

A Characterization Study of Morphology and Properties of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH)/Aloe Vera Fibers Biocomposites: Effect of Fiber Surface Treatments [†]

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Abstract: This paper aims to investigate the effect of different chemical modifications of biocomposites based on poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and aloe vera bio-fibers incorporated at 20 wt%. The fiber surface was modified with alkaline, organosilanes, and combined alkaline/organosilanes. Surface morphology, thermal stability, water absorption capacity, and rheological behavior of the modified biocomposite materials were studied, and the results compared to both unmodified biocomposites and neat PHBH. The study showed that the modified biocomposites with both alkaline and organosilanes exhibited an improved surface morphology, resulting in a good fiber/matrix interfacial adhesion. As a result, increases in complex viscosity, storage modulus, and loss modulus were observed, whereas water absorption was reduced. Thermal stability remained almost unchanged, with the exception of the biocomposite treated with alkaline, where this property decreased significantly. Finally, the coupling of alkaline and organosilane modification is an efficient route to enhance the properties of PHBH biocomposites.

Keywords: poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); bio-fibers; chemical modification; alkaline treatment; organosilanes treatment

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1. Introduction

During the past decade, biodegradable polymer composites reinforced with lignocellulosic fibers have attracted significant attention [1] because this new class of materials is a promising candidate for replacing synthetic polymers derived from fossil oil [2]. In this regard, polyhydroxyalkanoates (PHAs), which are aliphatic polyesters synthesized from bacteria under specific conditions [3], have been extensively investigated due to their advantageous properties in many applications, particularly involving the biomedical, food packaging, and agricultural fields [4]. Among the family of PHAs, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) copolymer is considered to be third generation, and is biodegradable and biocompatible, possessing a lower melting temperature (~135 °C), lower crystallinity index (~35–40%), and wider window process than polyhydroxybutyrate (PHB) and its copolymers [5]. As natural reinforcement in polymer composites, aloe vera fibers (AVF) offer significant potential in engineering materials. To date, however, AVF have not been investigated sufficiently in comparison with lignocellulosic fibers [6]. A small number of studies on AVF have been reported in the literature, often dealing with property characterization, surface modification, and applications as fillers in polylactides (PLA) [7–9]. Therefore, the objective of this study

was to examine the influence of chemical modification of aloe vera fibers on the morphology and properties of biocomposites based on PHBH/AVF, aiming to improve their matrix-filler compatibility and, subsequently, their functional properties. The bio-fibers incorporated at 20 wt%, were subjected to different chemical modifications, including alkaline, organosilane, and both alkaline and organosilane treatments.

2. Experiments

2.1. Materials

PHBH (11 mol% of HHx) in pellet form was purchased from Kaneka Corporation (Japan) and commercialized under the grade Aonilex X151A.

Aloe vera fibers (AVF) were extracted from locally harvested leaves. The preparation of bio-fibers is clearly described in Section 2.2.

Trimethoxy-octadecyl-silanes (TMOS) (Sigma Aldrich, France) and Sodium hydroxide (NaOH) (Biochem, United Kingdom) were used as received.

2.2. Extraction Procedure and Chemical Composition of bio-fibers

Aloe vera fibers were separated from the leaves using water retting according to the procedure described by Mannai et al. [10]: firstly, the leaves were washed and cut into small pieces, then immersed in a water bath at 90 °C for 2 h. Then, AVF were removed and placed in a closed water container for three weeks. Finally, the bio-fibers were washed several times and dried overnight at 70 °C.

The main constituents of AVF were determined by analytical methods according to Li et al. and Varma et al. [11,12]. The results were the following: lignin = 4.1 wt%, hemicellulose = 25.1 wt%, cellulose = 64.9 wt%, and waxes = 5.9 wt%. The bio-fibers had an average density of 1.4325, in concordance with the literature [7].

