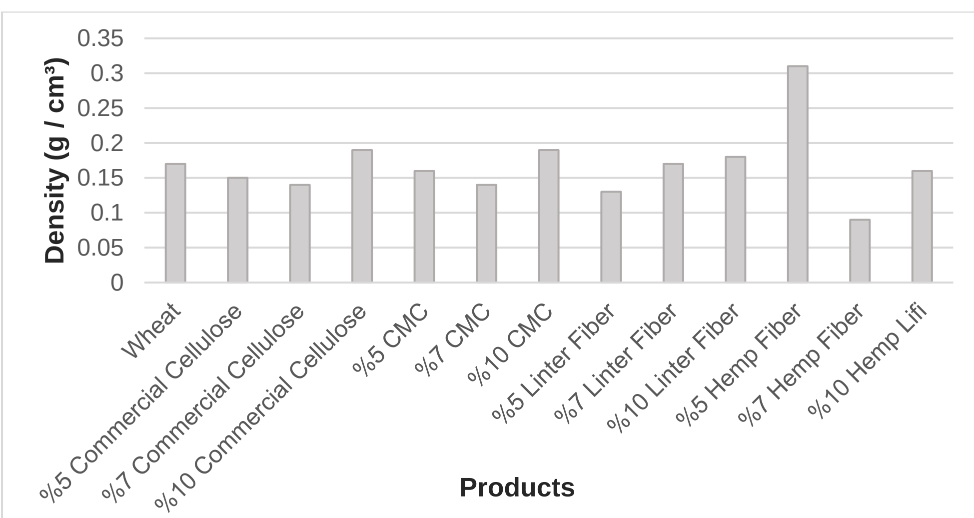


Fig. 1. Density values of composite plates

Amount of Percentage Water

Composite board produced with natural wheat starch contains more water than other boards produced from cross-linked wheat starch. It can be seen in Fig. 2 that the cellulosic fibers and other substances added to the sheet formulations may have slightly reduced the amount of moisture drawn from the air. The average water content of the composite boards produced as a result of the analysis was found to be 8.7%. In a different study, the water content of the corn starch boards was found to be 14.2% (Aygün 2013), and the moisture content of the foam boards made of glyoxal cross-linked corn starch was found to be 10.3% (Polat 2011).

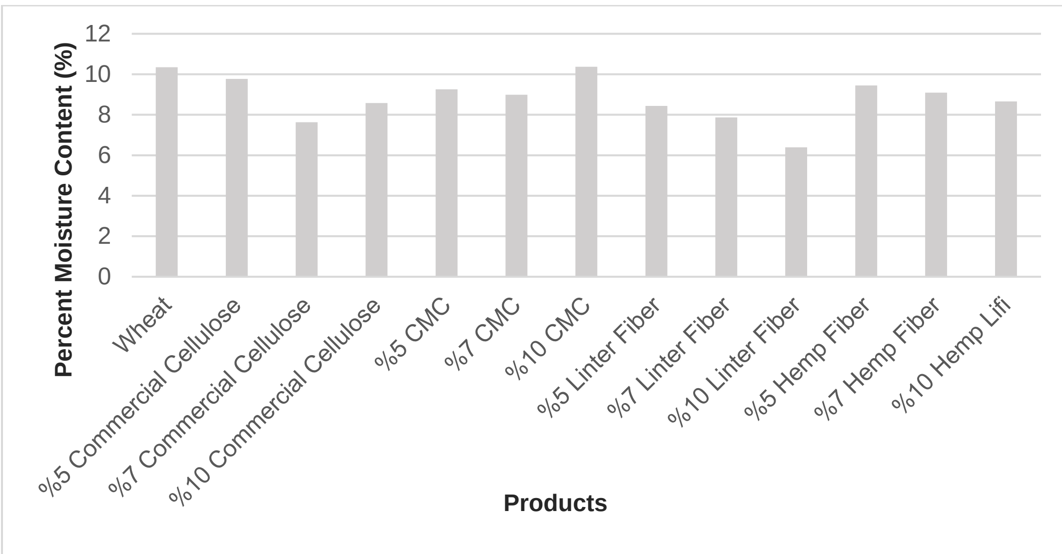


Fig. 2. Percentage of water in composite plates

Percent Water Absorption Amount

A composite board made from the cross-linked wheat starch sample was found to absorb more water than others.

