Improved packaging performance of olive tree-based biochar-loaded poly(lactic acid) films

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Petroleum-containing packaging materials have created serious ecological problems for the environment due to their resistance to biological degradation. In this context, the use of biodegradable films as alternative to packaging materials is gaining importance. Among various biopolymers, poly(lactide) (PLA) is an effective and durable material. However, the mechanical strength of PLA polymer is low. In addition, its vapor permeability is high, which limits the use of this material. Biochar (BC) is an additive that can be produced from many wastes and acts as a fertilizer in the soil. Adding it to the PLA material makes the packaging film completely compostable and improves its properties. In this study, biochar was synthesized from olive pruning waste by the slow pyrolysis method. Biochar was added to the PLA films in different ratios (5, 10, 15, 20 wt.%). The packaging properties of the films were investigated. Specific surface area (BET), biochar yield, and ash content, as well as tensile strength, swelling, water vapor permeability, and opacity of the films were determined. Owing to the high lignin rate and low volatile matter in the olive branch, biochar was produced with a yield of 29.75%. When the BC concentrations of the films increased, the water vapor permeability capacity gradually decreased from 4.43% to 1.36%. The maximum tensile strength value was obtained as 14.91 MPa for 5 wt.% biochar-loaded PLA films.

Keywords: polylactic acid packaging, biochar, composite films

INTRODUCTION

The increasing environmental problems and depletion of petroleum resources have led to an increase in the usage of renewable resources in the manufacture of biodegradable food packaging materials [1]. Traditionally used plastics are obtained by processing raw materials obtained from fossil resources such as oil, natural gas, and coal. The non-degradability of plastics in the environment has significantly increased waste accumulation. Disposal and recycling of waste have become the primary problems for waste management [2].

In recent years, the general trend in food packaging has been towards the use and development of biodegradable packaging. Biodegradable plastics are environmentally friendly plastics that can be used instead of traditional ones [3]. Biopolymers, also known as green polymers, are naturally occurring polymers derived from biomass, that can be broken down into their constituent parts by ambient microbes [4]. In nature, there are many different polymers in the structure of various plant and animal resources (trees, leaves, fruits, seeds, animal skin and bones, etc.). Although these polymers are environmentally friendly materials, the high water solubility of most of them is a significant disadvantage for applications that require long-term use. The most widely used resources in the production of biodegradable packaging materials are cellulose and starch [5].

An aliphatic polymer belonging to the poly(α-hydroxy acid) family, polylactic acid (PLA) is derived from sustainable and natural sources such as sugar cane, corn, and starch [4]. Lactic acid (LA) and ring-opening polymerization are the two processes used in industry to produce PLA [6]. PLA films are suitable for injection molding and vacuum forming and have low moisture permeability. When used as a food packaging material, PLA films have a high barrier property in preventing the loss of the aroma of the product. The disadvantage of unmodified PLA packaging is its fragility and limited use in hot product applications due to its degradation temperature of around 60 °C [4]. The advantages of PLA include strong sealing properties, low-temperature adhesion, heat sealability to paper or cardboard, stability, transparency, thermoplasticity, and easy processing. It has been reported that PLA packaging is used in products such as beverage cups, fresh pasta, bread and salad bags, thermoformed containers for bakery products, agricultural covers and boxes [4]. In addition, PLA is preferred in bread and bakery products because it does not fog [7].

Biochar is a black coal-like substance formed by the thermochemical conversion of various biomasses in an inert atmosphere [8]. Biomass loses its volatile matter content at high temperatures (400-500°C) and biochar remains [9]. Biochar is a porous,

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carbon-rich material with large specific surface area, containing a lot of aromatic carbon and functional groups (-OH, -COOH, C=O, and C-O) [10] and has unique physical, chemical, and biological properties [11].

