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Preparation and Characterization of Black Seed/Cassava Bagasse Fiber-Reinforced Cornstarch-Based Hybrid Composites

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Abstract: Great advances have been made in the preparation of bioplastics and crude oil replacements to create a better and more sustainable and eco-friendly future for all. Here, we used cassava bagasse fibers at different ratios as reinforcement material to enhance the properties of black seed w-cornstarch films using the facile solution casting technique. The reinforced films showed compact and relatively smoother structures without porosity. The crystallinity values increased from 34.6 ± 1.6% of the control to 38.8 ± 2.1% in sample CS-BS/CB 9%, which reflects the mechanical properties of the composite. A gradual increase in tensile strength and elastic modulus was observed, with an increase in loading amounts of 14.07 to 18.22 MPa and 83.65 to 118.32 MPa for the tensile strength and elastic modulus, respectively. The composite film also exhibited faster biodegradation in the soil burial test, in addition to lower water absorption capacity. Using bio-based reinforcement material could significantly enhance the properties of bio-based packaging materials. The prepared hybrid composite could have a promising potential in food packaging applications as a safe alternative for conventional packaging.

Keywords: cassava bagasse fiber; black seed; cornstarch; hybrid composite film; cellulose

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1. Introduction

The past few years witnessed greatly advanced in sustainable and ecologically friendly materials due to the huge environmental problems associated with conventional non-biodegradable plastics [1–3]. The conversion of biomass into valuable materials has attracted the attention of scientists, which has both substantial economic and environmental relevance [4–8]. Throughout the last two decades, several developments have been made on biocomposites, making them functioning and interesting alternatives to conventional materials [9–12]. Cornstarch (CS), among the biomaterials, is a highly preferable polysaccharide polymer in bioplastics and biomaterials fabrication due to its sustainability, high availability, and ability to form a continuous matrix [13–17]. Nevertheless, CS exhibits several drawbacks, including its relatively strong hydrophilic character, in addition to its poor mechanical properties, which limited its applications for packaging purposes [18,19].

Several attempts have used numerous bioresources and natural fibers to enhance the mechanical properties of biocomposites but still mimic that of synthetic and crude oil plastic [20–23]. Black seed (*Nigella sativa*) is a famous medicinal plant that has been used for centuries for therapeutic purposes due to its anti-microbial, anti-diabetic, anti-inflammatory, anti-cancer, and anti-hypertensive activities [24]. The large-scale black seed oil industry produces a significant amount of waste every year (about 70% of the raw material) [25,26]. Most of these wastes are landfilled and not being furtherly utilized. Thymoquinone is one of the main active compounds in black seed that possess most of the therapeutic activities of the seeds and is characterized by hydrophobic properties, making it poorly soluble in water [27]. It has been reported that most black seed oil extraction methods allow a significant loss of waste, making this waste highly valuable for further utilization [25,28]. Black seed fiber was used in this study to utilize as a protective material to resist soil acidity and microbial attack.

Cassava bagasse is another cheap and broadly available fiber of cassava plant (*Manihot esculenta*) in tropical countries, which is considered a byproduct of cassava starch production [29]. Cassava bagasse is mainly composed of cellulose fibers along with residual starch, which ranges 15 and 50 wt%, making it highly attractive in several industrial applications. The industrial exploitation of cassava mainly includes the elimination of soluble sugars in addition to fiber separation. This result in the formation of two materials; purified cassava starch and cassava bagasse fibers [30]. Apart from containing cellulose and hemicelluloses, cassava bagasse also contains a high amount of starch, a natural polymer that has a high polarity due to the presence of large amounts of hydroxyls in its macromolecules, which interact with lignocellulosic fibers, resulting in improved mechanical properties [31].

Hence, the present study aims to use cassava bagasse fibers (CB) as reinforcement material to improve the mechanical and biodegradability properties of black seed fiber/cornstarch films by using a facile solution casting technique. The morphological and mechanical properties were analyzed and related to water absorption and biodegradation profile. Surface morphology and crystallinity were also analyzed.

2. Materials and Methods

2.1. Materials

The Cornstarch was obtained from Thye Huat Chan Sdn. Bhd. located at Sungai Buloh, Selangor, Malaysia, while the black seed (*Nigella sativa*) was obtained from Berkat Madinah Sdn. Bhd. (Selangor, Malaysia), after extracting the oil from the seeds. Cassava bagasse was purchased from NSK Trade City Kuchai Lama (Kuala Lumpur, Malaysia).

