The Impact of Chemically-Treated Carbonized Wood Fiber (CWF) in Polyethylene Oxide (PEO)/Chitosan Blend Films

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Abstract. In this study, we investigated the effect of acid/alkaline-treated carbonized wood fiber (CWF) in polyethylene oxide (PEO)/Chitosan (70/30) blend film prepared by solution casting. We investigated the electrical conductivity, crystallinity percentage, crystal orientation, tensile properties, and morphology of the blend films filled with 25 wt% of untreated and acid/alkaline-treated CWF. From the results, the film filled with acid-treated CWF displayed the highest electrical conductivity when compared to the films filled with untreated and alkali-treated CWF. The x-ray diffraction (XRD) diffractograms reveal that the film filled with acid-treated CWF has the lowest crystallinity than the films filled untreated and alkaline-treated CWF. The reduction in d-spacing for the films filled treated CWF suggested improved crystal orientation for the promotion of electron transfer. The tensile properties were not affected much by the incorporation of CWF regardless of untreated or treated filler. The films with treated CWF showed slightly lower tensile strength and modulus but slightly higher elongation at break. The tensile results agree with reduced crystallinity for the blend films with both acid and alkaline treated CWF. The surface morphology of the films investigated by scanning electron microscopy (SEM) also displayed better dispersion of the conducting CWF inside the PEO/Chitosan matrix for the blends with treated CWF. The improved dispersion is due to less blockage with the presence of more amorphous regions. The presence of a broad network bridge smoothens the transfer of electrons and increases electrical conductivity.

1. Introduction
Conductive polymers have experienced tremendous development and turned into interest over the insulating properties because of its suitability with applications. The development of conducting polymers include the blending of two polymers to overcome the drawbacks in individual polymer properties. Blending provides a combination of properties, which is excellent compared to the individual polymers [1]. Mixing of two matrices with different types of polymers mechanically can produce a homogenous blend and increase the electrical conductivity of the polymer film by providing a better platform for electron transfer from the conductive filler. In this study, we opt for PEO as the main matrix because PEO has good film-forming ability [2]. PEO also fully miscible in water, making it low-cost and easy to handle. We can obtain enhanced conductivity in PEO-based films through blending with lower crystallinity polymer such as chitosan. Chitosan can enhance sensitivity and selectivity by changing the chitosan structure and able to transform as a film by the solution casting method as it dissolves in the acidic medium [3]. Chitosan is blended with a synthetic polymer to reduce production
cost and to enhance mechanical properties. Kadir et al. have obtained a homogenous blend from PEO and chitosan [4].

The incorporation of fillers as a conductive carrier within the insulating polymer matrix is identified as extrinsically conducting polymers. In this study, carbonized wood fiber (CWF) was used as a conductive filler. We anticipate that this filler allows the transfer of electrons by forming continuous conductive pathways [5]. Carbonization also increases conductivity performance due to the presence of carbon, which is up to 90% [6]. Chemical treatment is one of the pre-treatments conducted on fibers by using chemical solutions to modify properties. The treatment causes modification in terms of morphology, tensile properties, and also degradation towards thermal. Acidic and alkaline treatment mediums are commonly applied for natural fibers. Modification obtained through alkaline treatments enhances mechanical properties, resistance ability, and also high-quality composite films. Alkaline treatment increases tensile properties and surface roughness due to the removal of lignin, which improves the interaction between fiber and matrix, while acidic treatment modifies morphology and chemical properties [7]. Herein, in this work, we investigated the tensile properties, conductivity, and morphology of the PEO/Chitosan blend films filled CWF treated with two different chemical treatments. We also characterized the blend films by FTIR spectroscopy to elucidate the intermolecular interactions that occurred and the crystallinity of CWF filled blend film using XRD. A two-point probe determined the capability of the blend films to conduct electricity.

2. Methodology

2.1 Reagents
Sigma Aldrich supplied PEO, chitosan, acetic acid, sodium hydroxide, and glycerol as the polymer matrix and additive for a blend film produced by AR Alatan SDN. BHD. Kedah. PolyComposite SDN. BHD. Selangor provided the wood fiber with a size of 199 µm with grade B.