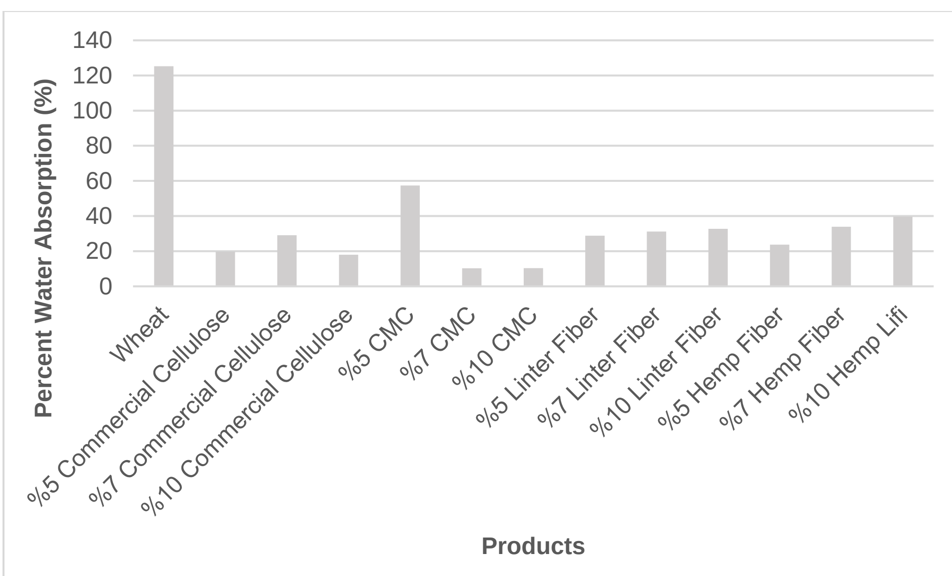


Fig. 3. The amount of water absorbed percentage by the composite plates

It can be seen from Fig. 3 that the water absorption rate decreased significantly with varying adjuvant addition rates. While the average water absorption amount of the composite boards obtained from natural starch was found as 125.3%, the average water absorption amount of the composite boards obtained from cross-linked wheat starch was found to be 27.9%.

Composite boards made from wheat starch absorbed more water than composite boards obtained with the addition of auxiliary substances due to their rough surfaces and wide cracks. This showed that the produced plates had an increased resistance to water.

As can be seen from Table 1, adding varying concentrations of cellulosic fibers to composite plate formulations made from natural starch resulted in significant changes in the elasticity and strength of the plates. The sheet produced with carboxymethyl cellulose from the composite sheets produced had superior properties compared to the others. With the addition of cellulosic fibers, the cracks on the surface of the sheet were significantly reduced and thus the mechanical properties were improved. The high amylopectin content of starch increased the diameter of the voids in the foam structure. For this reason, the bending strength of the foam board produced only from wheat starch was higher than the board produced from wheat-potato starch (Kısaç 2020). Composite boards made from starches with high amylose content have high tensile strength and durability (Shogren *et al.* 1998).

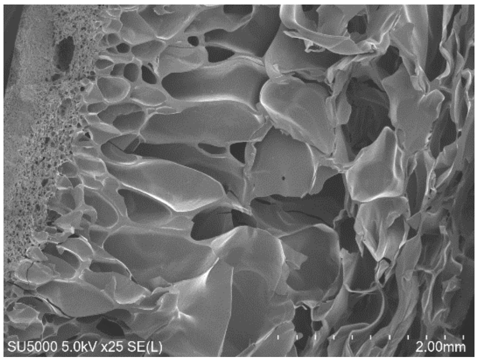
Table 1. Texture Analysis

Products	Hardness g Force 1	Brittleness / Flexibility Distance (mm)	Toughness (g/mm) Gradient F-D 1:2
Wheat	3700,85	16,09	432,96
%5 Commercial Cellulose	3064,21	15,21	369,89
%7 Commercial Cellulose	1546,57	4,3	347,35
%10 Commercial Cellulose	1589,75	24,97	61,57
%5 CMC	2735,59	3,12	875,03
%7 CMC	2526,39	1,9	1423,25
%10 CMC	3589,45	14,05	635,45
%5 Linter Fiber	2057,68	25	80,18
%7 Linter Fiber	1475,76	13,84	147
%10 Linter Fiber	4158,26	24,35	168,16
%5 Hemp Fiber	1280,03	6,4	241,79
%7 Hemp Fiber	1014,16	17,66	59,44
%10 Hemp Lifi	1305,04	16,1	96,29