2.2. Preparation of the Film

The composite films were prepared using the conventional solution casting technique; 10 g of pure cornstarch (CS) was dissolved in 180 mL distilled water and heated for 20 min at 85 °C with continuous stirring (using a thermal-magnetic mixture) to allow starch gelation. Two types of plasticizer (fructose, and glycerol) were added to the solution in a similar ratio of 30% (w/w powder starch) along with black seed (BS) 9% (w/w powder starch) [5]. Different loading of cassava bagasse fibers (0, 3, 6, 9%) of dry starch-based was used as a hybridized agent. The final mixture was heated for an additional 20 min with continuous stirring until a gelatinized solution formed, which was then discharged evenly in a thermal petri dish. The dish with a casted solution was desiccated in an air circulation oven for 15 h at 65 °C. The formed films were removed gently from the dishes and kept at ambient conditions for 7 days prior to characterization. The obtained films were labeled according to their compositions and concentration of cassava bagasse fibers (CB), as shown in Table 1.

Table 1. Mixing proportion of different black seed/cassava bagasse fiber-reinforced cornstarch hybrid composite film.

Film	Fructose and Glycerol g/g Dry Starch	Starch g/180 mL Distilled Water	BS g/100 g of Dry Starch	CB g/100 g of Dry Starch
Control(CS/BS)	0.3	10	9	0
CS-BS/CB3%	0.3	10	9	3
CS-BS/CB6%	0.3	10	9	6
CS-BS/CB9%	0.3	10	9	9

2.3. Characterization of Prepared Films

2.3.1. Physical and Morphological Analysis

The thickness of each film was calculated by an electronic caliper (Mitutoyo-Co., Kanagawa, Japan), using an inch accuracy of ±0.001. The density was directly measured from the weight and volume. Moisture content (MC) was calculated by weighing a constant dimension of each film (20 × 15 mm) and placed for 24 h in the dehydration oven at 105 °C. Then, the samples were weighed again and the difference in weights was determined as the MC of the sample. The film solubility was calculated using the same dimensions and drying step mentioned earlier and following the method described in Shojaee-Aliabadi et al. [32]. SEM (Hitachi S-3400 N, Nara, Japan) was used to observe the surface morphology of all the prepared samples by coating them with a thin golden layer to conduct electricity.

2.3.2. Surface Functional Groups and X-ray Diffraction Analysis

Fourier Transform Infrared Spectroscopy (FTIR) type (Bruker vector 22, Lancashire, UK) was used to investigate the surface functional group of prepared films, using 16 scans per sample and over a frequency range of 400 to 4000 cm^{-1}. In order to determine the crystallinity index of each sample, a 2500 X-ray diffractometer (Rigaku, Tokyo, Japan) was used to analyze the XRD diffraction and calculate the crystallinity index in the same method described by [33].

2.3.3. Mechanical Properties

The mechanical properties of the films were investigated by tensile test according to D882 (ASTM, 2002) standards. The test was performed at room temperature (30 °C) using 5KN INSTRON tensile machine. Constant strips (10 × 70 mm) were prepared from each film and then firmly mounted between tensile clamps. Five replicates for each sample were done, using 2 mm/min crosshead speed, tensile strength, elongation at break, and elastic modulus was finally calculated.

2.3.4. Thermal Properties

The thermal gravimetric analyzer (TGA) instrument type (Q500 V20.13 Build 39, Bellingham, WA, USA) was used to study the thermal stability of the prepared film samples. Each sample was subjected to a temperature ranging from room temperature to 600 °C at an ascending rate of 10 °C/min.

2.3.5. Water Absorption and Soil Burial Test

Water absorption was calculated at room temperature by preparing constant dimensions (20 × 15 mm) of all the films and oven dried them for 3 h at 105 °C to eliminate all the moisture. The samples then were immediately weighted and steeped in distilled water for 3 h and the excess was removed from the surface by using a soft cloth. Water absorption was then determined using the following equation:

$$\text{Water absorption } (\%) = \frac{\text{water loadedfilm} - \text{ initial weight}}{\text{initial weight}} \times 100$$

A soil burial test was conducted in polyethylene vials at room temperature in normal soil with the same method in [34].

2.4. Statistical Analyses

The statistical analyses of the findings were performed using Microsoft Excel 365, and the obtained data were plotted using Origin® 8.5 software (OriginLab Corporation, Northampton, MA, USA) for the graphical presentation of the results.

3. Results and Discussion

3.1. Physical and Morphological Analysis

The results of physical properties including moisture content (MC), density, thickness, and water solubility of the prepared film samples are presented in Table 2. The control had the highest MC, density, and water solubility, but it exhibited the lowest thickness. The addition of 3% CB increased the MC of the film from 7.54 ± 0.6 to only 6.81 ± 0.4%, but it reduced over again to 6.40 ± 0.2 and 6.02 ± 0.3% for CS-BS/CB6% and CS-BS/CB6% respectively. This could be attributed to the interaction that occurred between the BS and the CB; at a small amount, the interaction was limited, which led to an insufficient amount of interaction that was enhanced with loading more CB. The thickness clearly increased with the increase in loading amount from 0.272 ± 0.01 to 0.35 ± 0.04 µm, which also result in the reduction of the density value of the samples. The solubility of the film decreased from 34.23 to 31.47 ± 1.1% as the CB concentration increased, which could be due to the interaction that occurred between the materials that led to resistance of the water diffusion and enhance the film integrity [35].