2.3. Chemical modification of fibers surface

2.3.1. Alkaline modification

To separate from the cellulose, the hemicellulose, and partially the lignin, a treatment with NaOH was carried out with respect to the methods described by Balaji et al. [7] and Joyyi et al. [13]. Initially, the fiber length was cut to ~3 mm and dried at 70 °C overnight. AVF were immersed in a NaOH solution at 5 wt% for 1 h, while the temperature was kept at 27 °C. Then, AVF were removed and rinsed with distilled water followed by acetic acid solution at 2 wt% until reaching pH = 7. Finally, the fibers were dried at a temperature of 70 °C until obtaining a constant mass.

2.3.2. Chemical modification using TMOS

A chemical modification using TMOS was conducted according to the following procedure: the bio-fibers were placed in a solution mixture of water/ethanol (30/70 v/v) and stirred for 1 h. In parallel, 2% of TMOS (w/w) was dissolved in a solution mixture of water/ethanol (30/70 v/v) for 1 h at pH = 4. The bio-fibers were then immersed in the TMOS solution and stirred at 25 °C for 3 h [14,15]. AVF were filtered and dried at 110 °C for 12 h for a complete condensation of silanol groups [12].

2.3.3. Combined Alkaline–Organosilane Treatment

AVF fibers were subjected to both alkaline and organosilane treatments as described above.

2.4. Preparation of PHBH/AVF Biocomposites

Before processing, all materials were dried at 70 °C for 12 h to remove the moisture contained in the materials. PHBH/AVF biocomposites were melt compounded in a twin-screw extruder, Model DSM Xplore, according to the following processing condi-

tions: temperature = 145 °C and rotational speed= 50 rpm. Table 1 summarizes the various biocomposite formulations used.

Table 1. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH)/aloe vera fiber (AVF) biocomposite formulations used.

Formulations	PHBH (wt %)	AVF (wt %)	Designation
PHBH	100	-	Matrix
NTAVF	80	20	PHBH/non treated AVF
A-AVF	80	20	PHBH/alkaline treated AVF
S-AVF	80	20	PHBH/organosilanes treated AVF
AS-AVF	80	20	PHBH/combined alkaline and organosilanes treated AVF

2.5. Characterization Techniques

A scanning electron microscope, Jeol JSM-6031, was used to observe the morphology of the samples. Prior to any observation, a Polaron sputtering apparatus was used to coat the surface of the samples with a thin gold layer.

TGA was performed in a thermal analyzer (Setaram TGDTA92-10) at 10 °C/min under inert atmosphere (N₂) in the temperature range of 20 to 600 °C. Samples of almost 10 mg were tested in three replicates.

Rheological measurements were carried out at a temperature of 150 °C using an Anton Paar MCR301 rheometer on samples previously dried at 60 °C overnight. All measurements were performed in air.

Water absorption expressed as a percentage was measured on samples according to the ASTM D570-98 (2018) standard method. The procedure is well detailed in the literature [16]. The percentage of absorbed water (W_A %) was determined using Equation (1) [17].

$$W_A(\%) = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

where W_A is the % of absorbed water, m_t is the sample's weight at a particular immersion time, and m₀ is the sample's weight immediately after conditioning.

3. Results

3.1. Morphological Analysis of modified PHBH/AVF by SEM

SEM micrographs of the fracture surface of PHBH, and both unmodified and modified PHBH biocomposites samples, are shown in Figure 1a–e. In Figure 1a, the fracture surface of neat PHBH is homogenous and compact. Figure 1b relative to PHBH/NTAVF shows the presence of some aggregates with fibers pulled out from the matrix indicating the lack of adhesion. Furthermore, some surface irregularities such as voids are visible. For the PHBH/A-AVF biocomposite, the fracture surface shown in Figure 1c exhibits microscopic holes and cavities in the matrix where A-AVF are randomly distributed. Figure 1d shows clearly an improved surface morphology of PHBH/S-AVF biocomposite, resulting in a reduction of the number and size of aggregates. Figure 1e displays the fracture surface morphology of PHBH/AS-AVF biocomposite, which is characterized by a regular and homogenous surface having less defects and fiber pullouts compared with other PHBH biocomposites.

