

Biochar Reinforced Polyvinyl Alcohol /Corn Starch Biocomposites

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Biochar,
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Polyvinylalcohol,
Starch

Abstract: The utilization of biochar in polymer composites can be considered as a sustainable approach that provide valorization of a waste to a value-added material and at the same time diminish biowaste in a smart way. This study is focused on the evaluation of biochar as a filler in polyvinyl alcohol /corn starch composites. The composites were prepared via solution mixing and casting method using citric acid as a plasticizer and glutaraldehyde as a cross-linker. Distribution of biochar in the PVA/starch matrix was evaluated by optical microscopy. The structural features of composites were characterized using FTIR spectroscopy. Effects of biochar loading ratio (0-12 wt%) on the thermal stability of the PVA/starch blends were determined by differential scanning calorimetry and thermogravimetric analyses. The decomposition temperatures of the PVA/starch/biochar composites decreased in comparison to PVA/starch composites.

Biyokömür Takviyeli Polivinil Alkol /Mısır Nişastasası Biyokompozitler

Anahtar Kelimeler

Biyokömür,
Çapraz bağlı kompozit,
Polivinil alkol,
Nişasta

Özet: Biyokömürün polimer kompozitlerde kullanılması, atığın katma değerli bir malzeme olarak değerlendirilmesini sağlayan ve aynı zamanda biyo-atığı akıllıca azaltan sürdürülebilir bir yaklaşım olarak düşünülebilir. Bu çalışma, polivinil alkol /mısır nişastasası kompozitlerinde biyokömürün dolgu maddesi olarak değerlendirilmesine odaklanmıştır. Kompozitler, plastikleştirici olarak sitrik asit ve çapraz bağlayıcı olarak glutaraldehit kullanılarak çözelti karıştırma ve döküm yöntemi ile hazırlandı. PVA / nişasta matrisindeki biyokömür dağılımı optik mikroskop ile değerlendirildi. Kompozitlerin yapısal özellikleri FTIR spektroskopisi kullanılarak karakterize edildi. Biyokömür oranının (ağırlıkça %0-12) PVA/nişasta karışımının ısıl kararlılığı üzerindeki etkileri diferansiyel taramalı kalorimetre ve termogravimetrik analizle belirlendi. PVA/nişasta /biyokömür kompozitlerin bozunma sıcaklıkları, PVA/nişasta kompozitlerine kıyasla azaldı.

1. Introduction

Recently, there has been a growing interest in composite materials, with a particular focus on polymer based ones due to their superior and unique properties. At the same time, the replacement of traditional petroleum based plastics by eco-friendly polymers become attractive in scientific and technological communities with respect to environmental concerns [1, 2]. Therefore, extensive researches on polymer biocomposites are going on around the world.

Polymer biocomposites can be defined as materials formed by a biodegradable polymer matrix and a filler derived from natural biomass [3, 4]. Among the

various polymer biocomposites, polyvinyl alcohol (PVA) and starch based composites have been considered as one of the most promising biodegradable materials [5]. However, widespread applications of the blends of PVA and starch are limited because of their water sensitivity, poor thermal and mechanical properties. Earlier studies showed that incorporation of suitable reinforcement fillers is a way to overcome these drawbacks [6-8]. Over the last few years, the evaluation of carbon based fillers as carbon nanotubes [9, 10], graphene [11, 12] and graphene oxide[13] has become a hot research for enhancement of the properties of PVA/starch composites. Jose et al. [9] prepared carbon nanotube reinforced PVA/starch composites by solution casting method. Two carbon nanotube

addition ratios were used as 0.5 and 2 wt% of polymer blend. It was reported that the 2 wt% carbon nanotube addition improved the thermal stability due to increased compatibility of the blends. In the study of Massoumi et al. [10], poly(ethylene glycol)-functionalized multiwalled carbon nanotubes were used as filler for poly(vinyl alcohol)/starch nanocomposites. It was shown that the incorporation of functionalized multiwalled carbon nanotubes enhanced the mechanical properties of the composites which was related to the formation of strong interfacial forces and hydrogen bonds between the carbon nanotubes and the PVA/starch matrix. Bin-Dahman et al. [11] studied the electrical and dielectric features of PVA/starch/graphene nanocomposites. The results demonstrated that graphene addition increased the DC and AC conductivity of composites. Wu et al. [13] added graphene oxide to the PVA/starch composite films and found that increase in the graphene oxide concentration resulted in the enhancement of film's moisture resistance and slight improvement of the thermal stability. This has been attributed to the chemical interaction between nano-graphene oxide and PVA/starch composite film.