Table 2. Physical characteristics of black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

Sample Name	MC (%)	Density (g/cm^3)	Thickness (µm)	Solubility (%)
Control	7.546 ± 0.6	1.34 ± 0.02	0.272 ± 0.01	34.23 ± 2.0
CS-BS/CB3%	6.813 ± 0.4	1.31 ± 0.07	0.274 ± 0.08	32.93 ± 1.4
CS-BS/CB6%	6.406 ± 0.2	1.29 ± 0.01	0.332 ± 0.05	32.45 ± 0.9
CS-BS/CB9%	6.026 ± 0.3	1.25 ± 0.06	0.35 ± 0.04	31.47 ± 1.1

Figure 1 presents the scanning electron microscope (SEM) of the prepared film samples at same magnification. The difference in surface morphology between the control, which appeared more rough and porous compared with the reinforced ones, can be seen. Reinforced films showed compact and relatively smoother structures without porosity; the interaction between CB, BS and the CS could be the reason for the smooth surfaces and absence of porosity. The highest homogenous surface can be seen in the sample with the highest loading amount (CS-BS/CB9%), which supports our hypothesis. Although the CS-BS/CB3% sample was found to be more homogenous and smoother than the control, weak interfacial interaction, which is mainly related to the formation of hydrogen bonds through hydroxyl groups, could be the reason for this, compared with the higher loading samples [36,37]. The correspond results of mechanical and FTIR analysis to the increase of homogeneity will be remarked on in their own subsection.

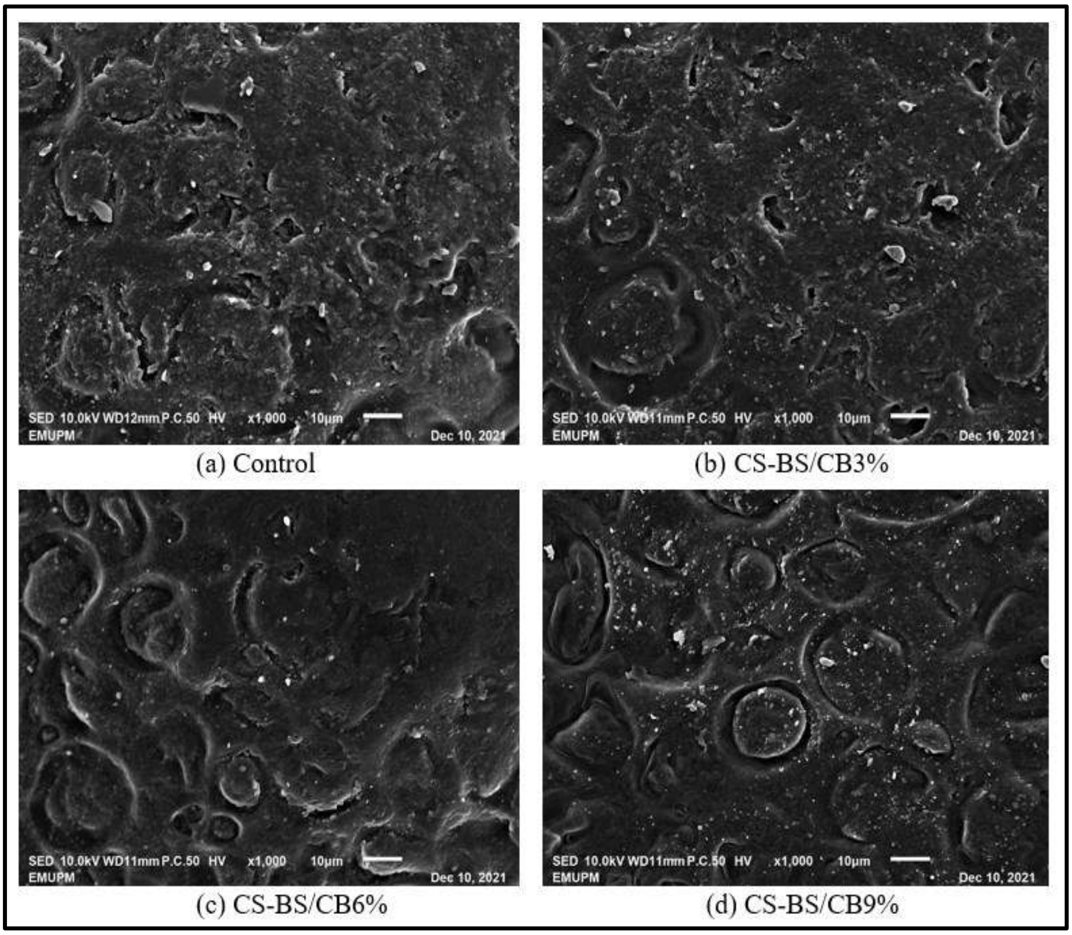

Figure 1. Surface morphology black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

