A Tough, Biodegradable and Water-resistant Plastic Alternative from Coconut Husk

Yihao Leow[1], Veronica Sequerah[1], Ying Chuan Tan[2], Yong Yu[1], Eric Charles Peterson[3], Changyun Jiang[1], Zheng Zhang[1], Le Yang[1], Xian Jun Loh[1], Dan Kai[1,2]*

[1]Institute of Materials Research and Engineering (IMRE), A*STAR, 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634 Singapore

[2]Institute of Sustainability for Chemicals, Energy and Environment (ISCE2), A*STAR, 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634

[3]Singapore Institute of Food and Biotechnology Innovation (SIFBI), A*STAR, 31 Biopolis Way, #01-02, Nanos, Singapore 138669

Email: kaid@imre.a-star.edu.sg

Abstract

Bioplastics from lignocellulosic biomass have gained great interests due to its renewable nature and biodegradability. However, poor mechanical performance and water stability limit their practical applications. Plastic resins are normally required to bond the biomass compounds. In this work, a high-performance bioplastic from coconut husk is developed *via* a simple top-down and resin-free approach; coconut husk fragments are directly processed into bioplastics through the partial removal of lignin, followed by hot-pressing. By optimization of delignification conditions, the generated bioplastics achieve a tensile Young's modulus of 2.1 ± 0.4 GPa and a tensile strength of 22.8 ± 4.4 MPa. More importantly, these bioplastics show excellent water stability (up to 28 days of soaking) and decent microbial biodegradability. Furthermore, the potential use of the bioplastics is demonstrated as solid planar substrates for miniaturized, disposable electrochemical biosensors. This work provides a promising and green approach to prepare strong, wet-stable, and biodegradable lignocellulosic bioplastic as a potential solution to replace petroleum-based plastics.

Keywords

Waste valorization, Cellulose, Lignin, Resin-free, Bioplastics, Biocomposites, Wearable devices

1. Introduction

Traditional plastics are putting a heavy toll on the environment due to the ever-rising amount of plastic waste that are accumulating in landfills and the natural environment, thus making plastic highly unsustainable. In order to provide a sustainable environment for the future generations, more efforts are thus needed to shift toward biodegradable plastics and reduce our reliance on conventional petroleum-based plastics [1].

Lignocellulosic biomass is an abundant and renewable resource from plants, which mainly comprise of cellulose, hemicellulose and lignin. Differing from petrochemical feedstock that mainly compose of C–C and C–H bonds, the chemical structures of lignocellulosic biomass contain a high amount of carbon-oxygen bonds. These unique structures could be used as new platforms to design functional and readily compostable/biodegradable polymers [2, 3]. Among the advancements, molded products made from pulp fibers have been widely explored [4]. However, due to the short, weak and hydrophilic characteristics of pulp fibers, current molded pulp products always show a poor performance with regard to low mechanical strength and weak resistance to water [5-7].

Therefore lignocellulosic biomass is commonly used as a filler material incorporated into a polymer matrix to form biocomposites [8-10]. Both petroleum-based and biodegradable resins have been widely employed to glue biomass to achieve material integration and acceptable performance. Mazur et al. studied the impact of various natural fibers (wood flour, basalt fibers, flax fibers, and walnut shell flour) when incorporated at 40 wt% as fillers into a green high-density poly(ethylene) matrix [11]. The stiffness of the composites increased, but long duration in water led to a decrease in tensile mechanical properties. Younesi-Kordkheili and Pizzi added lignin modified by ionic liquid as a natural binder to bagasse fiber-recycled poly(propylene) composites [12]. They found the composites with modified lignin performed better mechanically and offered higher dimensional stability in comparison to those with unmodified lignin. Bahrami et al. developed a strong and thermal resistant biocomposite by incorporating plasma-treated flax fibers in a biodegradable poly(butyl succinate) matrix [13]. Lu et al. further strengthen cotton stalks-high density poly(ethylene) composites with Kevlar fibers [14]. The mechanical strength improved greatly and the Kevlar fibers imparted the composites with self-extinguishing capabilities. However some challenges are still pending to overcome, including the incompatible nature of natural lignocellulose material with polymer matrices,

biodegradability and generation of microplastics [15]. Therefore, the development of resin-free bioplastics is a promising approach to fully valorize lignocellulosic biomass.

Recently, new technologies have been developed to produce high-performance bioplastics from lignocellulosic biomass. For example, a new top-down technology has been developed to make super-strong structural materials from wood and bamboo, via *in situ* lignin removal followed by hot-pressing [5, 6, 16, 17]. Specific tensile strengths of 400+ MPa cm^3 g^{-1} for wood and 750+ MPa cm^3 g^{-1} for bamboo were able to be achieved, which are much higher as compared to that of most structural metals and alloys. The process brings about a densely packed network of aligned cellulose nanofibers and promoted favourable interactions between the abundant hydroxyl groups. When compared to natural wood, the densified wood displayed a 12-fold increase in strength and exhibits strength performance that is substantially better than conventional load-bearing polymers. Likewise, using a similar method Li et al. showcased the enhancement of natural bulk bamboo [17]. A high tensile strength of 1 GPa and tensile modulus of 75 GPa was achieved. Clearly, this technology opens a new window for the development of lignocellulose-based bioplastics. However, considering its complex structure and heterogeneous characteristics, more studies need to be carried out on other biomass sources, in order to demonstrate the universality of the technology.

Coconuts represent an important economic crop for humid tropical regions, providing oil, food, animal feed, and coir fibers, and are widely found in Southeast Asia, the Pacific region, Latin America and Africa [18]. Globally, ~300 million tonnes of coconuts are produced in 2018, while ~50% of this harvest represent inedible coconut husk, which is either utilized to generate coir fibers, or discarded [19, 20]. Coconut husks are composed of ~40% cellulose, ~20% hemicellulose and ~30% lignin, similar to the composition of natural wood [21]. However, current studies rarely report technologies involving the conversion of coconut husk into novel functional materials.

In this study, we aimed to develop high-performance plastic alternatives from coconut husk via partial delignification and hot-pressing. Lignin is believed to play a key role in the regulation of the resulting materials considering that it functions as a binder in natural plants. Therefore, we prepared coconut husk bioplastics with different lignin contents by various delignifying condition to investigate the relationship between lignin composition and mechanical properties of the resulting bioplastics. The morphology, chemical, and mechanical properties of the

coconut husk bioplastics were studied. The water stability and biodegradability of the bioplastics were also evaluated. Moreover, the potential of using the coconut husk bioplastic as a biodegradable substrate for biosensor application was also demonstrated in the study.