Biochar is also a carbonaceous renewable material which can be obtained through pyrolysis of several wastes [14]. Biochar presents very attractive properties such as low cost, high chemical stability, high porosity and renewability [15]. It is primarily evaluated in soil amendment applications as fertilizer and carbon sequestration agent [16]. Another widespread usage area of biochar is adsorption of contaminants [17, 18]. In recent years, biochar has received significant attention as an effective filler to improve properties of various polymer materials including epoxy [19, 20], polyethylene [21, 22], polypropylene [23-26], polylactic acid [27], PVA [28-30] and nylon [31]. The biochar incorporation to the polymer matrix provides multiple advantages. Generally, the electrical and mechanical features of the resulting composite materials were finer compared with the neat polymers [4].

It is important to take into consideration that both PVA and starch have a polar nature [28]. Especially, the biochar addition to the PVA/starch blends can enhance the interaction between PVA and starch due to containing surface functional groups such as hydroxyl, aliphatic, etc. [28, 32, 33].

To the best of the authors' knowledge, no research has been reported yet in order to evaluate biochar incorporated PVA/starch biocomposites. The present study aims to investigate the effect of biochar addition on the thermal stability of PVA/starch biocomposites.

2. Material and Method

2.1. Materials

Biochar (particle size <500 μm) was a kind gift from Synpet Technologies (Istanbul, TURKEY). Poly (vinyl alcohol) (Mw 30,000, purity 95.4%, degree of hydrolysis 87.16%, viscosity 24.9 mPa.S) was purchased from Zag Kimya, TURKEY. Corn starch was obtained from Güneş Company, TURKEY. Citric acid was purchased from Aksu Company, TURKEY. Glutaraldehyde was purchased from Alfosol.

2.2. Preparation of biocomposites

PVA/starch biocomposites with different biochar concentrations (0, 3, 6, 9, 12 wt% of total polymer) was prepared in several steps. The blend ratio of PVA and starch was 80:20 (Table 1). The used total distilled water was 100 mL. First, an adequate amount of PVA was dissolved in water for at 90°C overnight. Separately, corn starch was gelatinized for 10 minutes at 100°C under continuous stirring. Afterward, gelatinized starch was added to the PVA solution and continuously stirred for 30 minutes at 70°C. Then, biochar dispersion in distilled water was ultrasonicated for 30 minutes using an ultrasonic probe (Bandelin Sonorex) and poured onto the PVA/starch mixture. The PVA/starch/biochar mixture was stirred for 30 min to obtain homogeneous solution in a 600 mL beaker. Citric acid (25 wt % of total polymer) was added to the solution and stirred for 10 minutes at 50°C. Finally, glutaraldehyde (500 μL) was added to the mixture with holding at 100°C for 5 minutes and the dried at 50°C in a vacuum oven (JEIO TECH/OV-11) for 16 hours. The composites were kept in zip lock polyethylene bags.

Table 1. The preparation formulation of polyvinyl alcohol /corn starch/biochar composites

Sample Code	PVA (wt %)	Starch (wt %)	Biochar (wt % of total polymer)	Citric acid (wt % of total polymer)
PSB0	80	20	0	25
PSB3	80	20	3	25
PSB6	80	20	6	25
PSB9	80	20	9	25
PSB12	80	20	12	25

2.3. Characterization of starting materials

The moisture, ash and volatile matter content of biochar were determined according to the European Biochar Certificate - Guidelines for a Sustainable Production of Biochar [34]. The moisture content of biochar and corn starch were determined by oven drying at 105°C, while the ash content was determined by combusting the samples at 550°C in an oven (Nabertherm LHT 08/18, Germany). The volatile matter of biochar was examined by heating at 950°C for 7 min in an oven. The results were calculated according to mass loss of samples.