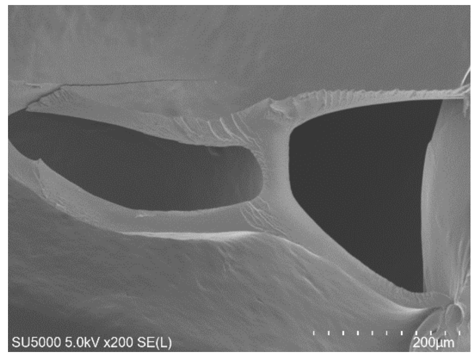
The tensile strength increases as the amount of added poplar fiber increases up to 15%, remains unchanged between 15% and 30%, and decreases when more than 30% fiber is added (Lawton *et al.* 1999). When the texture analysis results were examined, it was seen that the plate with the lowest brittleness and the plate with the highest fracture toughness value were produced from 7% carboxymethyl cellulose.

Scanning Electron Microscopy (SEM) Images

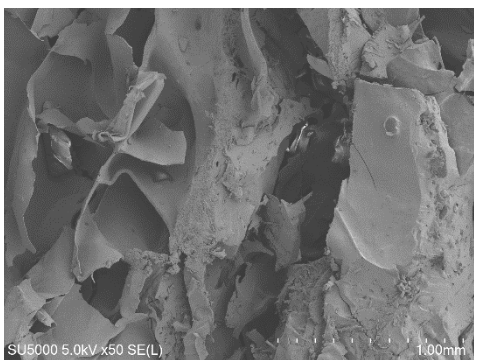
Figure 4 shows SEM images of composite plates made from modified wheat starch and glyoxal crosslinked cellulosic fibers. The rough surface area and wide surface cracks of the composite plate produced from natural wheat starch attract attention. With the addition of cellulosic fibers to cross-linked wheat starch, it is apparent that the gaps in the structure of wheat starch are closed, and thus the surface cracks of the composite plates are significantly reduced. As the amount of excipients in the suspensions of various dish formulations increase, the cracks decreased. However, cracks disappeared less in composite boards with hemp fiber added compared to other boards and the roughness on the board surface did not disappear. The amount of fiber in foam boards produced with potato starch reduced crack formation (Cinelli *et al.* 2006).



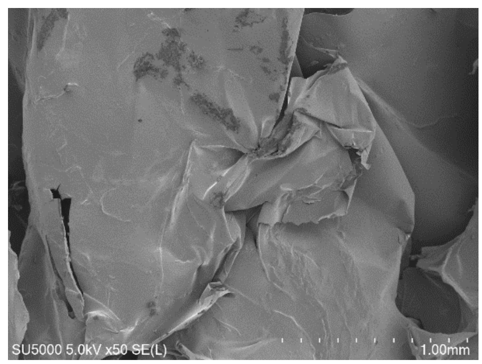
(Wheat)



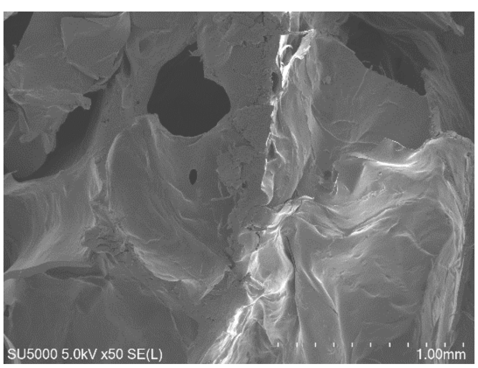
(Wheat)



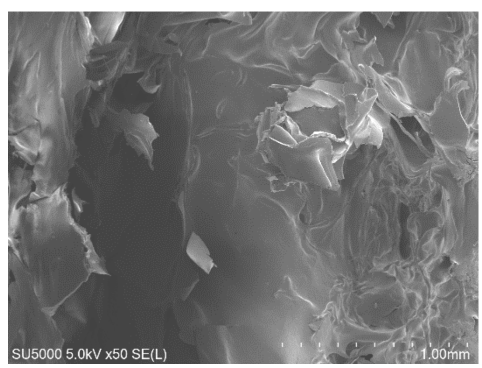
(5% Commercial Cel.)