2. Materials and Methods

2.1 Materials and Chemicals

Raw coconut husks were purchased from Nextevo. The obtained coconut husk was washed 3 times using deionized (DI) water to remove any dirt or dust. The coconut husk was left to soak overnight to help with the deshelling and was cut into smaller and manageable pieces. Subsequently, coconut husks were dehydrated in an oven at 100 °C overnight to remove all moisture. All chemicals were purchased from Sigma-Aldrich chemicals and used as received except when noted.

2.2 Preparation of coconut husk bioplastics

10 g of dry coconut husk was placed into a 500 ml round bottom flask (RBF) and then subjected to delignification where it was treated at 100 °C with 300 ml of aqueous mixture solution of 2.5 M sodium hydroxide and 0.4 M sodium sulfite at various time intervals (4 and 8 hours). The RBF was placed inside an oil bath and was set to 650 revolutions per minute (rpm), and a condenser setup was connected to the RBF to allow the solvent vapors to be condense back into liquid solvent. Next, the solvent was strained away from the delignified coconut husk and immersed in boiling DI water which was routinely changed with fresh DI water until a neutral pH was achieved.

For bleaching samples, the coconut husk that was previously delignified (8 h) was placed into a 500 ml RBF with 300 ml of sodium chlorite solution at 80 °C for 4 h at 650 rpm. The sodium chlorite solution was produced by mixing 1 wt.% of sodium chlorite and acetate buffer (pH of 4.6 – 5.6). The delignification process aims to remove hemicellulose and lignin binding the cellulose fibers and exposes the cellulose surface rich in hydroxyl groups. The abundance of hydroxyl groups facilitates hydrogen bonding between the neighbouring cellulose nanofibers, contributing to the formation of coconut husk bioplastics. After the bleaching process, the sodium chlorite solution was strained away from the bleached coconut husk, which was then immersed in DI water at 60 °C until the coconut husk reached a neutral pH. The processed coconut husk was soaked in ethanol and stored until it was ready for hot-pressing. Ethanol was

used as a storage medium to maintain the activity of –OH groups for hydrogen bonding. In addition, ethanol is also easily evaporated under hot-pressing conditions. A schematic of the fabrication of coconut husk bioplastics is displayed in Figure 1.

After soaking the processed coconut husk in ethanol and repeating the solvent exchange step three times, the processed coconut husk was thoroughly compressed into a mould where the excess ethanol is removed. The mould was then removed, which generated a compact processed coconut husk form ready for hot-pressing. The densification was conducted with a hot-press equipment (P 200 E, Collin, Germany) (Figure S1). The hot-press process has been adapted from Song et al. with a few modifications [5]. The parameters used in our study is hot-pressing with 100 °C at 50 bar for 1 h.

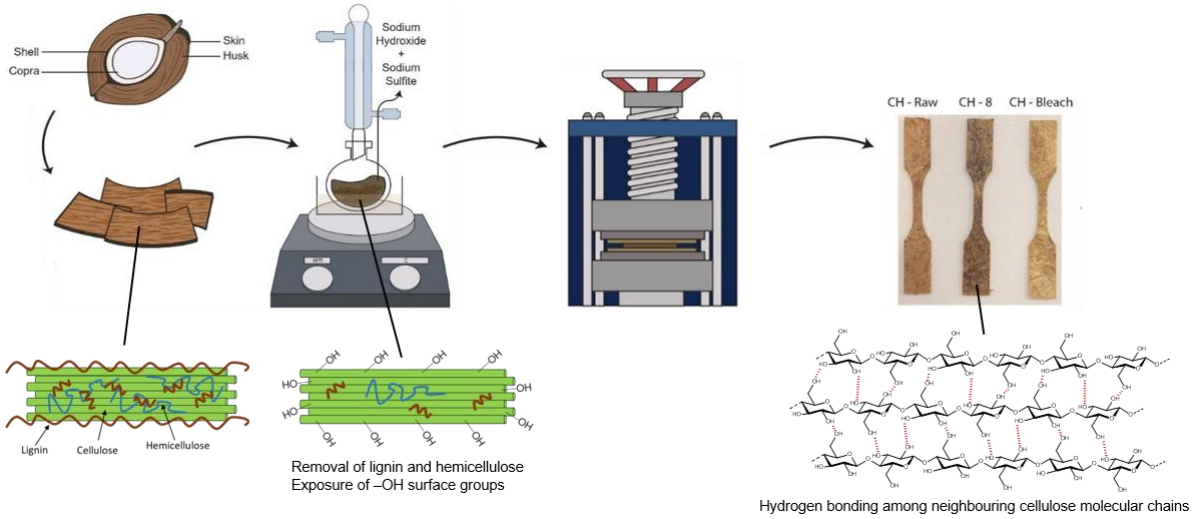

Figure 1. Processing steps and chemical treatment principles of preparing coconut husk bioplastics

2.3 Chemical characterization of delignified coconut husk

To determine the hemicellulose content, 1 g of dried processed coconut husk and 150 ml of 500 mol m^{-3} of NaOH solution was placed into a 250 ml Erlenmeyer flask and was boiled for 3.5 h at 500 rpm. After allowing the mixture to cool down to room temperature, the mixture was filtered using a vacuum filter and was continually washed with DI water until it reached a neutral pH. The remaining residue which contained lignin and cellulose content only were oven dried at 105 °C for overnight. The difference between the initial weight and the dried residue is the calculated hemicellulose content [22].

To determine the lignin content, 1 g of dried processed coconut husk and 15 ml of cold sulphuric acid (H_2SO_4) (72%) was placed in a beaker and aggressively stirred for 2 h. Next, 560 ml of DI water is added into the mixture to dilute the H_2SO_4 solution to 3 wt% and was boiled for 4 h. After allowing the mixture to cool down, the mixture was filtered using a vacuum filter and was repeated flushed with DI water until it reached a neutral pH. Lastly, the residue was dried in an oven at 105 °C overnight. The dried residue weight calculates represents the lignin content [23].

2.4 Physicochemical characterization of coconut husk film

The morphologies of the coconut husk samples were observed by using a scanning electron microscope (JSM6700F, JEOL, Japan). To prepare the cross-section of the coconut husk samples, the samples were flash-freeze and cut in liquid nitrogen.

Porosity, as expressed in Eq. 1, was determined using the density of the coconut husk film (D_x) calculated and the density of cellulose, D_c.

$$\text{Porosity } (\%) = \frac{D_c - D_x}{D_c} \times 100\% \quad - \quad (Eq.1)$$

Water contact angle test was conducted by using an injection syringe to drop 20 μL of DI water on to the coconut husk samples that are attached to the slides. A camera records where the drop of DI water comes in contact with the sample.