2.4. Characterization of biocomposites

All of the samples were characterized using an optical microscope (Nikon Eclipse LV150N) with 20X magnification.

Thermogravimetric analyses were carried out on a TGA Q500 thermogravimetric analyzer (TA SDT 650 Instruments, USA) to assess the relative thermal stabilities of the composites.

Differential scanning calorimetry (DSC) was also performed to determine the glass-transition and melting behavior of the biocomposites using a TA DSC 25 Instrument (USA). Samples (6-8 mg) were weighted into standard aluminum pans and then heated from 20°C to 300°C at a heating rate of 10°C/min under nitrogen atmosphere.

3. Results

The properties of starting materials have great influence on the final properties of produced materials. The proximate analyses of biochar and corn starch were summarized in Table 2. The moisture, ash and volatile matter of biochar were found to be 2.75, 1.00 and 25.12%, respectively. Moreover, the corn starch had 0.15 and 6.04% moisture and ash content, respectively.

Table 2. Moisture, volatile matter, and ash contents of biochar and corn starch

Sample	Moisture (%)	Ash (%)	Volatile matter (%)
Biochar	2.75	1.00	25.12
Corn starch	0.15	6.04	-

The digital photographs of the neat PVA/starch composite and PVA/starch/biochar (PSB6) composite are given in Figure 1a and 1b, respectively.

The IR spectra were measured with a Thermo scientific Nicolet i550 spectrophotometer at a resolution of 4 cm⁻¹ in the range of 4000-500 cm⁻¹. The other PSB composites had an appearance like PSB6 sample (not given). After the biochar addition, the color of the PVA/starch composite was changed from white to black. In addition, the thickness of neat PVA/starch and PSB3 sample were found to be similar (~5 mm). Further, the thickness of composites increased with the increment of biochar addition ratio. The thickness of PSB6 was 5.75 mm while the thickness was 6.10 and 6.25 mm for PSB9 and PSB12, respectively.

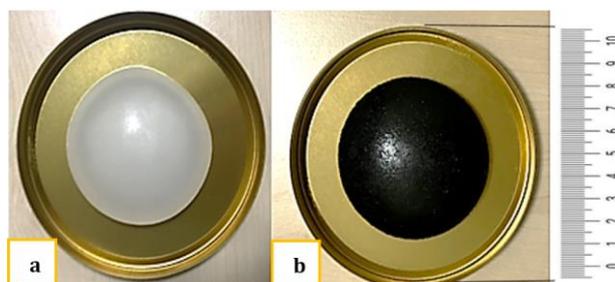


Figure 1. Digital image of (a) neat PVA/starch composite (b) PVA/starch/biochar (PSB6) composite

Figure 2 presents the optical micrographs of neat PVA/starch composite and PVA/starch/biochar composites with different addition levels. The neat PVA/starch composite had a relatively smooth surface containing small bubbles (Figure 2 a). There was an apparent change in the surface appearance and topography of the biochar added composites compared with the neat PVA/starch composite. The biochar can be clearly specified in the composites with bright particles which showed a tiny flake-like appearance. Additionally, the shapes of biochar particles were irregular with an average particle size distribution in the range of 70 to 150 µm. Optical micrographs of the PVA/starch/biochar composites showed that biochar particles are uniformly distributed throughout the surface (Fig. 2 b-e).