In recent years, biochar applications have received considerable attention in the fields of environment, agriculture, and industry. Biochar acts as a carbon sink in the soil, slowing down the chemical oxidation and reduction of biomass and preventing the release of carbon into the atmosphere [12]. Biochar-doped polymer composites take advantage of the porous structure of biochar. The polymer fills the pores in the biochar by flowing into them, thus creating a mechanical bond between the polymer and biochar. In addition, the large surface area of biochar aids particle dispersion within the polymer matrix. By imparting mechanical properties to polymer composites, biochar provides flame resistance to the composite due to its natural carbon content, stable C-C covalent bonds, and aromatic ring content [9]. There are several studies using biochar as an additive in different polymers such as polyamide, polycarbonate, polyvinyl alcohol, polyethylene, polypropylene, and epoxy [13]. In the literature, there are limited studies on the use of different source-based BC in the PLA matrix. Aup Negoen *et al*. [14] prepared carbon-rich biochar (CRB) samples of cassava rhizome, durian peel, pineapple peel, and corn cob BC by using a simple pyrolysis method. They used PLA as the matrix, added biochars in different proportions and examined the thermal and mechanical properties. They found that the cassava root composite, which has a higher carbon content, has a better elastic modulus and impact resistance. Huang *et al.* studied the physical and chemical properties of biochar produced from vine leaves by adding it to the PLA matrix. The strength and stress were found to be much higher in samples with biochar added, and their strength increased [15]. Kane *et al*. prepared biochar at 900 °C and added it into PLA and recycled high-density polyethylene (HDPE) in different ratios. The addition of biochar affected the properties of HDPE and PLA differently, but the key finding of the study was that food waste-derived biochar suffered almost twice a mass loss after 40 days in the subsoil in high biochar-loaded samples compared to pure PLA. In other words, the biodegradation of the film increased with the addition of biochar [16].

In this study, biochar-incorporated PLA films were produced and their potential for use as packaging was investigated. BC was produced from olive tree branches by the slow pyrolysis method. The surface area, efficiency, and ash content were measured. Characterization tests of PLA films with 5-20% BC loading were carried out and water and moisture retention, opacity, and mechanical strength were tested.

EXPERIMENTAL

Materials

Olive branches were collected from Çanakkale, Türkiye. Hydrochloric acid (HCl) and K_2CO_3 were obtained from Sigma Aldrich. PLA polymer (2003D) was purchased from NatureWork. Chloroform and N,N- dimethyl formamide (DMF) were obtained from Merck Chemicals, Türkiye.

Methods

- *BC preparation.* Olive tree branches were cut to ≈5 mm and dried in an oven at 60°C for 24 h. The dried olive branches were converted into biochar in a pyrolysis furnace. For this, dried olive branches, potassium carbonate (K_2CO_3), and pure water were mixed in a ratio of 1:2:4 and kept at room temperature for 24 h. Olive branches were removed by filtration and dried overnight in an oven at 105°C. The dried olive branches were pyrolyzed in a tube furnace at 650°C in N_2 atmosphere with a flow rate of 5 L/min at a temperature of 650°C, a temperature rise rate of 10°C/min, and a cooking time of 2 h. The product was washed with 10% HCl solution by mass and washed with distilled water until the pH value was about 7. The washed product was dried in the oven at 105°C for 24 h and kept in a desiccator. The BC yield and ash content were calculated as shown in Equation 1 and Equation 2, respectively [17]:

$$\text{BC Yield (\%)} = \frac{\text{Mf (g)}}{\text{Mi (g)}} * 100 \quad (1)$$

$$\text{Ash content (\%)} = \frac{Mr\ \text{(g)}}{\text{Mf(g)}} \times 100 \quad (2)$$

where Mi and Mf are the weights of biomass and biochar before and after pyrolysis, respectively. Mr is the ash content of BC after it was kept at 850 C in an ash oven for 4 h.

JEOL JSM-7100-F scanning electron microscope (SEM) was used to study the BC's structure. 30 kV was used for the SEM analysis. The pore characterization of BC was performed with the Quadrasorb SI Brunauer-Emmett-Teller (BET) equipment. The samples were vacuum-sealed and degassed for an hour at 200 °C. Nitrogen gas adsorption was used.