Thermal behaviours of the samples were also investigated. Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyser (Q500, TA Instruments, USA). Samples were heated at 20 °C min^{-1} from room temperature to 700 °C in a dynamic nitrogen atmosphere (flow rate = 60 ml min^{-1}). Differential Scanning Calorimeter (DSC) thermal analysis was performed on a DSC (Q100, TA Instruments, USA) equipped with an auto-cool accessory and calibrated using indium.

Crystallinity of the coconut husk bioplastics were investigated by X-ray diffraction (XRD) analysis. The diffractograms were collected between 2θ range from 5° to 85° at 100 counts s^{-1}. Crystallinity index (CI) is obtained with the following equation (Eq. 2),

$$\text{CI} = \frac{I_{101} - I_{Am}}{I_{101}} \times 100\% \quad - \quad (Eq.2)$$

where I_{101} is the diffraction intensity of (101) plane and I_{Am} is the diffraction intensity of the amorphous phase.

Surface chemistry of CH membranes was characterized using attenuated total reflection (ATR) technique on an infrared spectrometer (Spectrum 2000, PerkinElmer, USA) and its Fourier transform infrared spectrum (FT-IR) spectra recorded. The spectra data were collected across a range of 600 to 4000 cm^{-1}.

2.5 Mechanical properties measurement

The tensile and bending properties of coconut husk bioplastics were measured via a universal testing machine (Instron 5569, USA) with a 50 kN load cell. The tensile test was conducted according to ISO 527 test standard. Tensile samples were prepared into dog-bone shape with dimensions of 3.15 × 10 mm and subjected to tensile stress until fracture at crosshead speed of 1 mm min^{-1}. The flexural test was conducted according to ASTM 790 test standard. The flexural samples were cut out into dimensions of 45 × 10 mm and tested to the point of failure. Flexural testing was set-up with a fixed span of 40 mm and crosshead speed of 1 mm min^{-1}. Average values were obtained from five replicated samples for both tensile and flexural testing.

The dynamic mechanical properties were attained using TA Instrument Q800. The dimensions for tensile samples were 30 × 5 mm and flexural samples were 45 × 10 mm. The tensile and flexural samples were measured using a tension and single cantilever mode respectively. Both studies were conducted under temperature ramp test mode from −50 to 150 °C with a constant heating rate of 3 °C/min, at a frequency of 1 Hz and amplitude of 20 μm.

2.6 Stability test and degradation

The swelling test was conducted by cutting up the coconut husk film samples with dimensions of 1 cm × 1 cm and weighing each sample. The samples are then immersed into vials containing 20 ml of DI water. There are 3 sets of swelling test done with different time intervals of 7 days and 28 days, where every two days the DI water in the vial is exchange with fresh DI water. The weight was measured before the start of the experiment and at the end of the end of the experiment. The coconut husk samples are later put into an oven for 24 h to remove all moisture. After the dehydration, the coconut husk samples are weighed again.

2.7 Biodegradation experiment

To determine biodegradability of untreated and treated coconut fiber, *Clostridium thermocellum*, a rapid cellulolytic anaerobe, was cultivated on experimental samples. Briefly, a seed culture of *C. thermocellum* (ATCC 27405) was prepared by aseptically inoculating a 2 mL −80 °C freezer stocks into 50 mL of RM medium, comprised of 2 g L^{-1} urea, 2 g L^{-1} KH_2PO_4, 3 g L^{-1} K_2HPO_4, 5 g L^{-1} yeast extract, 0.2 g L^{-1} $MgCl_2{\cdot}6H_2O$, 0.05 g L^{-1} $CaCl_2{\cdot}2H_2O$, 0.0025 g L^{-1} $FeSO_4{\cdot}7H_2O$ [24]. The medium was prepared anaerobically via Hungate technique in 250 mL serum bottles, using 5 g L^{-1} crystalline cellulose (Avicel PH-101, Sigma Aldrich) as sole carbon source, and incubated at 60 °C for 48 h after inoculation [25]. Subsequently, this seed culture was used as inoculum (5 % v/v) on triplicate bottles prepared in an identical manner, using 5 g L^{-1} raw CH-Raw, CH-8, and CH-Bleach as the sole carbon source, with Avicel included as a positive control, and incubated at 60 °C for 48 h. All samples were ground and sieved to ensure a maximum particle diameter of 100 µm.

To determine biomass degradation, a modified acid detergent fiber (ADF) method was used [26]. In short, after 48 h incubation, triplicate bottles were opened, and 100 mL of ADF solution (20 g L^{-1} cetyltriamethylammonium bromide (CTAB), 50 mM H_2SO_4) were added, with the bottles then resealed and autoclaved for 45 min at 121 °C and 115 PSI. After this, the hot contents of each bottle were shaken vigorously and filtered through a 47 mm A/E Glass Fiber filter (Pall Corp., USA), and washed with 3 equivalent volumes of boiling water. Filters were then dried overnight to determine residual biomass dry weight. Uninoculated bottles with 5 g L^{-1} cellulose were used as a negative control.

2.8 Coconut husk as substrate for electrochemical biosensor

The electrodes used in this work were fabricated by a blade-coating method on the coconut husk bioplastic (CH-8) cut into dimensions of 30 × 10 × 0.5 mm^3 (length × width × thickness), which adopts a three-electrode configuration consisting of a round-shaped working electrode (W.E.) of 4 mm in diameter, surrounded by a partial circle of a counter electrode (C.E.) and a reference electrode (R.E.) (Figure 5A). A commercial silver (Ag) based ink was used to define the conductive underlayer as well as the R.E., while a homemade carbon-based ink was utilized to define the W.E. and C.E. The coconut bioplastic-based carbon electrodes were then dried at 120 °C for 2 h.

Glucose sensors were prepared by using glucose oxidase (GOx) as a catalyst and Prussian blue (PB) as a mediator. The CBCE was first modified with a thin layer of Prussian blue (PB) by electrodeposition. Specifically, the CBCE was immersed in an aqueous solution containing 0.1 M KCl, 0.1 M HCl, 2.5×10^{-3} M $K_3Fe(CN)_6$ and 2.5×10^{-3} M $FeCl_3$, and the potential was swept from –0.2 to 0.6 V for three segments at a scanning rate of 0.05 V s^{-1}. After PB deposition, 2 μL solution of glucose oxidase (Catalogue number 2133, Sigma-Aldrich), which was dissolved in aqueous solution of chitosan (1 wt%, Catalogue number C3646, Sigma-Aldrich), acetic acid (2 wt%, Catalogue number 695092, Sigma Aldrich), and BSA (5 mg mL^{-1}, Catalogue number A2153, Sigma Aldrich), was drop-casted on the W.E. and dried at 4 °C overnight. All electrochemical experiments were performed on a μStat 8000 Multi Potentiostat/Galvanostat from Metrohm.