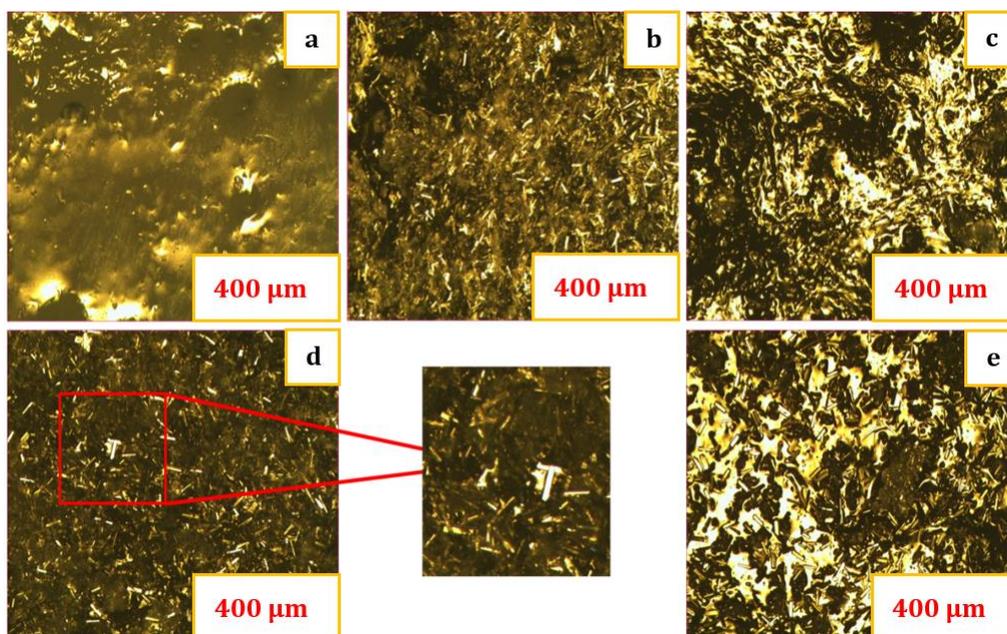


Figure 2. Optical micrographs of the surfaces of (a) neat PVA/starch composite and PVA/starch/biochar composites (b)PSB3 (c) PSB6 (d)PSB9 (e)PSB12 (20x)

The FTIR spectra of the initial components (PVA, starch and biochar) and composites are illustrated in Figure 3 and the functional groups of composites are listed in Table 3. The changes in the functional groups were the evidence of the chemical modifications in the blends.

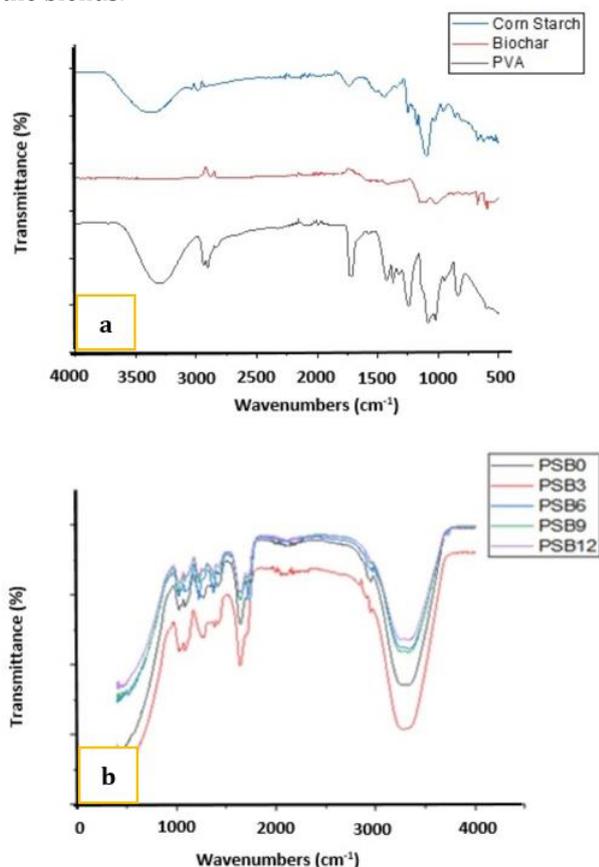


Figure 3. FT-IR spectrum of (a) PVA, starch, and biochar; (b) PVA/corn starch and PVA/corn starch/biochar composites

In the spectra of biochar, the $-OH$ peak centered at 3330 cm^{-1} was missing indicating that the biochar had lower moisture than PVA and starch. The peaks at 2920 and 2850 cm^{-1} represent the $-CH_2$ groups [35].