3.2. Surface Functional Groups

Since the chemical composition and the portions of all the films are well known, the FT-IR spectra (Figure 2) exhibited characteristic absorption peaks associated with the three materials of the hybrid components. The well-dispersed fillers caused the formation of similar spectra patterns, indicating the formation of alike chemical bonds within all samples. All the films showed the typical characteristic bands of starch O-H stretching, C-H, and C-O stretching at 3298, 2998, and 1151 cm^{-1}, with slight shifting among them. The peak at 989.48 cm^{-1} appeared in all the samples corresponding to alkenes, which are the characteristics of black seed active compounds in addition to the aliphatic amines at 1033 and 1089 cm^{-1} [38]. Although the reinforced films did not show a significant difference between the three loading amounts, the slight shifting of peaks between the control and CS-BS/CB9% can be observed, which could be due to the effect of interaction between the three materials in the film. Higher CB loading formed greater hydrogen bonds quantitatively generated higher peak intensity. The band 1423 cm^{-1} appeared in all the samples, which corresponds to glycerol, while the ones between 1944 and 1649 cm^{-1} refer to bound water [39].

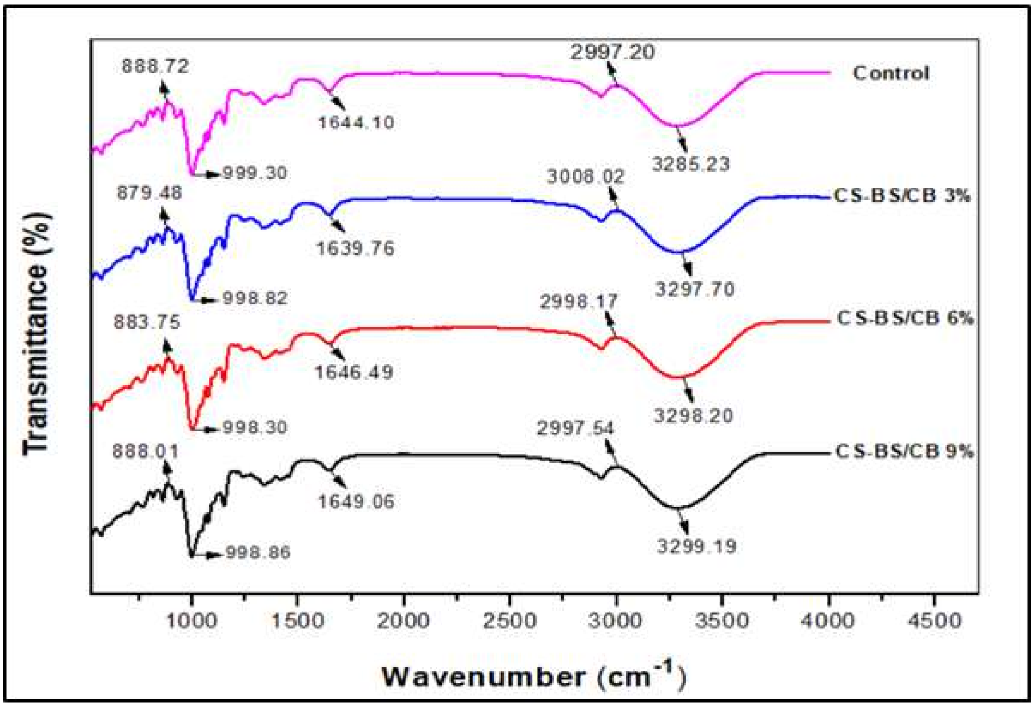

Figure 2. FT−IR curves of black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

3.3. X-ray Diffraction (XRD)

The XRD curves of the black seed/cassava bagasse fiber reinforced cornstarch film composites are presented in Figure 3. The difference between the control and the three reinforced samples can be observed; the control increased the intensity of the two main peaks at 17 and 20°. However, among the reinforced fibers, CS-BS/CB 9% had significantly higher intensity compared with the other two samples. Owing to the gelatinization of starch molecules, sharper peaks can be observed in CS-BS/CB 9% at angles 17.82° and 20.47° in addition to 22.72°, which is the typical pattern of A-type plant starches [40]. The crystallinity values of the control were only 34.6 $\pm$ 1.6%, which increased with the increase of reinforcement percentage to become 38.8 $\pm$ 2.1% in sample CS-BS/CB 9%. The difference in crystallinity values could be attributed to the effect of starch reinforcement on the structure, which was also explained earlier by the mechanical properties. Natural fibers of black seed are oriented materials; they are able to combine with the starch molecules and thus improve the crystallinity of the film composite [41].