3. Results and Discussion

Table 1. Chemical composition and physical characteristics of the coconut husk bioplastics.

Sample	Treatment	Chemical composition (C:H:L)[a)]	Density (g cm^{-3})	Porosity (%)	Contact Angle (°)	T_d (°)[b)]	Tg (°)[c)]	O/C ratio[d)]	**CI[e)]**
CH-Raw	No treatment	17:34:49	1.09 ± 0.18	27.4	70.7 ± 7.9	258	99.1	0.34	85.0
CH-4	4 h kraft	47:13:40	1.09 ± 0.13	27.1	39.1 ± 4.7	266	81.8	0.34	86.6
CH-8	8 h kraft	59:12:29	1.14 ± 0.11	23.8	36.5 ± 1.8	263	72.1	0.42	89.9
CH-Bleach	8 h kraft + $NaClO_2$	80:10:10	1.17 ± 0.11	21.9	55.0 ± 5.6	265	55.2	0.45	93.4

[a)]Content of cellulose (C), hemicellulose (H), and lignin (L) in each sample; [b)]determined by TGA at 5% weight loss; [c)]determined by DMA; [d)]determined by XPS; [e)]crystallinity indices (CI) determined by XRD.

3.1 Fabrication of coconut husk bioplastics

Coconut husk contains three key components, para-crystalline cellulose fibril, amorphous hemicellulose, and lignin. They intertwine with each other to form a strong and functional vascular structure to transport water and nutrients and protect the core. As shown in Table 1, after 8 h of the kraft treatment, the lignin and hemicellulose content was reduced to 29 % and 12 %, respectively, while cellulose content increased to 71 %. The additional $NaClO_2$ treatment

further decreased the lignin content down to 10 %. Here, we did not fully remove lignin or hemicellulose, in order to preserve the fibrous microstructure and the hierarchal alignment of the coconut fibers (Figure 2A). Moreover, the removal of lignin and hemicellulose created more pores in the coconut fibers and soften them to facilitate processing and molding. After the delignification, the coconut husk samples were hot-pressed at 100 °C. The process enabled the collapse of the coconut fiber cell and enhanced hydrogen bond formation among neighboring cellulose nanofibers. The coconut husk bioplastics were determined to be suitable for hot-pressing at 100 °C without under undergoing thermal degradation (Table 1 and Figure 2F).

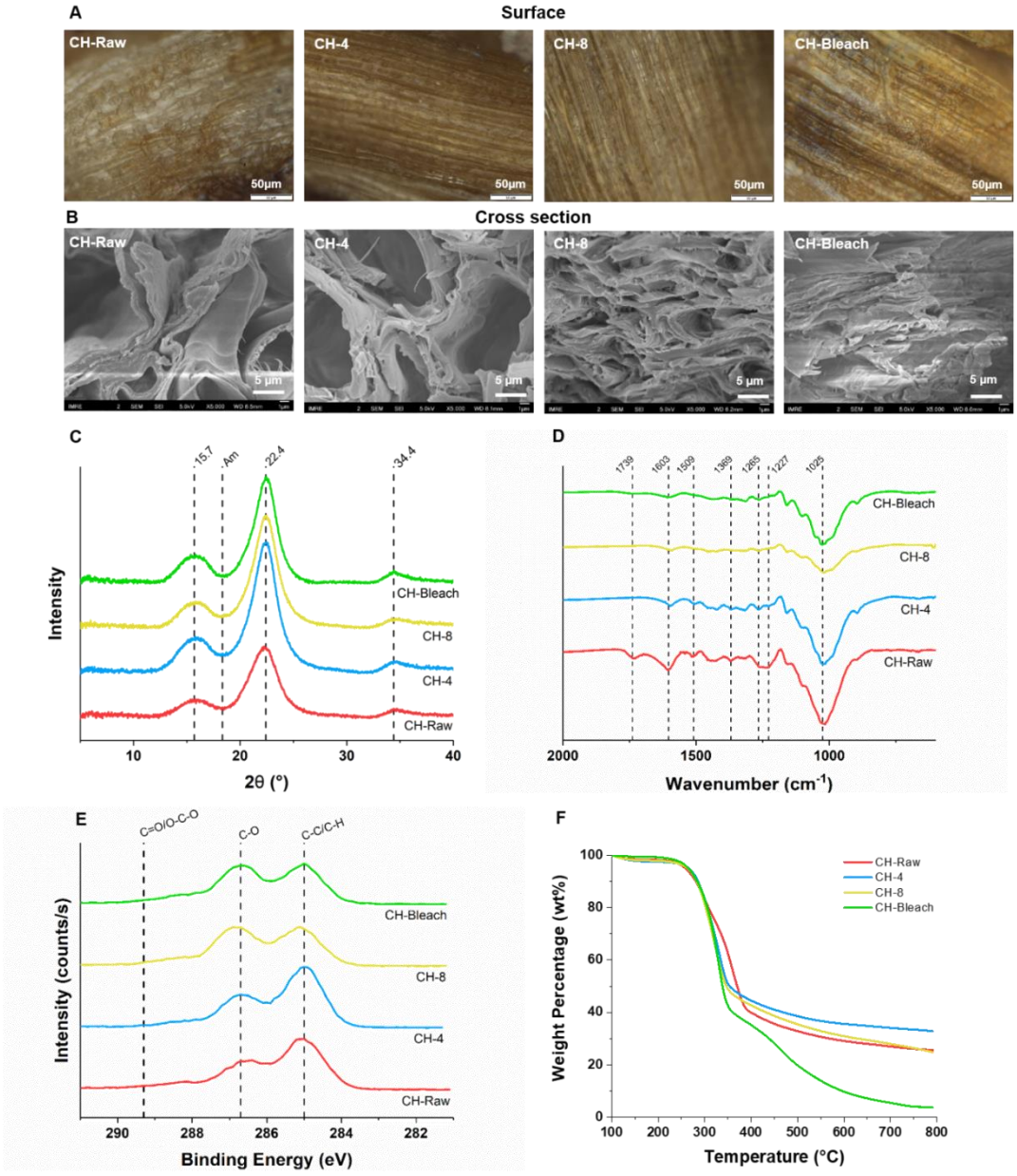

Figure 2. Morphology and chemical properties of hot-pressed coconut husk bioplastics. (A) Optical microscopy images of the surface of the coconut husk. (B) SEM images of the cross –

section of the coconut husk; (C) XRD spectra, (D) FTIR spectra, (E) XPS spectra, and (F) TGA graph.