- *Film preparation.* The polymer solution containing 10% PLA by mass, 90% chloroform and 10% DMF by volume was stirred at 40 °C until completely dissolved. Separately, 0-20% biochar (by mass of polymer) was dissolved in 5 ml of DMF and dispersed by mixing with a homogenizer for 30 min. Then it was added to the PLA-DMF-chloroform solution and mixed at room temperature for 2 h, the mixture was poured into a glass Petri dish and the films were immersed in a water bath to complete the phase separation. Then, the films were removed and dried at 60 °C in the oven.

- *Film characterization.* The swelling test is used to determine the water resistance of films or the porosity of films, i.e. how much water they can trap in water. To test the swelling properties of the films, each sample was soaked in 25 mL of deionized water for 24 h and the values before (Wi) and after (Ws) water retention were recorded. The swelling degree calculation is given as Equation 3:

$$SD\ (\%) = \frac{Wi - Ws\ (g)}{Wi\ (g)} * 100 \quad (3)$$

Water vapor uptake values (WVU) of the film samples were determined by the ASTM E96-95 standard method. Using permeation cups, the obtained films were exposed to pure water vapor without contact for 24 h at 25°C. The vapor uptake values of the films were determined by weighing the final (Wf) and initial (Wi) of the films, respectively.

$$WVU\ (\%) = \frac{Wf - Wi\ (g)}{Wi\ (g)} * 100 \quad (4)$$

The opacity, i.e. light transmittance, of the films was determined using a UV-Vis spectrophotometer (Shimadzu-1280). After being prepared, the films were cut into rectangular strips and put on the spectrophotometer cell's two outer surfaces. A wavelength of 600 nm was used to measure the absorbance (A) value. The opacity was calculated per thickness of film (l) as shown in Equation 5:

$$Opacity = \frac{A}{l} \quad (5)$$

Tensile strength and elongation at break values of the films were determined by a Universal Testing Machine (Ankarin) with ASTM D882 standard. After the width and thickness of the prepared films were measured, they were placed between two clamps, and the distance was measured. The test started and the strength values were measured.

RESULTS AND DISCUSSION

In this study, biochar was synthesized by the slow pyrolysis method and then added to the PLA matrix at different rates, and its film properties were examined. When the efficiency of the produced biochars was analyzed, its value was found to be 29.75%. It has been observed that this value generally varies between 20-35% depending on the lignin and cellulose structure in the biomass content [10, 11, 17-19]. Efficiency also decreases, especially at high pyrolysis temperatures. However, in this study, although the temperature was 650 °C, nearly 30% efficiency was achieved. In this case, highly efficient BC can be obtained from olive pruning waste. The ash content was found to be 3.37%. This value is similar to that in the literature [20, 21].

One of the most important characteristics in BC synthesis is the porous and morphological structure of BC. In this way, the film properties of PLA can be improved. When SEM images are examined for BC, it is seen that BC has a uniform pore structure. The activation process contributes to enhancing the homogeneous pore structure as shown in Figure 1. It can be said that K_2CO_3 is distributed in the cellulosic structure on the surface and inside of the olive branch. The resulting metallic potassium increases porosity through intercalation through carbon layers [21].

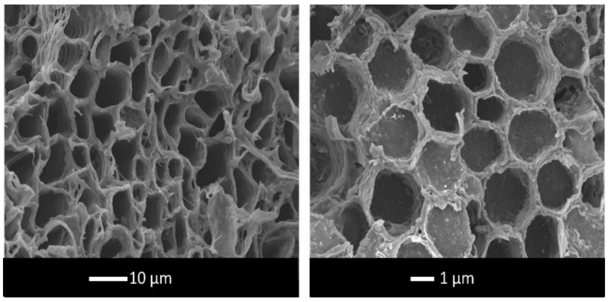

Fig. 1. SEM analysis of the BC

The increase in surface area provides many advantages depending on the usage area of BC. Increasing surface area increases the performance of BC, especially in important experimental studies such as moisture retention, water retention, and gas permeability. Therefore, a high surface area is an expected and desired result. In this study, the activation process was applied to increase the surface area of BC. The surface areas of non-activated BC and K_2CO_3-activated BC were obtained as 1.44 m^2/g and 659,255 m^2/g, respectively. Activation increases the specific surface area of biochar by increasing the number of mesopores.