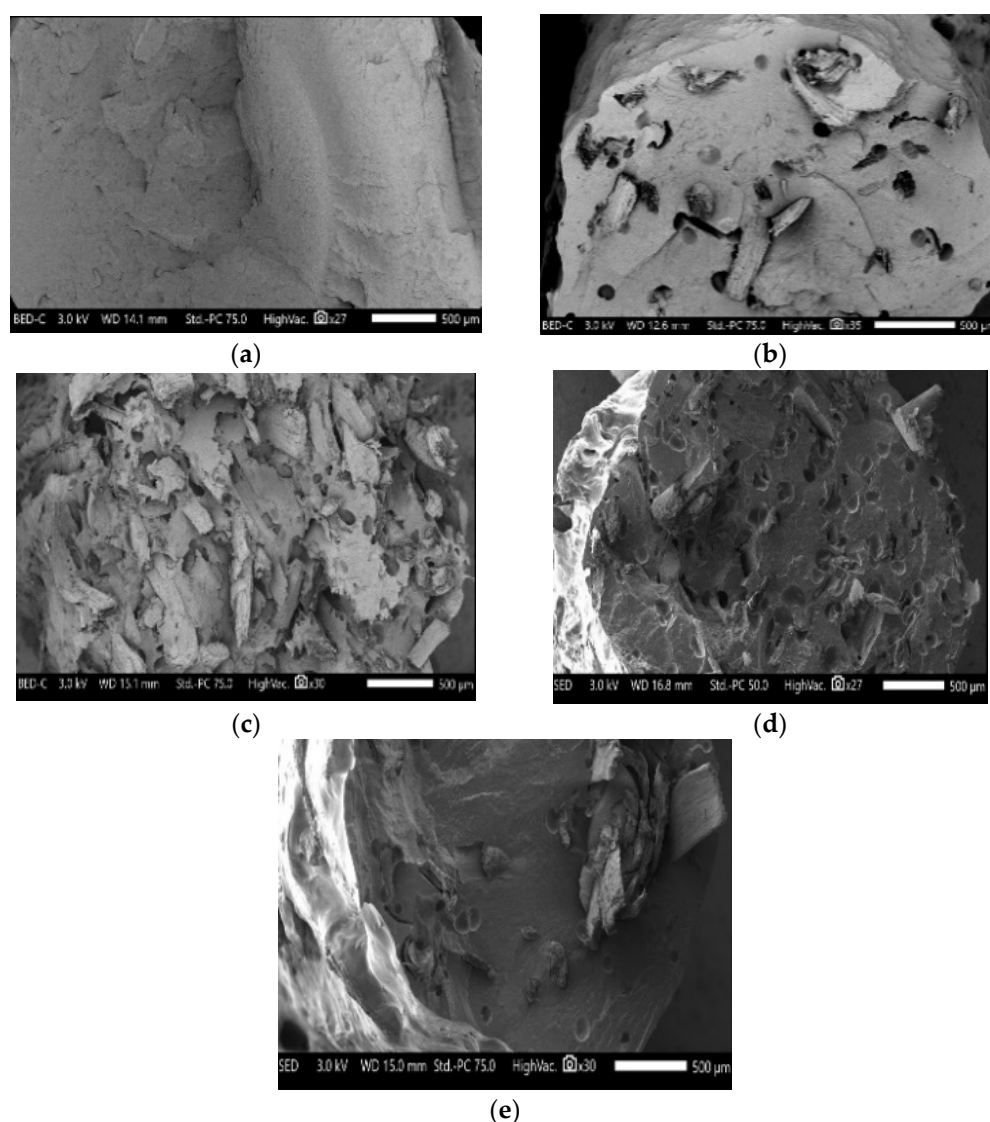


Figure 1. SEM micrographs of: (a) neat PHBH, (b) PHBH/NTAVF, (c) PHBH/A-AVF, (d) PHBH/S-AVF, (e) PHBH/AS-AVF. Copyright 2020. Reproduced with permission from Elsevier Ltd.