As shown in Figure 2A and Figure S2, the surface of all samples appears to be smooth where husk fibers were densely impacted with each other with very few pores. For the cross-sectional microstructure of CH-Raw and CH-4 (Figure 2B), the pores are still present, indicating that hot-pressing of high lignin content samples can only modestly densify the coconut husk, leaving many gaps in between collapsed cell walls. On the other hand, the CH-8 and CH-Bleach samples showed a densified microstructure with the fully collapsed fiber cell walls tightly intertwining along their cross-section. Therefore, the density of samples increased, while their porosity decreased with the decreasing lignin content in the samples (Table 1). The CH-Bleach showed the highest density of 1.17 ± 0.11 g cm^{-3} and the lowest porosity of 21.9 %.

3.2 Chemical and surface properties

To understand the chemical structure of coconut husk bioplastics, X-ray diffraction (XRD) was carried out and shown in Figure 2C. The diffraction peaks at 14.7 °, 16.6 °, 22.8 °, and 34.9 °, associated with the crystal lattice type I structure of the native cellulose, were clearly observed from all samples. Similarly, the peak at 21.5 °, corresponding to amorphous cellulose, is also present for all samples. Compared to CH-Raw, the delignified coconut husk samples displayed more intense and sharper cellulose I peaks. More specifically, the delignification process increased crystallinity indices (CI) of cellulose I structures from 85.0 for CH-Raw to 94.3 for CH-Bleach. The result confirmed that this process effectively removed amorphous lignin and hemicellulose without destroying the crystal structures present in raw coconut husks. Fourier transform infrared (FTIR) analysis (Figure 2D) showed that the functional groups of coconut husk assigned to hemicellulose and lignin (G-lignin: 1025 cm^{-1} and 1265 cm^{-1}, aromatic skeletal vibration: 1603 cm^{-1}) became less intense with the increasing delignification time, and finally not detectable in CH-Bleach.

To further understand the chemical structure of the treated coconut husk materials, X-ray photoelectron spectroscopy (XPS) was conducted, and the C 1*s* spectra of the coconut husk samples are shown in Figure 2E. The XPS spectrum of the CH-Bleach has a high energy shift as compared to the raw material CH-Raw, which signifies a reduction of C–C groups and an increase in C–O groups. The calculated oxygen to carbon (O/C) ratio in the treated coconut husk bioplastics increased from 0.34 to 0.45 after kraft and bleach treatment. The change in

elemental compositions is attributed to the loss of high-carbon components, i.e. lignin and hemicellulose, suggesting that the remaining material after the treatment is mainly cellulose.

In order to study the surface interaction with water, the as-prepared samples were subjected to water contact angle measurement. CH-Raw has a higher water contact angle of 70.7 ^{o} as compared to that of the delignified samples with the lowest at 36.5 ^{o} for CH-8 (Table 1 and Figure S3). For the delignified coconut husk, the droplet of water quickly penetrated the hydrophilic surface while the CH-Raw film was more water-repellent due to the presence of lignin. However, it is observed that the water contact angle of CH-Bleach increased to 55 ° and becomes more hydrophobic. It is probably attributed to the denser structure of CH-Bleach, which slowed the water penetration.

3.3 Mechanical and viscoelastic properties

The mechanical performance of coconut husk bioplastics was evaluated via an Instron universal testing machine, and the results were tabulated in Figure 3, S4 and Table S1. The macro failure of both tensile and flexural samples was displayed in Figure S5. Significant improvements to tensile and flexural properties were observed for all delignified coconut husk bioplastics compared to CH-Raw. When compared to CH-Raw (808 ± 369 MPa), tensile Young's modulus displayed a minimum two-fold increase for all treated CH (1751 ± 192 to 2093 ± 243 MPa). A gentle increasing trend was noticed when the coconut husk samples were delignified longer or bleached. More prominently, treated coconut husk bioplastics exhibited an increase of at least 2.75 times, with a maximum of close to five-fold increase in flexural Young's modulus in comparison to CH-Raw (634 ± 258 MPa). In this case, the difference between treatment duration or method did not appear to play a role in the modulus outcome. A similar trend is observed for the tensile and flexural strength. In general, a longer delignification time led to an increase in mechanical strength, with the best result obtained after 8 h of treatment. The additional bleaching step reduced tensile strength slightly when compared to CH-8. For the three-point bending test, both CH-8 and CH-Bleach have a comparable flexural strength of approximately 40 MPa. Our best performing coconut husk bioplastics, CH-8, was compared to some biocomposites (polymer resin incorporated with lignocellulose biomass fillers) and notable research on densified wood (Figure 3G and Table S2). The tensile strength (22.79 ± 4.36 MPa) demonstrated comparable strength against PP-biomass composites and exceeds that of PLA-biomass composites. The flexural strength of the CH-8 (40.71 ± 11.82)

displayed remarkable higher strength compared to all the biocomposites and even neat polymers.