3.4. Mechanical Properties

The mechanical properties of the film are very important in order to be applicable for most practical applications. In this study, tensile testing of the film composites was done to measure each tensile strength, elastic modulus, and elongation at the break. As illustrated in Figure 4, it can be observed that the lowest tensile strength was reported for the control with only 14.07 MPa, which increased to 15.04, 16.65, and 18.22 MPa for the CS-BS/CB3%, CS-BS/CB6% and CS-BS/CB9%, respectively. Similarly, the elastic modulus increased from 83.65 MPa to 118.32 MPa. The gradual increase in tensile strength and elastic modulus is due to the homogeneous mixture and the interaction that occurred between the three materials, leading to an increase in rigidness and stiffness of the composite film with less flexibility, which was confirmed by the reduction in elongation at the break values [42]. The enhancement in the mechanical properties could have occurred due to the relative crystallinity, as we reported earlier and described by Salaberria et al.; the increase in the crystallinity of the film promotes the rigidity and stiffness of the film, leading to a reduction in elongation at the peak and thus better performance [43]. Black seed fibers also play a significant role by bonding the hydroxyl group with both CS and CB, leading to better transfer of stress from the film matrix to the fibers and thus higher tensile strength [33]. Furthermore, the significant reduction in film elongation can be explained by rebuilding the intermolecular bonding of the film, which improves its stiffness and rigidity, as described by da Rosa Zavareze et al., and also decreases the composite film flexibility by eliminating chain mobility [44–48]. Table 3 expresses the tensile strength and elongation at the break of several starch-based composites.

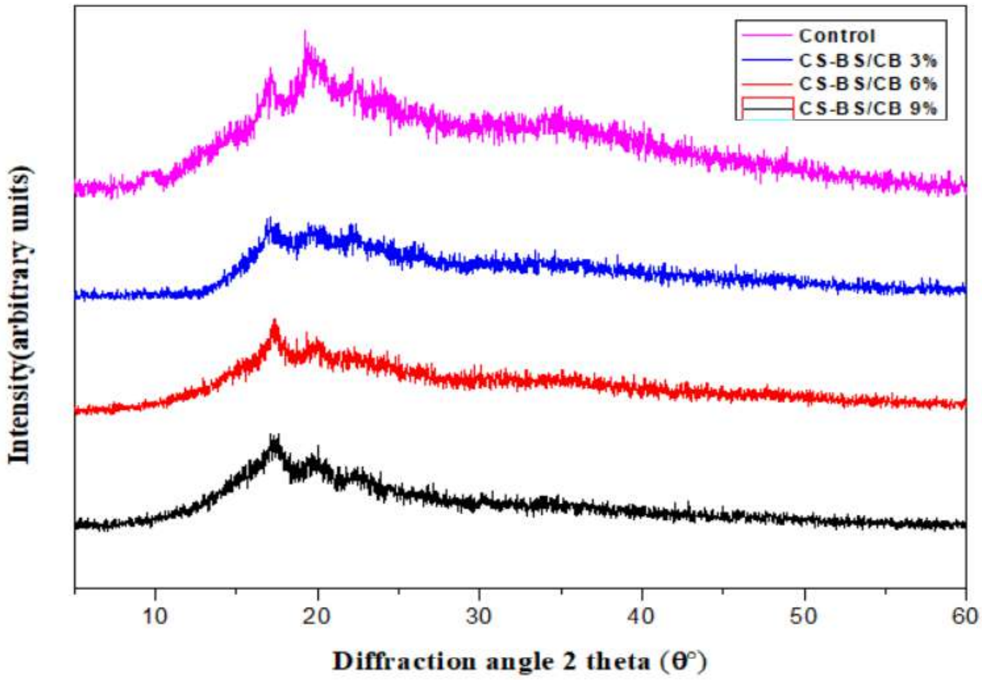

Figure 3. X-ray diffraction curves of black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