2.2 Preparation of blend films
CWF fillers were treated with acetic acid for acidic medium and sodium hydroxide for alkaline medium at concentrations of 5 wt% for 2 hours at room temperature by stirring. After treatment, treated CWF filtered, washed using distilled water for several times until its pH turns neutral and then kept in oven at 80°C for 24 hours. PEO and chitosan powder dissolved in 0.1 M of acetic acid separately according to their weight ratio. Stir the solution using magnetic stirrer until homogenous. After 8 hours of stirring, the solution of PEO and chitosan were mixed together and allowed to stir for another half an hour at room temperature. After that, 25 wt% of untreated and treated CWF also dissolved in 0.1 M of acetic acid together with 5 drops of glycerol and added to PEO/Chitosan blend and stirred for 1 hour to ensure homogenous mixture is obtained. Lastly, untreated and treated CWF filled PEO/Chitosan blend film were prepared using solution casting and allowed to dry in room temperature to form a film.

2.3 Characterization and Measurements.

Electrical Conductivity with two probe I-V measurement system model Keithley Model 4200 Semiconductor Characterization System. The samples were measured with voltage varied from 0–10 V. The conductivity was calculated using its relationship with resistivity. The resistivity can be calculated using the Equation 1 and 2 below:

\[ \rho = R \left( \frac{w \times t}{l} \right) \]  

\[ \sigma = \frac{1}{\rho} \]  

where; t is the sample thickness, R is the resistance difference in charge between two points and w is the width of the sample and l is the length of the sample.
Fourier Transform Infrared (FTIR) Spectroscopy Test with model Perkin-Elmer Spectrum 400 Series equipment. The thin blend films FTIR resolution of the spectrum and the scanning range of 650-4000 cm⁻¹.

X-Ray Diffraction (XRD) with model Shimadzu XRD-6000 Analyzer. Voltage of 35 kV and 25 mA with CuKa (\(\lambda = 1.5406 \text{ nm}\)) radiation source, in the scale of 10–60° (2\(\theta\)) under scan rate of 10X/°/min were used. Ratio of crystal orientation (Equation 3) was used to describe the X-ray interference by crystals, while the interlayer gap was determined by the diffraction peak using the Law formula of Bragg (Equation 4).

\[
I = \frac{I_2}{I_1} \\
\text{where } I_1 \text{ and } I_2 \text{ is the intensity peak number 1 and 2}
\]

\[
n \lambda = 2d \sin \theta \\
\text{where } d \text{ indicates distance between atoms, } n \text{ shows number of lengthways (n=1), } \lambda \text{ is the wavelength of the incident radiation, and } \theta \text{ is the angle of incidence.}
\]

Tensile Test with model Instron 5567 Universal Testing Machine according to ASTM D882 with crosshead speed was set of 10 mm/min. Blend of rectangular film specimens with dimensions of 100 mm x 15 mm used for analysis.

Scanning Electron Microscope (SEM) with model (JEOL JSM-6460LA). The surface morphologies of the blend film surfaces and filler distribution were studied. Before testing, the films were soaked for 24 hours using toluene at room temperature. The film specimens were coated with palladiums by using to prevent electrostatic charge during testing.

3. Results and Discussions

3.1 Electrical Conductivity

The electrical conductivity of PEO/Chitosan blend film filled with untreated and treated CWF with different treatment are shown in figure 1. Blend film without treatment exhibited insulation properties with conductivity at around 10⁻⁸ S/cm. During both chemicals treatment, CWF filler turned to form amorphous region with reduction O-H groups in the hemicellulose and lignin contents as a resulted the treated CWF filler in the hydrophobicity phase. The conductivity increased to 10⁻⁴ S/cm upon incorporation of treatment alkali and acid on CWF filler. This was due to the formation of a better conducting path in the film by the dispersion of the CWF agglomerates through the blend films. In addition, electron mobility will be easier when there is sufficient space for electrical network via acid compared alkali treatment. Based on XRD analysis, the percentage crystallinity by using chemical acid is lower than alkali. This is successfully achieved through amorphous region as reduced blockages which preventing electron flow network for acid treatment. Sufficient space for flowing of electrons through polymer matrix with the help of conducting filler will provide greater conductivity [17]. Required percolation value will decrease with better dispersion of conducting filler is able to increase conductivity [18]. Free mobility of electrons from conducting filler through matrix efficiently enable to achieve good conductivity according to percolation threshold value [19].