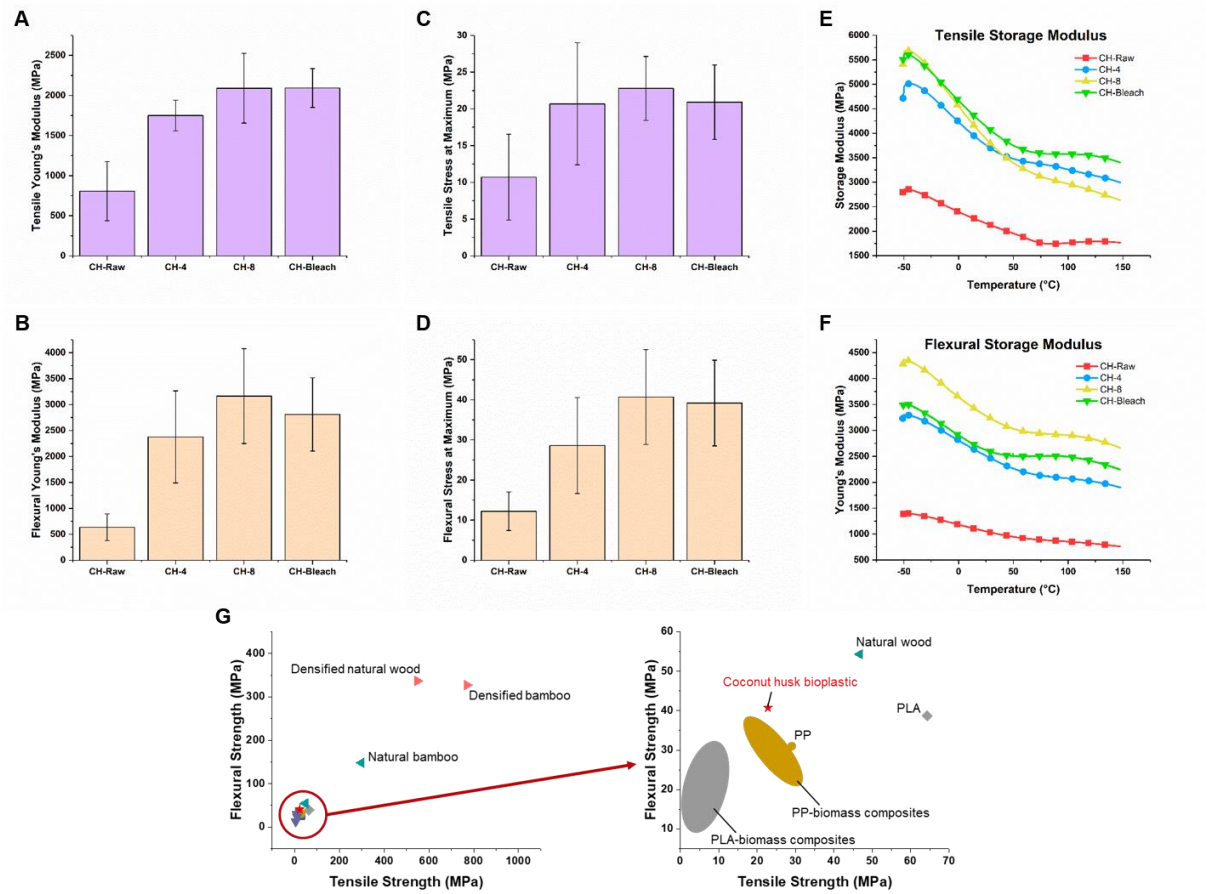

Figure 3. Mechanical and viscoelastic properties of coconut husk bioplastics. (A) tensile modulus, (B) flexural modulus, (C) maximum tensile stress, (D) maximum flexural stress, (E) tensile storage modulus, (F) flexural storage modulus, and (G) comparison among some polymer resin composites filled with lignocellulose biomass. The detailed information and references could be found in Table S2.

The viscoelastic behaviour of coconut husk bioplastics was investigated as a function of temperature and plotted in Figure 3E, F, S6, and S7. All coconut husk bioplastics experience a decrease in storage modulus when transitioning from −50 to 150 °C under both tensile and flexural DMA modes. The reduction can be attributed to the higher molecular chain mobility as the polymeric components of the coconut husk cell walls transit from a glassy state to an amorphous nature when the relaxation increases. Interestingly, the different lignin content in the materials influenced the viscoelastic property of coconut husk bioplastics. CH-Raw

performs the weakest possibly due to high lignin content and large gaps among coconut husk, preventing good interfacial hydrogen bonding between the cellulose fibers. After undergoing delignification and bleaching, the storage modulus for the delignified bioplastics (CH-4, CH-8, and CH-Bleach) significantly improved across the entire temperature range. This observation confirms that partial lignin removal and densification could effectively improve the performance of the resulting materials in term of mechanical and viscoelastic properties.

Overall, we demonstrated that partially removing lignin is a key process to achieve improved mechanical properties of the coconut husk bioplastics. With the full presence of lignin, hot-pressing raw CH into densified sheet is challenging as the stiff lignin protects voids between cell walls and individual fibers from densification. On the other hand, the hot-pressing of delignified samples minimizes the presence and size of defects which improves mechanical properties. As shown in the SEM images (Figure 2), both CH-8 and CH-Bleach possess a densely packed microstructure with intertwined cell walls, which results in a high degree of alignment of cellulose fibers and drastically increase interfacial interactions among those nanofibrils. Moreover, as the delignified coconut husk bioplastics are largely composed of cellulose after the removal of lignin, the strengthening effect can be amplified by the abundance of hydroxyl groups on the cellulosic nanofibers. The densification process brings the fibers together and facilitate the hydrogen bonding formation among the cellulose molecular chains. Therefore, the overall energy required to fracture the treated coconut husk bioplastics is greater than that of CH-Raw.

3.4 Water stability

Water instability is one of the major challenges that limit the applications of lignocellulosic materials in various fields. To test the water stability of our bioplastics, we soaked the samples in deionized (DI) water for 7 days. As shown in Figure 4, the surface of all coconut husk bioplastics become rough and wrinkled due to the water erosion, and the porous structure can still be observed especially for CH-Raw. For delignified samples, the cellulose fibers still bind tight to each other with a good orientation. Similar results are observed in the cross-section SEM images (Figure 4B). For CH-Raw, the pores expanded, and the size increased as compared to the unsoaked sample, indicating the sample significantly swelled in water. On the other hand, the densely packed and intertwined coconut husk fiber structure in microscale maintained in CH-8 and CH-Bleach, though only a few minor gaps or slight delamination appeared.