There was an increased intensity decrease for hydroxyl band ($3100\text{--}3400\text{ cm}^{-1}$) with the increment of biochar ratio. The band also became narrower. This phenomenon is attributed to the good compatibility of PVA, starch and biochar, as shown in their increased hydrogen bonding [36]. The other shifts and slight intensity changes (1645 and 1250 cm^{-1}) were possibly resulting from intramolecular and intermolecular bonding between starting materials. Compared the PSB0 in the spectrum with the PSB3-PSB12, a new peak (1217 cm^{-1}) appeared with the incorporation of biochar at 6, 9 and 12 wt %, while the 3 wt % biochar incorporated sample (PSB3) had a similar band pattern with PSB0. The peak at 1700 cm^{-1} was due to $C=O$ functional group and the peak moved to the low frequency region with the incorporation of biochar (PSB6-PSB12).

The results revealed that there was a strong interaction between PVA/starch with biochar because of the formation of hydrogen bond between the oxygen-containing groups in biochar and $-OH$ groups available in either starch or PVA. A similar result was encountered by other researchers during the incorporation of graphene to the PVA/starch blends [9].

Thermal degradation behavior is taken into consideration as a significant and simple tool to determine thermal stability of polymer-composites during thermal processing [43]. TGA analysis curves of PVA/starch and PVA/starch/biochar composites are represented in Figure 4. Moreover, 10% weight

loss temperature (T_{d10}), 50% weight loss temperature (T_{d50}) and 90% weight loss temperature (T_{d90}) are presented in Table 4. As expected, the weight loss of PVA/starch composite was higher than the biochar reinforced composites. Neat PVA/starch decomposed without solid residue formation while PSB3-PSB12 biocomposites produced around 4.0-10.7 and 0.7-1.9% solid residue at 500°C and 900°C, respectively (Table 4). This consequence indicating that the biochar may display a condensed phase flame retardant mechanism [39]. There is an increase in the residue with increased biochar incorporation ratio.

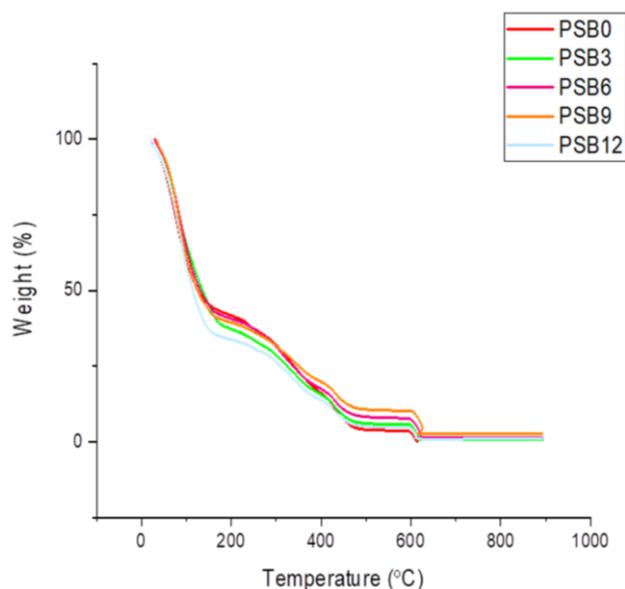


Figure 4. TGA curves of PVA/starch and PVA/starch/biochar composites

Table 3. Assignment of FT-IR bands for PVA/starch, and PVA/starch/biochar composites

Frequency (cm ⁻¹)		Assignment
PSB0-PSB3	PSB6-PSB12	
1022	1022	C-O stretching of the glucose ring [2, 37]
1080	1080	C-O-H stretching vibration [38]
-	1217	C-H stretching vibration [39]
1250	1250	CH ₂ wagging vibration [40]
1374	1374	CH ₂ bending vibration[40]
1420	1420	CH ₂ bending vibrations [40,41]
1645	1645	O-H bending vibration, C=O asymmetric stretching [40]
1700	1690	C=O functional group [42]
2985	2985	CH ₂ symmetric stretching [29]
2940	2940	CH ₂ asymmetric stretching [30]
3100-3400	3100-3400	O-H stretching vibration, free hydroxyl [42]

Table 4. Degradation temperature of PVA/starch, and PVA/starch/biochar composites at residual weight 90% (T_{d90}), 50% (T_{d50}) and 10% (T_{d10})