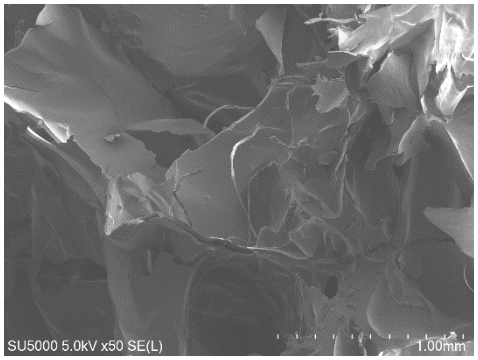
(7% Commercial Cel.)



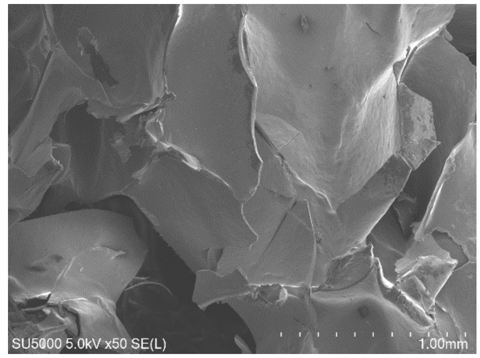
(10% Commercial Cel.)



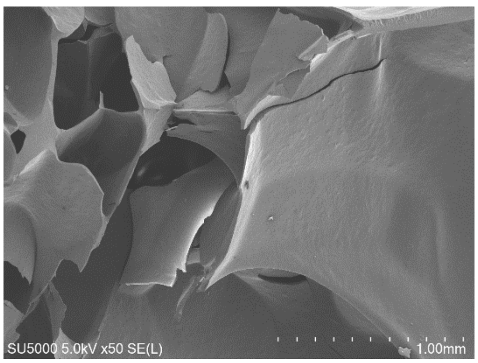
(5% Linter)



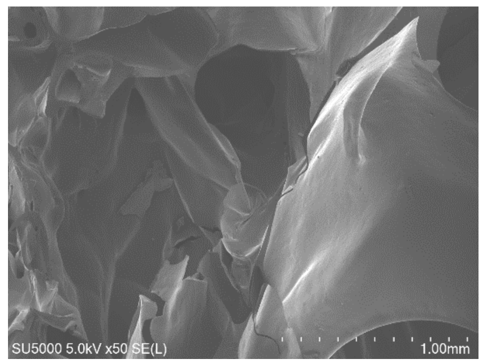
(7% Linter)



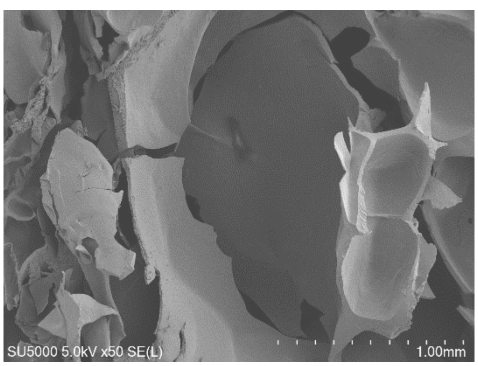
(10% Linter)



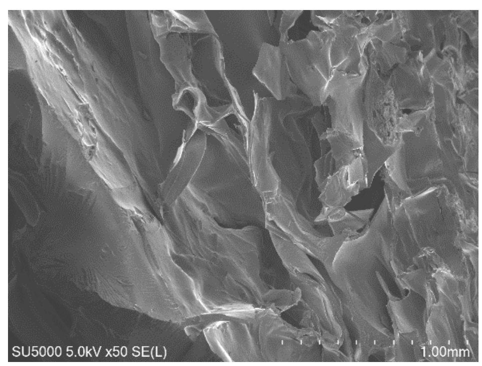
(5% CMC)



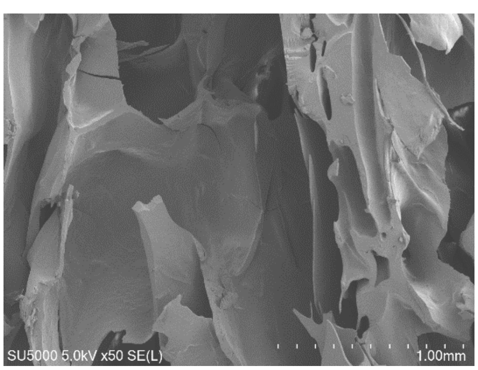
(7% CMC)