Another important factor for preparing composites is the homogeneous distribution of fillers in the polymer matrix. This depends on both the size of the particles and the polymer-particle compatibility. The BC used in this study has a meso-structure. For this reason, especially in cast-film preparation, it can provide a more durable structure by allowing the polymers to fill the pores. However, on the other hand, the inhomogeneity of the particle size may cause a decrease in mechanical strength. BC distribution in PLA was observed by an optical microscope (SOIF-BK5000) (Figure 2). At a low loading rate (wt. 5% and 10 %), a homogenous distribution can be clearly seen. As the biochar concentration increased, agglomeration increased, as seen from the microscope images. Although biochars were distributed in an ultrasonic mixer and stirred in a magnetic stirrer, a heterogeneous appearance was obtained at the high loading rate [22]. According to these results, it was predicted that mechanical strength may also decrease, especially at high additive rates.

Additionally, it was observed that biochar particles had a circular shape. As a result of the distance measurements of the particles, the highest distance was measured as 4.8 μm in the 5% BC-PLA packaging film, while this value was measured as 17.0 μm for the PLA packaging film containing 20% BC. This situation is due to the concentration difference [23].

The efficiency of packaging as a barrier against food deterioration, nutrient loss, and flavor degradation when exposed to visible and ultraviolet light depends on its optical qualities. Foods are long-lasting and shielded from light in this way. The opacity results of the films are given in Figure 3. It is observed that as the BC ratio in PLA films increases, their opacity increases. This result is attributed to the light absorption capacity of BC. The reason for this is higher than that of PLA films. Depending on the increasing particle size, this increase is normal, although not very regular [24].