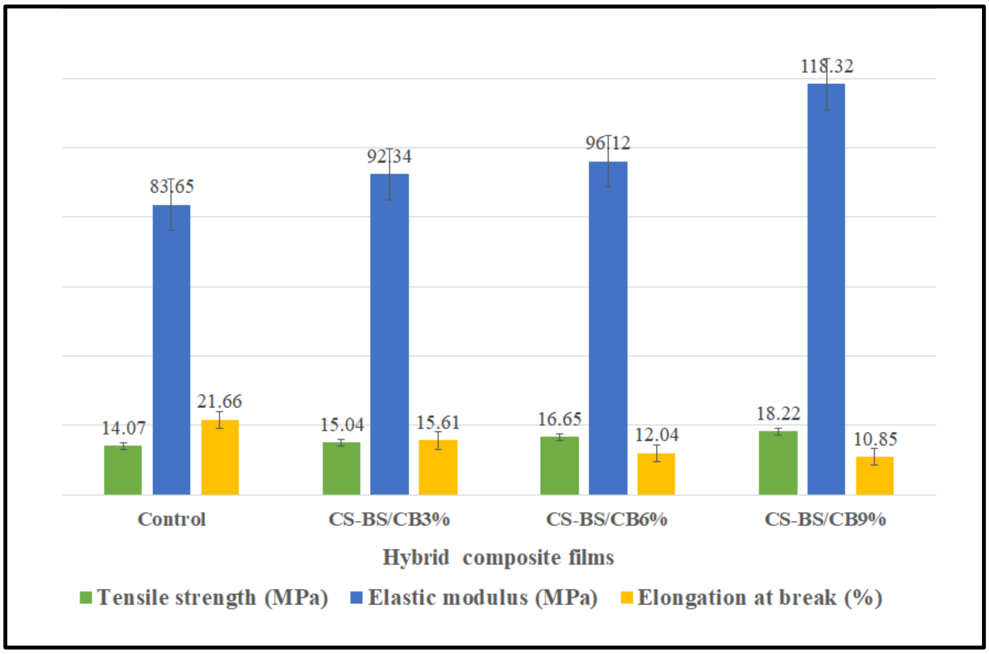

Figure 4. The mechanical properties of black seed/cassava bagasse fiber-reinforced cornstarch hybrid composite film.

Table 3. The tensile strength (TS) and elongation at break (E) of various starch-based composites.

Polymer	Fiber	Plasticizer	TS	E	Reference
Cassava starch	Cassava bagasse (6 wt.%)	Fructose	10.78 MPa	3.19 mm	[49]
Corn starch	Corn Husk (8 wt.%)	Fructose	12.84 MPa	3.7%	[50]
Corn starch	Kenaf fiber (6 wt.%)	Sorbitol	17.74 MPa	48.79%	[51]
Cassava starch	Banana pseudostem powder (10 wt.%)	-	16 MPa	113.5%	[52]
Dioscorea hispida starch	*Dioscorea hispida* Fiber (6 wt.%)	Sorbitol	9.29 MPa	25.44%	[53]
Sugar palm starch	Sugar palm cellulose fiber (10 wt.%)	Glycerol and sorbitol	19.68 MPa	32.8%	[54]

3.5. Thermal Properties

Thermal degradation of the prepared film composites mainly occurs in three different stages (Figure 5). The first stage corresponds to the moisture removal and sample dehydration, which started from 52 ± 2.6 °C until 163.5 ± 3.2 °C. At this stage, a clear difference can be observed in weight loss between the control, which had the highest weight loss, and CS-BS/CB9%, which showed the lowest. The second stage corresponds to the decomposition of starch molecules within the films, which occurred between 282 and 340 °C. The initial decomposition at 282 °C is attributed to the amylopectin and amylose differential degradation rate [55,56]. A similar effect for the reinforcement can be observed at this stage; the addition of CB into the film enhanced its thermal stability and reduced the weight loss due to the interactions in the composite matrix between the three materials. The greatest differences between the four investigated samples were observed in the third phase of degradation, which correlated to several oxygen-based reactions of carbonaceous residues—known as "glowing combustion" [57]. The control had the most significant weight loss at this stage; however, the reinforcement enhanced the stability and reduce the decomposition, in a similar way to what was reported by Florencia et al. [1]. Higher reinforcement samples CS-BS/CB6% and CS-BS/CB9% were clearly more stable by 12% than the control, owing to their higher residual carbohydrate content.

3.6. Water Absorption and Soil Burial Test

Water absorption is an important characteristic in packaging materials and is considered a major drawback in many bio-based films. Figure 6 presents the results of the water absorption investigation in this study, in which can be seen the effect of reinforcement on the water sensitivity of the films. At the initial assay (20 min of immersion), CS-BS/CB3% exhibited more water absorption than the control, which then reduced after 40 min of immersion to 63% compared to the control, which reported 67%. However, after the films reached the maximum degree of water saturation (180 min of immersion), a huge difference can be observed: the control showed the highest water absorption, at 64.7%, followed by CS-BS/CB3%, at 62.8%. The 6 and 9% CB reinforcement significantly reduced the water absorption to 51 and 42%, respectively, which could be due to the hydrogen bonding that occurred, resulting in the slight hydrophobic nature of the films [58]. Furthermore, the reduction of water absorption rate caused by CB reinforcement could be also attributed to the creation of interfacial bonding in the hybrid composite, which was confirmed earlier by the results of mechanical analysis. Such interfacial bonding hinders the water penetration through the film matrix and thus reduces its water absorption [59].