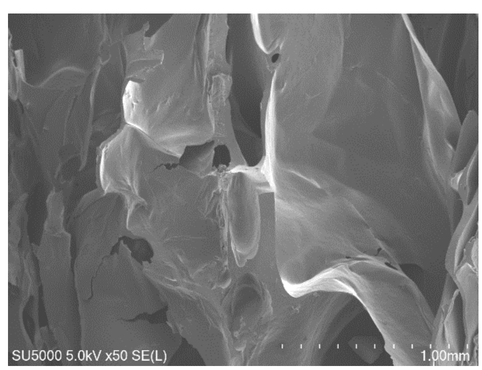
(10% CMC)



(5% Hemp)



(7% Hemp)



(10% Hemp)

Fig. 4. SEM images of plates produced with cross-linked wheat starch and cellulosic fibers in different ratios (B: Plates made from wheat starch, TS: Commercial cellulose added, L: Linter fiber added, CMC: Carboxymethyl added cellulose and K: hemp fiber addition)

Biodegradability

Figure 5 shows photographs depicting the changes in the samples obtained from the composite plates made from cross-linked modified wheat starch. When the samples under the soil were examined after 10 days, it was seen that the composite plate produced with 10% commercial cellulose was completely destroyed.

(30.08.2022)

(09.09.2022)

(19.09.2022)

(29.09.2022)

(15.10.2022)

Fig. 5. Images of the photographs taken with an interval of 10 days within the scope of the biodegradability test of the produced composite plates.

The plates produced from 5% commercial cellulose, 7% commercial cellulose, hemp fiber, linter fiber, and carboxymethyl cellulose in different proportions did not shrink at very clear rates. After 20 days, the composite plates comprised of 7% commercial cellulose and 10% carboxymethyl cellulose deteriorated. When the samples under the soil were examined after 30 days, it was seen that the plate produced with 10% linter fiber completely disappeared, and about half of the plate pieces with 5% commercial cellulose and 10% hemp fiber. After 40 days, it was observed that half of the plate samples produced with 10% carboxymethyl cellulose, 5% commercial cellulose, 7% commercial cellulose and 10% hemp fiber preserved their integrity, while the other samples were completely destroyed.

CONCLUSIONS

1. Composite plates made from cross-linked wheat starch and cellulosic fibers were observed to have superior properties to natural starch plates. The density of the plates decreased as cellulosic fibers and filler were introduced. The resistance to water increases with the added substances (linter fiber, hemp fiber, commercial cellulose and carboxymethyl cellulose).
2. While there were wide cracks on the surface of the plates made of natural starch, it was observed that the cross-linking process significantly reduced the cracks on the surface, that is, improved the rough surface area of the composite plates. It has been found that the plates obtained from cross-linked starch have a more homogeneous structure and less rough surface area and cracks than those obtained from natural starch. However, it is possible to use the produced plates for solid foods; for liquid foods, the plates should be covered.
3. When the biodegradability of the plates was evaluated, it was determined that all plates made from linter fiber were completely decomposed in the natural environment within forty days. Due to its high strength, low density, and low water absorption in comparison to other plates, the plate made with 7% carboxymethyl cellulose was found to be the finest in the study.

ACKNOWLEDGMENTS

The authors thank to support of the Karamanoglu Mehmetbey University Scientific Research Projects Management Unit-Karaman of Turkey (No: 33-YL-21). This research is based on a master's thesis of Sebahir Ülpki. Prof. Dr. Mustafa Kemal Uslu provided laboratory facilities and significant intellectual support for this investigation. The authors appreciate their significant contribution.

REFERENCES CITED

Baker, I. (2018). “Polystyrene,” in: *Fifty Materials That Make the World*, F. Ashby (ed.), Springer International Publishing, Cham, Switzerland, pp. 111-115. DOI: 10.1007/978-3-319-38925-7

Chaireh, S., Ngasatool, P., and Kaewtatip, K. (2020). "Novel composite foam made from starch and water hyacinth with beeswax coating for food packaging applications," *International Journal of Biological Macromolecules* 165, 1382-1391. DOI: 10.1016/j.ijbiomac.2020.10.007

Cinelli, P., Chiellini, E., Lawton, J. W., and Imam, S. H. (2006). "Foamed articles based on potato starch, corn fibers and poly (vinyl alcohol)," *Polymer Degradation and Stability* 91(5), 1147-1155. DOI: 10.1016/j.polymdegradstab.2005.07.001

Dauvergne, P. (2018). Why is the global governance of plastic failing the oceans?," *Global Environmental Change* 51, 22-31. DOI: 10.1016/j.gloenvcha.2018.05.002

Franz, R., and Welle, F. (2003). "Recycling packaging materials," in: *Novel Food Packaging Techniques*, R. Ahvenainen (ed.), Elsevier, Amsterdam, pp. 497-518.