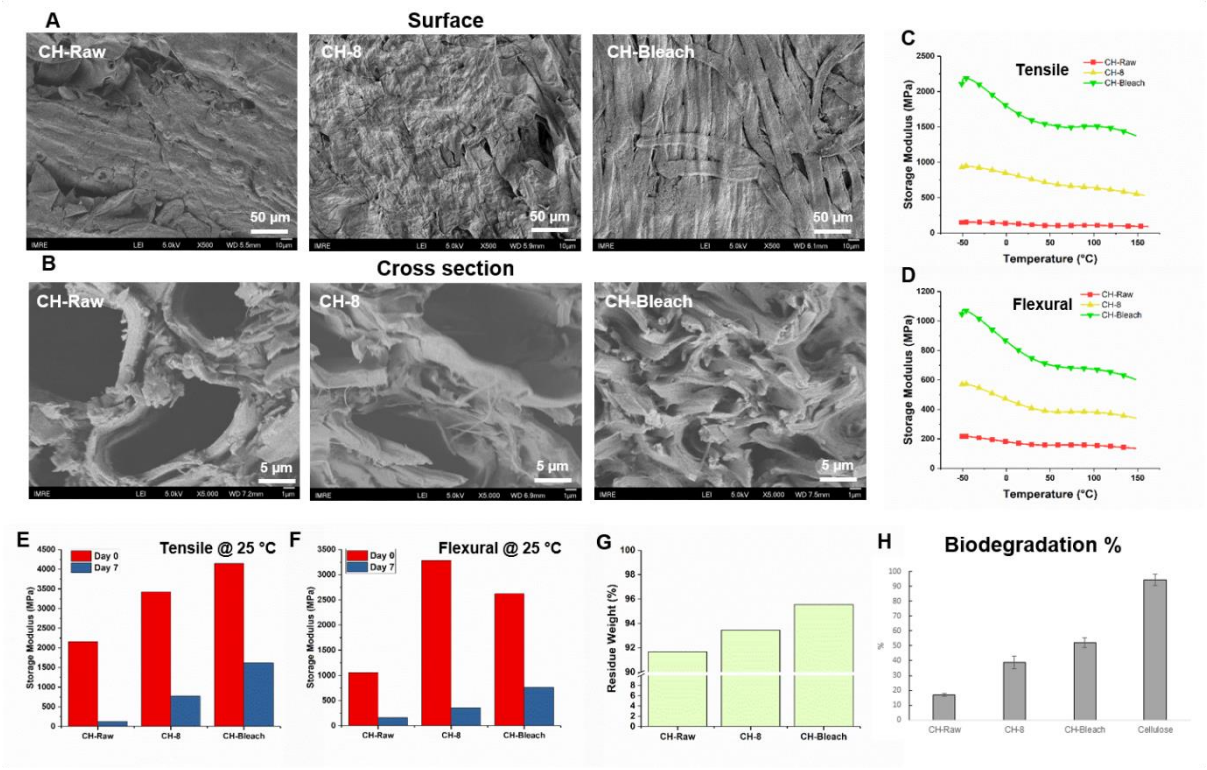

Figure 4. Water stability (7 days of soaking in water) and biodegradability of coconut husk bioplastics. Morphology (SEM images) of the (A) surface and (B) cross-section of the coconut husk bioplastics. Storage modulus of water-treated coconut husk bioplastics: (C) tensile and (D) flexural storage modulus over temperature; (E) tensile and (F) flexural storage modulus at 25 °C. (G) Weight residual after 7 days of soaking in water. (H) Biodegradation of coconut husk bioplastics by *Clostridium thermocellum* after 48 h.

We tested the mechanical properties of the bioplastics after soaking treatment via DMA, and the results shows that all the samples are not as strong as before (Figure 4C, D, S8, S9 and Table S3). However, it is demonstrated that the delignification processing improves the water stability of the bioplastics. CH-Bleach predominate over all the other samples after water treatment, where its tensile and flexible storage modulus are 13.7 times and 4.7 times higher than those of CH-Raw, respectively. Conventional bottom-up pulp technologies manufacture lignocellulosic products mainly based on the hydrogen bonds between cellulose microfibers. Unfortunately, when they get wet, those strong hydrogen bonds are disrupted, therefore leading to fiber separation and paper disintegration. As a result, crosslinkers or adhesive polymers (citric acid, epichlorohydrin or glutaraldehyde) are commonly incorporated into the material systems in order to improve their water stability [27-29]. Here, we used the top-down approach

to produce coconut husk bioplastics without any binder or crosslinking agent. The partial delignification is able to retain certain amount of lignin in the system as a natural binder to maintain the integration and strength of the coconut husk tissue (Sclerenchyma). After 7 days of soaking, the CH-Bleach only lost < 5 % of its original mass while CH-Raw lost about 10 % (Figure 4E). Even after 28 days of soaking, no significant difference in microstructure was observed when the surface and cross-sectional SEM images (Figure S10) were compared to those soaked for 7 days. DMA results showed that the tensile storage moduli of the samples continue decreasing over the soaking time. (Figure S11). After 28 days, the storage modulus of CH-Raw dropped 34.9%, while the treated coconut plastics (CH-8 and CH-Bleach) only reduced ~15% compared to those soaked for 7 days. CH-Bleach can still retain 93 % of its original weight (Figure S12 and S13). This implies that these coconut husk bioplastics exhibit adequate water stability up to 28 days.

3.5 Biodegradation test

To determine the biodegradability of these treated coconut husk materials, the prepared samples were incubated in the presence of *Clostridium thermocellum*, with commercial cellulose as a control sample (5 g L^{-1}). As can be seen in Figure 4H, a distinct reduction in biomass was observable for treated samples. Whereas CH-Raw shows a residual biomass concentration of 3.89 ± 0.04 g L^{-1}, which translates to a biomass reduction of 17.0 ± 0.99 %, it can be observed that residues remaining after degradation decrease with delignification, with CH-8 (2.84 ± 0.19 g L^{-1}) and CH-Bleach (2.21 ± 0.15 g L^{-1}) reducing initial biomass by 38.7 ± 4.3% and 52.3 ± 3.27% respectively. It must be noted that the commercial cellulose control sample achieved a reduction of 94.3 ± 3.8% of total biomass as *C. thermocellum* is a niche organism that breaks down cellulose specifically, and thus the presence of presence of lignin and hemicellulose would limit the degradation [30]. Although the treated materials have a markedly lower amount of these components compared to the untreated material (Table 1), this does partially limit degradation. Regardless, this work shows that the proposed treatment of coconut husks promotes degradation, rather than limiting it, and does not represent a persistent material. Furthermore, the fermentation products of *C. thermocellum* are primarily short-chain fatty acids (i.e. acetate, lactate, and formate) and ethanol, and these products could be of value in a circular bioeconomy [30].