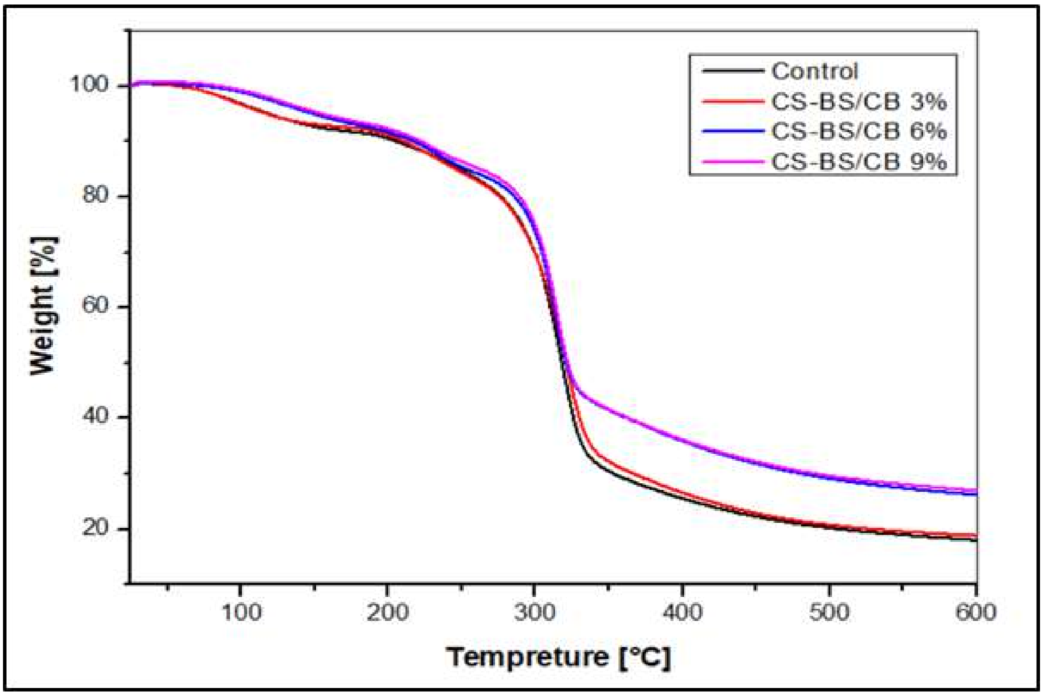

Figure 5. TGA curves of black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

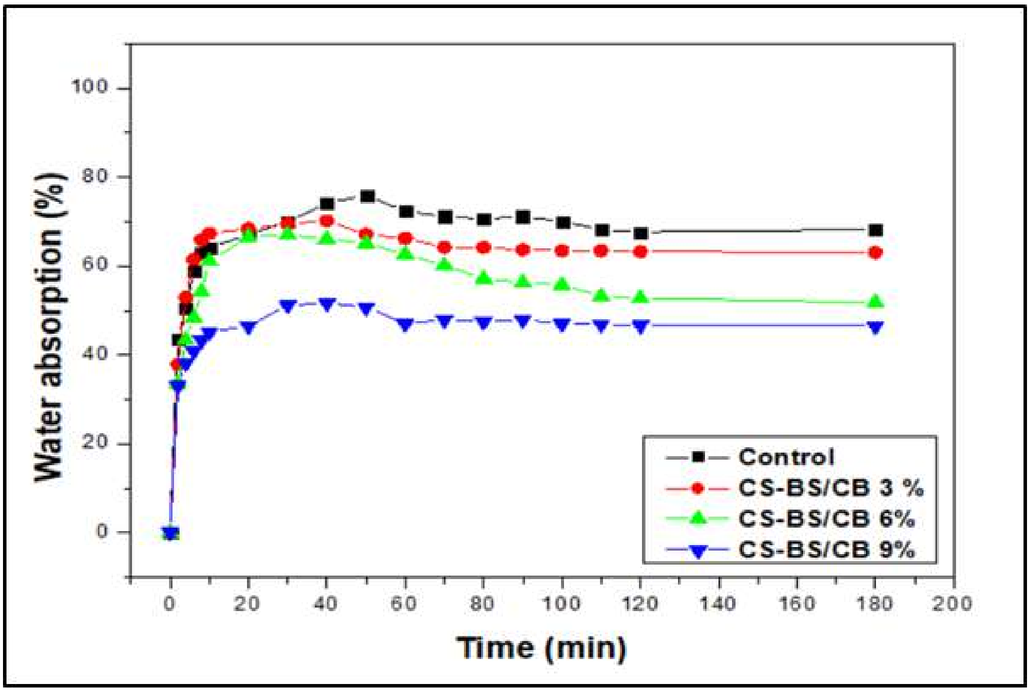

Figure 6. Water absorption of black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

