Influence of Filler Loading and in Situ Salicylic Acid Treatment on Corn Husk Fiber Filled Poly(Hydroxybutyrate-Co-Valerate)

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Abstract. The effect of filler loading and in situ salicylic acid treatment on the mechanical properties and morphology of poly(hydroxybutyrate-co-valerate)/ corn husk fiber (PHBV/CHF) biocomposites was studied. Both untreated and salicylic acid treated PHBV/CHF biocomposites were prepared by using heated two roll mill followed by compression moulding. It was found that the addition of CHF to PHBV biocomposites increased the tensile strength and Young’s modulus while the elongation at break decreased. Salicylic acid treated PHBV/CHF biocomposite display superior tensile strength and Young’s modulus than untreated PHBV/CHF biocomposite due to the enhanced filler–matrix interaction. The better interfacial adhesion between CHF and PHBV matrix was confirmed through scanning electron microscope (SEM) analysis.

1. Introduction

The use of natural fibers as reinforcement in polymers has significantly increased over the last three decades due to important advantages such as lightweight, non-toxicity, high stiffness and easy processing [1]. Current environmental concern over landfill issues and degradability of petroleum based plastics has led to the use of more sustainable polymers derived from renewable resources having specific characteristics such as biodegradability and biocompatibility [2]. Poly(hydroxybutyrate-co-valerate) (PHBV), an aliphatic co-polyester produced through bacterial fermentation of sugar and lipids, is gaining increasing attention due to its complete biodegradability in different environments, satisfactory mechanical properties, low moisture permeability and processing versatility [3-4]. However, large-scale application of PHBV is restricted by its relatively higher cost in comparison with most commodity polymers like polyethylene or polypropylene, as well as its brittleness, thermal instability, and narrow processing window [5,14].

The reinforcement of PHBV with natural fibers offers some advantages such as cost reduction, improved mechanical properties and higher thermal stability while ensuring its original biodegradation performance [6,7]. However, natural fibers contain a large number of hydrophilic polar groups that leads to low fiber-matrix interfacial bond strength and poor wetting of the fibers by the matrix which usually results in poor mechanical properties of the composites compared to steel fiber [13,15]. To overcome this drawback, chemical surface modifications such as mercerization, acetylation and silane treatments have been used [8-10]. While various chemical surface modifications of natural fibers biocomposites were previously studied, research on the effect of using salicylic acid as chemical
surface treatment is hardly found. Salicylic acid treatment could be considered as low-cost process to modify the surface of natural fibers by disrupting the hydrogen bonding and henceforth enhancing the wettability of the fibers with the matrix [11]. This research investigated the effect of in situ salicylic acid treatment and corn husk fiber (CHF) loading variation on the mechanical properties and morphology of PHBV/CHF biocomposites [16-18].

2. Methodology

2.1. Material
Corn husks waste was collected from corn fields in Mata Ayer, Perlis. The corn husks were washed, chopped to slightly smaller pieces followed by drying at 80°C for 24 hours. The dried corn husks were then grounded to obtain finer corn husk powder of around 63 μm in particles size. PHBV in fine powder form was supplied by Ningbo Tianan Biologic Material Co., LTD in Ningbo, China under the trade name of ENMAT Y1000. Salicylic acid in solid form was supplied by AR Alatan Sdn. Bhd. Alor Setar, Kedah.

2.2. Biocomposites Preparation
The compounding of PHBV/CHF biocomposite was carried out by using a heated two roll mill mixer at 185 °C with rotor speed of 15 rpm. PHBV was charged into the heated mixing roll and melted for 15 minutes. CHF was then added and the mixing was continued for another 15 minutes. The formulation of the PHBV/CHF biocomposites is listed in table 1. For in situ salicylic acid treatment of PHBV/CHF biocomposite at 20 wt% CHF loading, PHBV was firstly charged into the mixing roll for 15 minutes. Then, 6% salicylic acid was added into the heated mixing roll followed by CHF filler. The mixing was continued for another 15 minutes until it was homogeneous. The compounded PHBV/CHF biocomposite was then compression moulded using a hot press machine (Model:GT-7014-H) to obtain uniform sheet of biocomposite. PHBV/CHF biocomposite was preheated for 15 minutes at 185°C before completely pressed for 10 minutes under 20 kPa pressure. Afterwards, the biocomposite sheet was cooled in cold press for 5 minutes before the specimens were cut for mechanical testing according to ASTM standard.

| Sample          | PHBV (wt%) | Untreated CHF (wt%) | Salicylic acid treated CHF (wt%) |
|-----------------|------------|---------------------|----------------------------------|
| PHBV            | 100        | 0                   | -                                |
| PHBV / CHF5     | 95         | 5                   | -                                |
| PHBV / CHF10    | 90         | 10                  | -                                |
| PHBV / CHF20    | 80         | 20                  | -                                |
| PHBV / CHF30    | 70         | 30                  | -                                |
| PHBV / CHF20_T  | 80         | -                   | 20                               |

2.3. Testing and characterization
Tensile properties were determined according to ASTM D 882 by using Instron 5569 with a cross-head speed of 5 mm/min. Five rectangular shaped samples (15 mm × 100 mm) were used and the mean values of tensile strength, Young’s modulus, and elongation at break of each composite were obtained from the test. The fractured surface morphology of PHBV/CHF biocomposites was observed with SEM (Model: TM3000 & Bruker). Auto Fine Coater (Model: JEOL JFC – 1600) is used for platinum-coated specimen to eliminate the electron charging effects.
3. Results and Discussion

3.1. Tensile properties

The effect of filler loading on the tensile strength of PHBV/CHF biocomposites is shown in figure 1. It can be seen from figure 1 that the tensile strength of PHBV/CHF biocomposites increased with increased filler loading. As the amount of CHF filler loading increases to 30 wt%, tensile strength of PHBV/CHF biocomposites increased by 165% as compared to that of pure PHBV. The increase in the tensile strength of PHBV/CHF biocomposites could be attributed to the good adhesion between CHF filler and PHBV matrix interface that leads to better stress transfer from the matrix to the filler.