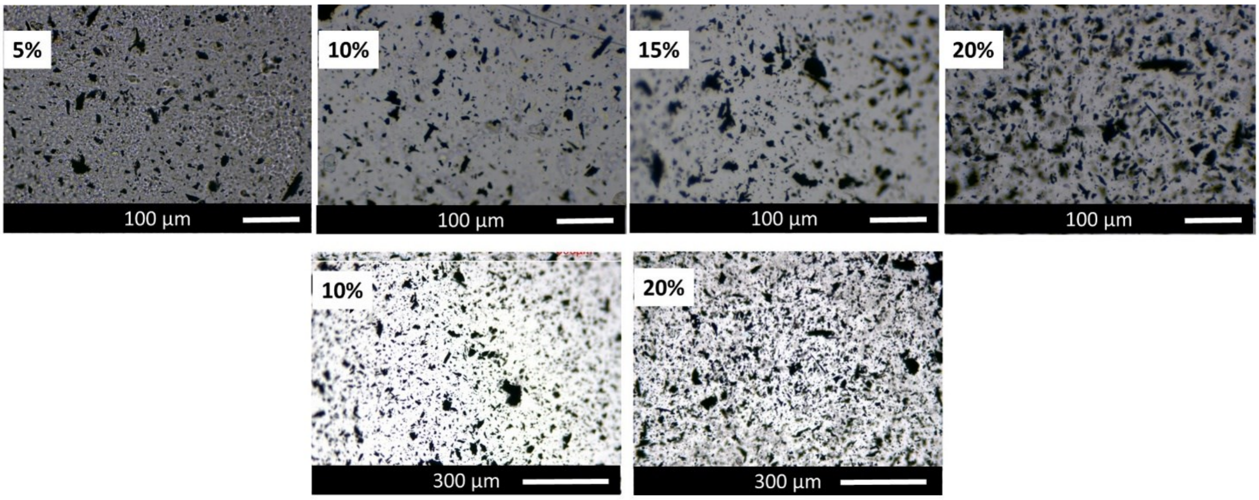

Fig. 2. Optical microscopy analysis of the BC loaded PLA films

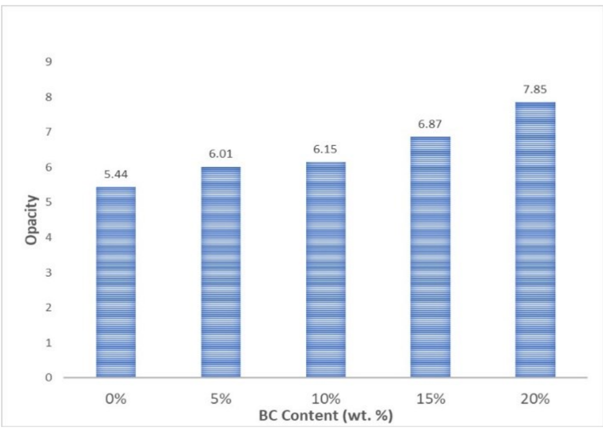

Fig. 3. Opacity results of BC-PLA films

The swelling test provides information about the water solubility of the film. However, it is not desired that this value be too high. Otherwise, they will lose their properties in contact with water during use. In this study, PLA was used as the matrix and this polymer is quite rigid and has high water resistance. It has no solubility in water. However, in this case, it takes a long time for it to become biodegradable after use. For this reason, BC additive increases its affinity for water and provides a structure that is durable in use and easily degradable after use. Biochar is a hydrophilic material due to the presence of hydrophilic groups [24]. Therefore, it has the ability to absorb water. It is expected that the swelling ratios of the formed PLA films increase as the BC concentrations increase. Figure 4 indicates the swelling degree of the films. According to the swelling test results, it was observed that the swelling ratio increased as the BC concentration increased. It was found that the swelling rate of the PLA packaging film containing 0% BC was 1.29%, while it was 10.10% in the film containing 20% BC. According to the results, it is clear that the water solubility of packaging films in the soil is improved by BC addition [25]. This shows that the films are biodegradable in nature and will decompose faster than other petroleum-derived plastics [26].

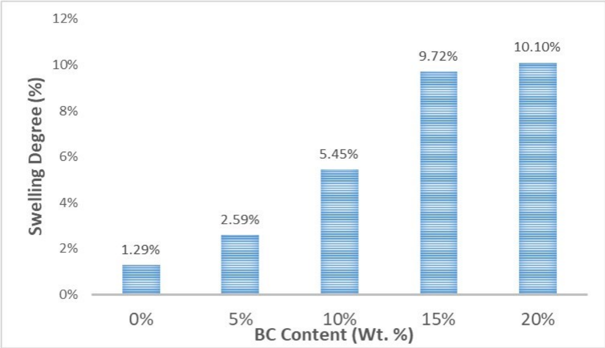

Fig. 4. Swelling degree results of BC-PLA films

Another important feature of the packaging film is the water vapor permeability or water vapor uptake. The water vapor barrier properties of a physically or chemically biodegradable packaged product are related to moisture balance and are of great importance in preserving or extending its shelf life [27]. The movement of water between food goods and their surroundings has a direct impact on how long they last on the shelf. For the packaging to have greater durability, the films' water transfer capacity should be minimal [28]. Vapor permeability is an undesirable feature in the case of vapor transport from outside to inside because it causes deterioration of food inside the package. On the other hand, vapor permeability from inside to outside is desired because it ensures that the food remains dry in the package. Therefore, it is quite difficult to characterize these two features. In this study, water vapor uptake (WVU) was calculated instead of permeability. During this test, the films were naturally exposed to water vapor at room temperature. Figure 5 shows the WVU values of the films with and without BC. According to the test results, the water vapor permeability capacity of the films gradually decreases as BC concentrations increase. The reason for this is that the biochar in the films absorbs water and restricts the passage of water vapor through the film. This is a desired result [24]. It was also related to the fact that the biochar slows down the diffusion of water vapor and makes pores in composite films more tortuous [29].