3.6 Coconut husk bioplastic as a substrate for electrochemical biosensor

The electrochemical behaviors of coconut bioplastic-based carbon electrodes (CBCEs) were examined by cyclic voltammometry (CV) using Fe^{3+}/Fe^{2+} as a model redox couple. Typically, a CBCE was immersed in a solution of $K_3Fe(CN)_6$ (5×10^{-3} M in 0.1 M KCl) with the potential sweeping from –0.2 to 0.6 V at various different scan rates (0.01 – 0.1 V s^{-1}), and the current in response to sweeping potential was recorded. Figure 5B shows the resultant cyclic voltammograms. The cathodic peak was observed at 0.134 V when the scan rate was 0.01 V s^{-1}, which gradually shifted to 0.118 V as the scan rate increased to 0.1 V s^{-1}. On the other hand, the anodic peak was first observed at 0.186 V at 0.01 V s^{-1} and gradually shifted to 0.208 V as the scan rate increased to 0.1 V s^{-1}. The peak-to-peak separation (ΔEp) value was calculated to be 0.052 V at 0.01 V s^{-1}, which is slightly smaller than the theoretically predicted value of 0.057 V for a reversible one-electron redox process according to the Nernst equation [31]. The narrower ΔEp can be attributed to the high surface area at the interface formed by porous structure of the coir board as well as the intrinsic edge plane-like sites/defects of the graphite flakes in the ink, which facilitates a faster electron transfer. The widening of ΔEp (i.e., 0.052 to 0.09 V) in response to the increase in scan rate indicates the time constant for electron transfer becomes comparable to the time scale of the potential sweep at higher scan rates. In addition, the plots of anodic (i_{pa}) and cathodic peak currents (i_{pc}) against the square root of scan rate ($v^{1/2}$) show a good linearity (Figure 5C), indicating the electrochemical process is diffusion controlled, as described by the Randles-Sevcik equation [32]. Considering its availability, low production cost and biodegradability, the CBCEs may find great potential in developing disposable and biodegradable electrochemical biosensors for wearable healthcare devices.

As a proof-of-concept, the CBCEs were functionalized with glucose oxidase and its electrochemical glucose detection capability were tested. Briefly, a thin layer of Prussian blue (PB) was first formed on the CBCEs as a mediator by electrodeposition. A tiny drop of glucose oxidase solution was then drop-casted on the working electrode. The as-formed sensor was then connected to the potentiostat with the three electrodes immersed in phosphate buffer solution, and polarized at 0.1 V vs Ag/AgCl. The current in response to addition of glucose was then monitored. As shown in Figure 5D, the current density increases (in terms of absolute value) accordingly when aliquots of glucose (~40×10^{-6} M) were introduced to the system at regular intervals (50 s). The signal (i.e. change in current density) shows a good linear relationship with respect to the concentration of glucose (Figure 5E), which further confirms the feasibility of employing CBCEs for glucose-sensing applications.

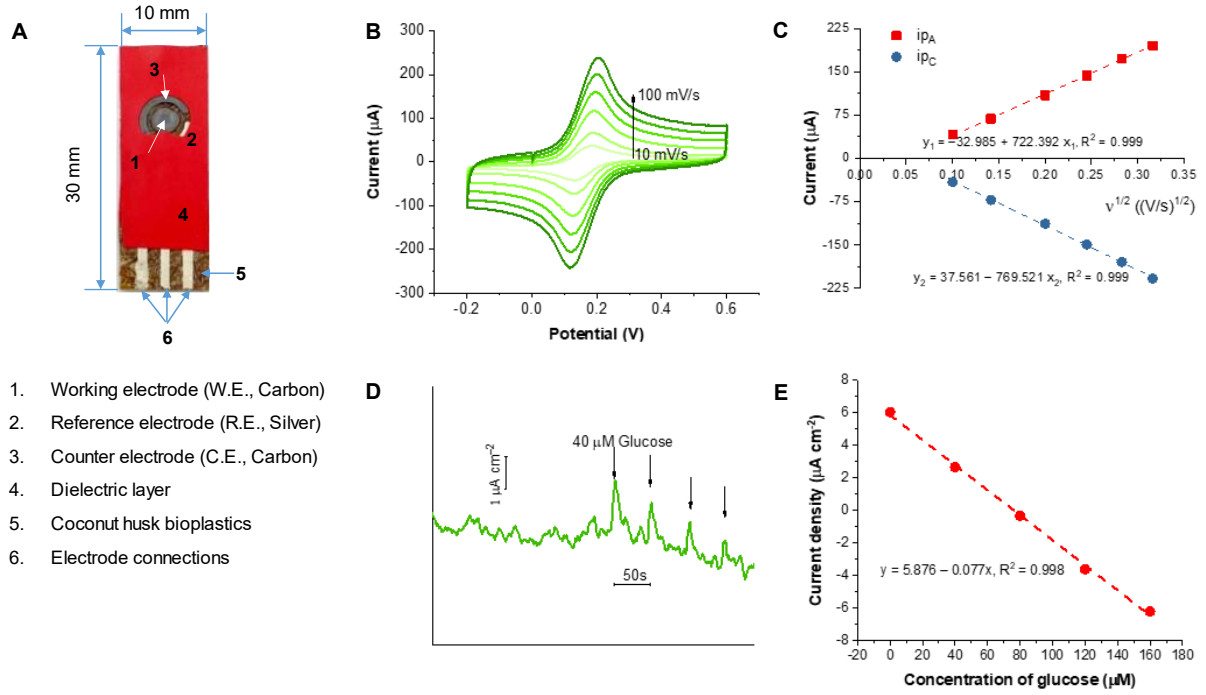

Figure 5. (A) Photoimage of a CBCE with its detailed specification labelled. (B) Typical cyclic voltammograms of the CBCEs in 5×10^{-3} M $K_3Fe(CN)_6$ (prepared in 0.1 M KCl) at a scan rate of 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 V s^{-1} (from inner to outer), respectively. (C) Plots of anodic (red square) and cathodic (blue sphere) peak currents against the square root of scan rate and their respective linear regression results (dot lines). (D) Real time amperometric trace in response to aliquots addition of glucose (2 μL, 1×10^{-3} M) into PBS (0.01 M, 50 μL) at regular intervals. The electrode was polarized at 0.1 V vs Ag/AgCl. (E) Plot of current density against the glucose concentration (sphere) and its linear regression result (dot line).

4. Conclusion

In this project, a high-performance bioplastic based on a food/agri-waste product has been developed via a green and cost-effective approach. Without adding any synthetic resin binder, the coconut husk bioplastics exhibited good mechanical properties, excellent water stability, and improved biodegradability over the untreated raw material. Via optimization of the delignification process, the ideal final lignin content necessary to achieve desirable properties was identified by facilitating interfacial hydrogen bonds and maximizing the integration of cellulose fibers, even under wet conditions. It was also demonstrated that these bioplastics can be used as a substrate for engineering disposable and biodegradable electrochemical biosensors for wearable healthcare devices. The work presented here expands the usage of these

innovative and sustainable approaches (delignification and hot-press) to a wider range of natural materials, and thus opens new opportunities to design novel advanced functional materials from lignocellulose biomass.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table of Contents

Bioplastics derived from waste coconut husks are fabricated via a top-down approach of partial lignin removal and densification. The process improved the mechanical properties via extensive hydrogen bonding. The treated bioplastics are also stable in water and displayed better biodegradability. The bioplastics are demonstrated to be a suitable substrate for glucose biosensor.