![Figure 1. Tensile strength of PHBV/CHF biocomposites at different filler loading](image)

The tensile properties of PHBV/CHF20 biocomposites before and after salicylic acid treatment are shown in table 2. At 20 wt% of CHF filler loading, salicylic acid treated PHBV/CHF biocomposites exhibited a slightly higher tensile strength compared to that of untreated PHBV/CHF biocomposite. This behaviour is attributed to the improved interfacial adhesion between CHF filler and PHBV matrix in PHBV/CHF20T biocomposites as evidenced by the decreased fibers pull-out (see figure 2). According to De et al., citric acid treatment of bamboo fiber improved the wettability of fiber, resulting in stronger fiber-matrix adhesion [11].

| Sample       | Tensile Strength (MPa) | Young’s Modulus (MPa) | Elongation at break (%) |
|--------------|------------------------|-----------------------|-------------------------|
| PHBV / CHF20 | 3.7                    | 99.1                  | 7.5                     |
| PHBV / CHF20T| 4.5                    | 161                   | 6.3                     |

As shown in figure 2, a similar trend of increasing Young’s modulus with filler loading was observed in PHBV/CHF biocomposites. It was found that Young’s modulus of PHBV/CHF biocomposites increased from 27.6 MPa to 269 MPa as the filler content increased from 0 to 30 wt%. The increase in the Young’s modulus of the biocomposites is due to the introduction of the stiffer CHF into the PHBV matrix. Similar observations were obtained by Mazur et al. who studied mechanical properties of wood fibers and basalt fibers introduced to the PHBV matrix [12]. In addition, the
Young’s modulus for PHBV/CHF20 T biocomposites was found to be higher than for PHBV/CHF20 biocomposites which indicates that more efficient stress transfer from PHBV matrix to stiffer CHF occurs resulting from the stronger fiber-matrix adhesion induced by salicylic acid treatment.

Figure 2. Young’s modulus of PHBV/CHF biocomposites at different filler loading

On the other hand, the elongation at break of PHBV/CHF biocomposites decreased significantly as the CHF content is increased as illustrated in figure 3. Increased CHF filler loading in the PHBV matrix resulted in the stiffening and hardening of the biocomposites. This reduced the biocomposites resilience and toughness, and led to lower elongation at the break. In addition, the elongation at break of salicylic acid treated PHBV/CHF biocomposite was lower than the corresponding value for the untreated PHBV/CHF biocomposite. This is due to salicylic acid treatment, which further stiffened the biocomposite and thus decreases the chain mobility of the biocomposite.

Figure 3. Elongation at break of PHBV/CHF biocomposites at different filler loading
3.2. Scanning Electron Microscopic (SEM) analysis

SEM micrographs of the tensile fracture surfaces of PHBV/CHF biocomposites are presented in figure 4 (a) to (d). Figure 4 (a) shows a smooth fracture surface of PHBV matrix which commonly indicates a brittle failure mode.

![SEM micrographs of tensile fracture surfaces of PHBV/CHF biocomposites: (a) PHBV, (b) PHBV/CHF30, (c) PHBV/CHF20 and (d) PHBV/CHF20T](image)

Figure 4. SEM micrographs of tensile fracture surfaces of PHBV/CHF biocomposites: (a) PHBV, (b) PHBV/CHF30, (c) PHBV/CHF20 and (d) PHBV/CHF20T

Figure 4 (b) and (c) show rougher fracture surfaces of PHBV/CHF biocomposites with minimal presence of microvoids from fibers pull-out. Lesser fibers pull-out indicates a good interfacial adhesion occurred between CHF and PHBV matrix which leads to a significant improvement in the mechanical properties of PHBV/CHF biocomposites upon the addition of CHF filler. As can be seen in figure 4 (d), PHBV/CHF20T biocomposite showed more homogeneous surface and reduced microvoids appearance upon in situ salicylic acid treatment. This indicates that the CHF filler is well blended within the PHBV matrix and thus promotes stronger interfacial adhesion between PHBV and CHF. As a result, the tensile strength of salicylic acid treated PHBV/CHF20 biocomposite was found to be higher than the untreated PHBV/CHF20 biocomposite.

4. Conclusion

Tensile strengths and Young’s modulus of PHBV/CHF biocomposites increase while elongations at break decrease with increasing filler content. It was found that salicylic acid treatment facilitates good interfacial adhesion between CHF and PHBV. As a result, salicylic acid treated PHBV/CHF biocomposite yielded better tensile strength and Young’s modulus. The enhancement of filler-matrix interaction induced by in situ salicylic acid treatment was confirmed through SEM.
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