Another important feature desired in a packaging film, regardless of the purpose it is used for, is its mechanical strength. Mechanical strength preserves the shape and rigidity of films during transportation and packaging.

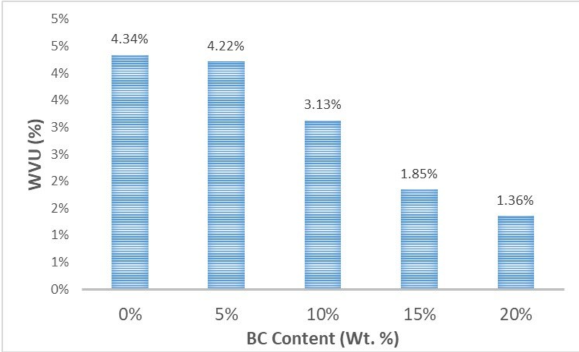

Fig. 5. Water vapor uptake results of BC-PLA films

However, if a polymer film is used for transport purposes, this value becomes more important. For use only for packaging purposes, lower mechanical strength is acceptable. Food packaging can typically take the shape of an elastic film for various uses or a non-deformable material to guarantee structural integrity or reinforce the food structure [27]. Tensile strength depends on film content, film thickness, moisture content, and additives. Figure 6 shows the mechanical test results of films with and without BC.

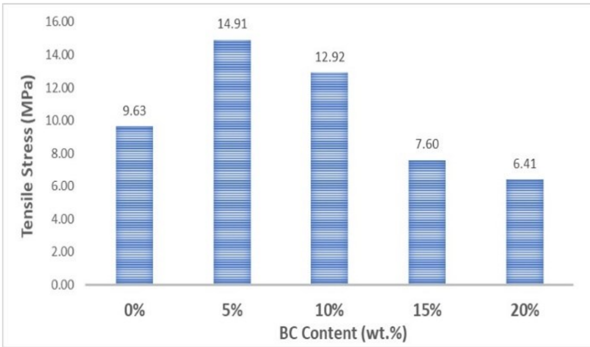

Fig. 6. Mechanical test results of BC-PLA films

As seen in the figure, mechanical strength increased compared to pure film at 5% loading rate. This result is attributed to the equal load transfer between the PLA and BC. During the film preparation, PLA solution fills the BC pores. According to the rule of mixture phenomena, the strength of PLA increased. However, after this loading rate, the mechanical strength began to gradually decrease. Although the strength achieved at 10 wt.% loading rate is lower than that at 5 wt.%, it is higher compared to the pure PLA. It may be acceptable to use. However, the strength obtained at 15 wt.% and 20 wt.% loading rates is lower than that of pure PLA film, which indicates that the material structure is deteriorated. As confirmed from microscopic analysis, particle distributions and sizes were not homogeneous at high loading rates. This shows that the load transfer within the film was not distributed properly and adhesion problems occurred between the polymer and BC [14, 22]. Therefore, no matter how much the other properties improve, it is not appropriate to use these ratios in the PLA matrix.

CONCLUSION

In this study, biochar was obtained from olive branch waste, characterized, and added to PLA to obtain a natural packaging material. The usability of the composite material obtained was investigated by performing some of the tests required for packaging. According to the swelling test results, it was observed that the swelling ratio increased from 1.29% to 10.10% when the BC enhanced from 0 wt% to 20 wt.%. This result allows to conclude that the BC additive increases the solubility of the composite material in nature. It was observed that the BC improves the vapor resistance. The increased ratio decreased the water vapor uptake from 4.43% to 1.36%. BC also significantly increased the mechanical strength of the films. However, the strengths decreased, especially after 10 wt.% loading. This shows that BC loading above 10% is not suitable for packaging. Based on all these results, it may be concluded that converting olive branches into biochar enables the acquisition of a very important additive material, and the use of this material in packaging is very beneficial.

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