A soil burial test was conducted in normal soil at room temperature over a period of 12 days. Figure 7 presents the results of films' biodegradability, in which can be seen the difference between them in the degradation rate. The CB reinforcement enhanced the biodegradation rate of the films; the highest rate was reported for CS-BS/CB9% with 99% degradation after 12 days. A previous study reported that the degradation of cassava film is greater than the corn-based one [60]; in our study, the biodegradation enhancement that occurred by CB reinforcement could be due to Cola cordifolia, which was found in both cassava and corn. Furthermore, the consumption of hydrogen bonding makes the film highly sensitive to microbial attacks and thus biodegrades easily [61]. In the case of control and CS-BS/CB3%, which absorbed a higher amount of water, the microorganisms are known for CO_2 and water production as a result of bio-based material consumption. However, the Solvation of CO_2 in the soil leads to the formation of H_2CO_3, forming an acidic environment around the film, which eventually reduces the microbial activity and thus limits the film's biodegradation [62]. Although the presence of black seeds fiber helps in resisting soil acidity and microbial attack [63], the significant biodegradability of CS-BS/CB9% could be due to their limited water absorption, which maintains microbial activity, and also to the crystalline structure of the CB reinforcement.

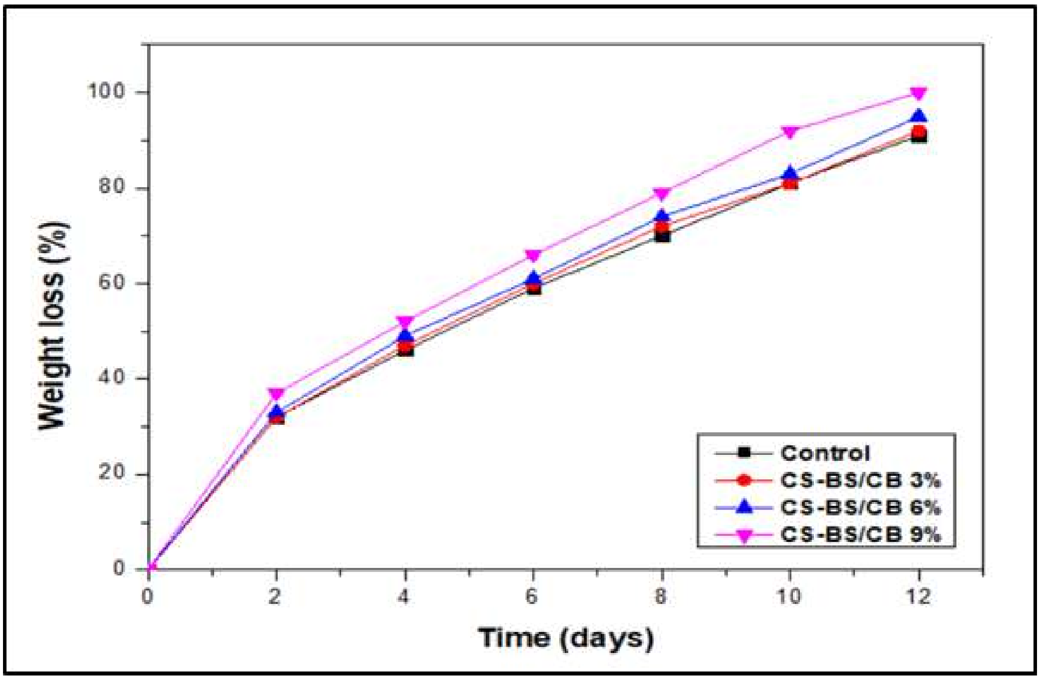

Figure 7. Soil burial test of black seed/cassava bagasse fiber reinforced cornstarch hybrid composite film.

4. Conclusions

Intensive studies have been conducted on waste utilization and the development of enhanced materials able to mimic synthetic plastic to overcome its associated environmental issue. In this study, cassava bagasse fibers at different ratios were used as a reinforcement to enhance the properties of black seed fiber-cornstarch films. The addition of fibers significantly enhanced the mechanical properties of the film and a gradual increase in tensile strength and elastic modulus was observed with an increase in loading amount. The composite film also exhibited faster biodegradation in the soil burial test in addition to lower water absorption capacity. Using fibers as reinforcement could significantly enhance the properties of bioplastics in terms of mechanical, water absorption, and biodegradation properties. The prepared hybrid composite could have promising potential in food packaging applications as a safe alternative to conventional packaging.

Author Contributions: Conceptualization, W.A. and S.M.S.; methodology, W.A.; formal analysis, W.A. and S.M.S.; writing original draft preparation, W.A.; writing—review and editing, W.A., S.M.S., M.T.H.S., M.F.M.A. and R.A.I.; visualization, W.A.; project administration, W.A., S.M.S. and R.A.I.; funding acquisition, S.M.S., W.A. and R.A.I. All authors have read and agreed to the published version of the manuscript.

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