Glenn, G., Orts, W., and Nobes, G. A. (2001). "Starch, fiber and $CaCO_3$ effects on the physical properties of foams made by a baking process," *Industrial Crops and Products* 14(3), 201-212.

Ji, M, Li, F., Li, J., Li, J., Zhang, C., Sun, K., and Guo, Z. (2021). "Enhanced mechanical properties, water resistance, thermal stability, and biodegradation of the starch-sisal fibre composites with various fillers," *Materials and Design* 198, article 109373. DOI: 10.1016/j.matdes.2020.109373

Kaisangsri, N., Kerdchoechuen, O., and Laohakunjit, N. (2012). "Biodegradable foam tray from cassava starch blended with natural fiber and chitosan," *Industrial Crops and Products* 37(1), 542-546. DOI: 10.1016/j.indcrop.2011.07.034

Kaisangsri, N., Kerdchoechuen, O., and Laohakunjit, N. (2014). "Characterization of cassava starch based foam blended with plant proteins, kraft fiber, and palm oil," *Carbohydrate Polymers* 110, 70-77. DOI: 10.1016/j.carbpol.2014.03.067

Lawton, J. W., Shogren, R. L., and Tiefenbacher, K. F. (1999). "Effect of batter solids and starch type on the structure of baked starch foams," *Cereal Chem*. 76, 682-687.

Kısaç, Y. E, and Uslu, M. K. (2022). "Nişasta Bazlı Köpük Tabakların Hidrofobik Malzemelerle Kaplanması," *Akademik Gıda* 20(4), 365-373. DOI: 10.24323/akademik-gida.1224341

Kısaç, Y. E. (2020). Hidrofobik Malzemelerle Kaplanmış Nişasta Bazlı Köpük Tabak Üretimi. (Yüksek Lisans Tezi) Akdeniz Üniversitesi Mühendislik Fakültesi.

Polat, S. (2011). Gıda Ambalajlaması ve Servisinde Kullanılabilecek Nişasta Bazlı Köpük Tabak Üretimi, (Yüksek Lisans Tezi), Akdeniz Üniversitesi Mühendislik Fakültesi.

Preechawong, D., Peesan, M., Supaphol, P., and Rujiravanit, R. (2004). "Characterization of starch/poly(ε-caprolactone) hybrid foams," *Polymer Testing* 23(6), 651-657

Salgado, P. R., Schmidt, V. C, Molina, O. S. E., Mauri, A. N., and Laurindo, J. B. (2008). "Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibers obtained by a baking process," *Journal of Food Engineering* 85(3), 435-443. DOI: 10.1016/j.jfoodeng.2007.08.005

Shey, J., Imam, S. H., Glenn, G. M., and Orts, W. J. (2006). "Properties of baked starch foam with natural rubber latex," *Industrial Crops and Products* 24(1), 34-40. DOI: 10.1016/j.indcrop.2005.12.001

Shogren, R. L., Lawton, J. W., Doane, W. M., and Tiefenbacher, K. F. (1998). “Structure and morphology of baked starch foams,” *Polymer* 39(25), 6649-6655.
Soykeabkaew, N., Supaphol, P., and Rujiravanit, R. (2004). “Preparation and characterization of jute-and flax-reinforced starch-based composite foams,” *Carbohydrate Polymers* 58(1), 53-63. DOI: 10.1016/j.carbpol.2004.06.037
Uslu, M. K., and Polat, S. (2012). Effects of glyoxal crosslinking on baked starch foam,” *Carbohydrate Polymers* 87(3), 1994-1999. DOI: 10.1016/j.carbpol.2011.10.008

Article submitted: April 11, 2023; Peer review completed: May 20, 2023; Revised version received and accepted: June 20, 2023; Published: August 3, 2023.
DOI: 10.15376/biores.18.4.6772-6783