3.2. Rheological Measurements

Table 2 summarizes the values of the main rheological properties (η^* , G' , and G'') of neat PHBH and various PHBH/AVF biocomposites, recorded at 0.01 Hz. AVF considerably affect the rheological properties of the biocomposites. Indeed, η^* increases from 4100 Pa.s for the neat PHBH to more than 111×10^3 Pa.s for the PHBH/NTAVF biocomposite, and even more for the treated samples, indicating the restriction of chain mobility of PHBH. This behavior is more pronounced for the biocomposite filled with AS-AVF. Moreover, G' and G'' exhibit the same behavior.

Table 2. The values of complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') of PHBH and PHBH/AVF recorded at 0.01 Hz.

Sample	η^* (Pa.s)	G' (Pa)	G'' (Pa)
PHBH	4100	6.18	258
PHBH/NTAVF	111,000	5100	4760
PHBH/A-AVF	835,000	50,500	14,000
PHBH/S-AVF	228,000	9610	10,600
PHBH/AS-AVF	1,240,000	66,500	40,800

3.3. TGA Data

Thermal stability analysis of both modified and unmodified PHBH/AVF biocomposites was performed by TGA and the results compared to those of neat PHBH. Table 3 shows the temperature values of T_{10} and T_{50} corresponding to 10% and 50% mass loss, respectively, and T_{mdr} is the temperature relative to the maximum decomposition rate. TGA data indicate that the presence of AVF in PHBH slightly decreases the thermal stability of the biocomposite materials independently of the chemical modification. Indeed, the main degradation temperatures, i.e., T_{10} , T_{50} , and T_{mdr} , exhibit lower values. Further, the PHBH/A-AVF biocomposite presents the lowest thermal stability.

Table 3. TGA data of neat PHBH and various PHBH/AVF biocomposites before and after fiber surface treatment.

Samples	T_{10} (°C)	T_{50} (°C)	T_{mdr} (°C)	Residue (%)
PHBH	280 ± 0.5	294 ± 1.8	295 ± 1.1	0.2 ± 0.05
PHBH/NTAVF	274 ± 0.8	288 ± 1.9	288 ± 0.8	4.2 ± 0.6
PHBH/A-AVF	260 ± 0.7	274 ± 1.7	276 ± 0.9	4.3 ± 0.4
PHBH/S-AVF	278 ± 0.4	293 ± 1.3	293 ± 0.3	1.9 ± 0.1
PHBH/AS-AVF	277 ± 0.2	289 ± 1.1	292 ± 0.3	1.6 ± 0.1

3.4. Water Absorption (WA)

Figure 2 shows the water uptake of neat PHBH and PHBH/AVF biocomposites before and after chemical modification. All WA curves exhibit a similar trend, which is characterized by a fast increase in WA during the first 24 h of immersion before reaching saturation. As expected, PHBH has the lowest water absorption, whereas that of the PHBH/A-AVF biocomposite is the highest.