Sample ID	Biochar Content (%)	T_{d10} (°C)	T_{d50} (°C)	T_{d90} (°C)	V_{max} at T_{max} (min % at °C)	Char at 500 °C (wt %)	Char at 900 °C (wt %)
PSB0	0	75.7	296.7	455.3	3.07 at 424.61	4.07	0
PSB3	3	58.9	136.4	440.2	2.08 at 428.85	6.14	0.68
PSB6	6	59.5	131.4	457.8	1.76 at 431.8	8.31	1.47
PSB9	9	59.9	124.2	499.8	1.81 at 427.24	10.72	1.78
PSB12	12	51.8	114.4	431.8	1.63 at 431.38	9.95	1.92

Under gradually increased temperature, the TGA curves demonstrated that all the biochar reinforced biocomposites decomposed in a four-step weight loss process, while PVA/starch composite showed three-stage degradation. It was observed that higher moisture adsorption was found in all biochar incorporated composites. The biochar reinforced PVA/starch composites decomposed earlier than neat PVA/starch composite.

Similar results were obtained for bamboo charcoal loaded polylactic acid composites [29] and sewage sludge biochar loaded wood/polypropylene biocomposites [14].

For PSB3-PSB12, the first region at a temperature of 80–150°C is due to the evaporation of water. The other two steps above 150°C were due to the melting and degradation of the side chains and main backbone cleavage of polymer matrix. The final stage was the thermo-oxidation of carbonized residue. The starting temperatures of the different decomposition steps for biochar reinforced biocomposites were lower than the neat PVA/starch composite.

These findings indicated that the incorporation of biochar to the PVA/starch matrix can lower the thermal stability of the biocomposites. This can be explained by the slight outgassing of CO, CO₂, and H₂O from inside due to biochar reduction may finally lead to a quick breakdown of the PVA/starch matrix [44]. The result was in accordance with the previous findings reported by Wang et al. [44] on the graphene oxide loaded poly(vinyl alcohol) composites.

The results of the DSC analyses are summarized in Table 5. The PSB3 sample showed approximately similar behavior with the PSB0 sample, which was also realized in the FT-IR spectrum. Merely, the addition of 3 wt% biochar increased the glass-transition temperature (T_g) from 157.81°C to 165.49°C. T_g is highly related to the flexibility of polymeric segments and thus segmental chain motion [45]. The increased T_g represents new hydrogen bond interactions between the polymer matrix and biochar which may result in the limited mobility of polymer chains with the incorporation of biochar. This consequence had an agreement with the study of Sedaghat et al. [46] for the 2.5 wt% of graphene oxide incorporated poly (vinyl alcohol)/starch nanocomposites. As the amount of biochar in the blend increased from 3 wt% to 6-12 wt% the T_g decreased. This is probably related to the weakening of the hydrogen bonding between starch and PVA as a consequence of addition of higher amount of biochar as mentioned in the literature for poly(vinyl alcohol)/starch/graphene nanocomposites [11]. Moreover, the melting temperature of PSB0 and PSB3 samples were found to be 197°C which were slightly higher than the other biochar incorporated composites. Similarly, it was reported that there were decrease in the T_m of biochar incorporated PVA composites [28]. Higher values of melting enthalpies were determined for the 6-12 wt% biochar incorporated biocomposites as compared to the pure and 3wt% biochar incorporated samples.

Table 5. DSC results of PVA/starch blend and its biocomposites containing different amounts of biochar

Sample Code	T _g (°C)	T _m (°C)	Heat of melting, ΔH _m (J/g)
PSB0	157.81	197.40	118.33
PSB3	165.49	197.64	84.14
PSB6	141.08	172.12	412.24
PSB9	143.72	177.75	323.83
PSB12	143.07	182.43	366.86

4. Discussion and Conclusion

PVA/starch/biochar composites were successfully prepared with a simple method in the presence of citric acid and glutaraldehyde. The thermal behavior of the biocomposites was investigated using TGA and DSC. The biochar incorporation significantly affected the degradation pattern of PVA/starch composite. The thermal stability of PVA/starch/biochar composites was lower compared to that of PVA/starch composite. It is worth noting that the glass-transition and melting temperature did not increase in the composites with biochar content higher than 3 wt%. Therefore, further studies should focus on the effect biochar incorporation with lower ratio and biochar particle size on the properties of PVA/starch composites.

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