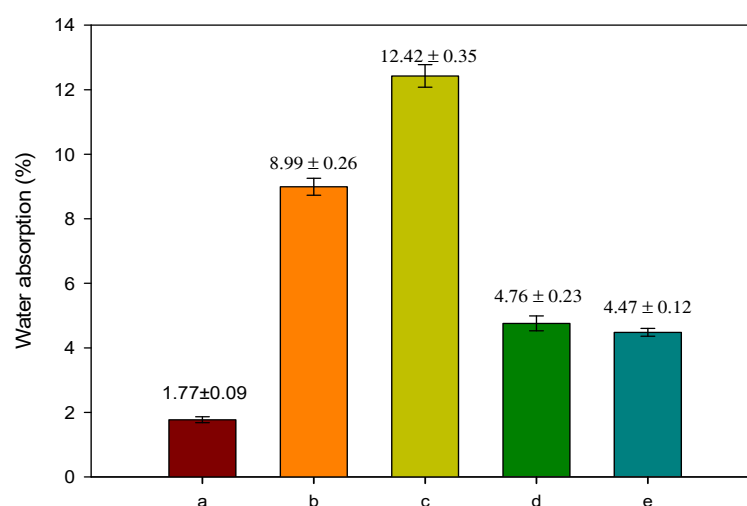


Figure 2. Water absorption (%) at saturation (a) neat PHBH, (b) PHBH/NTAVF, (c) PHBH/A-AVF, (d) PHBH/S-AVF, and (e) PHBH/AS-AVF.

4. Discussion

A homogeneous morphology is observed in Figure 1a relative to neat PHBH, whereas in Figure 1b, NTAVF aggregates are present in the matrix with some fiber pullouts and microvoids. This behavior is typical of an incompatible system, characterized by a poor interfacial adhesion between highly hydrophilic bio-fibers and a hydrophobic polymer matrix [18]. However, the chemical modification involving both the alkaline and organosilane treatments enhances the morphology, resulting in enhancement

of the fibers' wettability, and subsequently on strong interactions between AVF and PHBH. Indeed, according to Orue et al. [14], the grafted TMOS on the AVF surface promotes the interfacial adhesion due to its bifunctional structure.

Rheological measurements show a significant increase in η^* at a lower frequency (0.01 Hz), which is attributed to a hindering effect on the chains' mobility after adding AVF. Similar behaviors are reported for G' and G'' , which indicate a good interfacial bonding between PHBH and AVF; however, this is more pronounced for the PHBH biocomposite filled with AS-AVF, in agreement with the literature data [19].

TGA data indicate that the thermal stability of modified and unmodified biocomposites decreases on adding AVF to PHBH. This could be explained as a result of the moisture contained in the materials [20] and also to a slight alteration of the cellulose structure during the chemical treatment [21].

PHBH shows the lowest water uptake due to its hydrophobic nature, whereas PHBH/A-AVF shows the highest percentage owing to the alkaline treatment, which causes the surface irregularities and fibrillation of the bio-fibers, thus increasing reactive sites [22]. The remainder of the PHBH biocomposites have intermediate values. PHBH/NTAVF has the highest WA% attributed to the presence of hydroxyl groups in the chemical structure of AVF [23], whereas PHBH/S-AVF and PHBH/AS-AVF exhibit lower values, resulting from the presence of silanol groups which prevent fiber swelling [24,25].

5. Conclusions

In the current study, the influence of chemical modification on aloe vera fibers and their impact on morphology and properties of PHBH biocomposites, elaborated by melt mixing in a twin-screw mini-extruder, were investigated. Morphological data showed the importance of this chemical modification to prevent the formation of filler aggregates, thus enhancing the filler-matrix interfacial adhesion. Furthermore, the biocomposite of AVF treated with a combination of alkaline and organosilanes displayed better thermal stability, rheological properties, and lower water uptake in comparison with the other biocomposites.

Author Contributions: C.I. realized the set of experiments, treated the experimental data and wrote the paper; M.K. conceived and designed the experiments; and N.D., I.Z. and S.B. analyzed and validated the data. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

PHBH	poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)
Aloe Vera Fiber	AVF
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
SEM	Scanning Electron Microscopy
TMOS	Trimethoxy-octadecyl-silanes
NTAVF	Not treated Aloe Vera fiber
A-AVF	Alkaline treated Aloe Vera Fiber
S-AVF	Organosilanes treated Aloe Vera Fiber
AS-AVF	Combined alkaline organosilanes treated fiber
TGA	Thermogravimetric analysis

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