![Figure 1. Electrical conductivity of PEO/Chitosan blend films filled different CWF.](image-url)
3.2 Fourier Transform Infrared (FTIR) Analysis

In figure 2 (a), the spectrum of the untreated CWF filled PEO/Chitosan blend film shows peak characteristic peaks of 3356 cm\(^{-1}\) and 2927 cm\(^{-1}\), which indicates the presence of O-H and C-H stretching vibrations, respectively. Strong O-H stretching vibrations reveal hydroxyl groups which are involved in hydrogen bonds while presence of aliphatic methylene group represents by strong C-H stretching vibration [11]. The spectrum indicates the asymmetric CH\(_2\) of PEO structure range at 3356 cm\(^{-1}\) and 2927 cm\(^{-1}\) absorption. Correspondingly, the peak at 1581 cm\(^{-1}\), due to C-H, CH\(_2\), C-O bending vibrations in cellulose are observed in untreated CWF and it also attributed to C=C sketching vibration from aromatic that indicated CWF contains fatty acids from lignin [12]. The spectroscopy at 796 cm\(^{-1}\) shows the overlapping C-H bending and PEO ether group. The proposed illustration of the mechanism of interaction of PEO/Chitosan/CWF blend film is shown in figure 3.

Figure 2(b) shows that, the sketching vibration of O-H and C-H, respectively reduces in CWF treated with alkali filled PEO/Chitosan blend film [13]. Spectrum of asymmetric CH\(_2\) stretching slightly decreased and shifted to right compared to untreated. New peak formed at 1641 cm\(^{-1}\) and it’s due to the C=O range of the hemicellulose acetyl groups. Intensity of C-H, CH\(_2\), C-O bending vibrations in cellulose and C=C sketching vibration in lignin reduced after treatment and shifted to right. Figure 2(c) demonstrate that intensity of O-H shows minimal stretch in acid treated CWF filled blend film as content of lignin is removed. The sharp peak of C-H bending vibrations in cellulose decreased and shifted to right, while the peak at 1256 cm\(^{-1}\) reflects the lignin stretching C-O-C asymmetric bridge [14]. There is new sharp peak present at 1015.43 cm\(^{-1}\) indicates stretching of C-C bond.

![Figure 2](ftir_spectra.png)  ![Figure 3](interaction_mechanism.png)

3.3 X-ray Diffraction (XRD) Analysis

Figure 4 demonstrates the XRD pattern of PEO/Chitosan blend film filled with untreated and treated CWF with different treatment. Crystalline peaks of untreated CWF slightly moved to right compared to both treated and peak’s intensity also linearly reduced. The crystal orientation ratio, average interparticle spacing and percentage crystallinity values are displayed in table 1. Smaller interparticle spacing provide better dispersion as more amorphous region is available and tendency to agglomerate of CWF will decrease. As d-spacing is decreases, space between filler and matrix will reduces and provide better
interaction as less crystals orientated. Untreated CWF exhibit highest percentage of crystallinity as it cementing materials act as tie to encapsulate all the crystalline elements. Higher crystallinity causes the planes to orientation in more ordered structure, resulting in enhanced strength. Alkaline treatment caused bonding held by hydrogen to decrease by treatment involving extraction of cellulose materials [15]. This modification occurs causes reduction in the intermolecular hydrogen bonds while changing the cellulose morphology. Acetic acid cause esterification reaction to occur, which in result decrease the crystallinity of fiber [16]. Crystallinity is decreasing, as acid able to break hydrogen bonds that enable penetration into crystalline areas of cellulose.

![Figure 4. X-ray diffractograms of PEO/Chitosan blend film filled different CWF.](image)

**Table 1** Crystal orientation ratio, interparticle spacing, and crystallinity percentage of different treatment on PEO/Chitosan blend films filled CWF

| Blend Films             | Intensity (counts) | Interparticle Spacing | Crystallinity (%) |
|-------------------------|--------------------|-----------------------|-------------------|
|                         | $I_1$  | $I_2$  | $I_2/I_1$ | $d$ (nm)     |          |
| PEO/Chitosan/CWF       | 3509   | 730    | 0.21      | 4.4403       | 43.3     |
| PEO/Chitosan/CWF-Alkali| 5064   | 1016   | 0.20      | 3.3556       | 41.5     |
| PEO/Chitosan/CWF-Acid  | 4059   | 873    | 0.22      | 3.3567       | 41.1     |

3.4 Tensile Properties

Figure 5 shows blend films on virgin and different treatment of alkali and acid on CWF filled PEO/Chitosan on tensile properties. Tensile properties influenced by crystalline region of the film due to presence of higher crystallinity. The content of cellulose, hemicellulose and lignin exist in higher amount before treatment process, thus these fiber elements provide rigid structure for the filler [8]. Tensile strength and modulus are higher for virgin CWF due to higher rigidity and both treatment medium the tensile strength and modulus of blend film reduced. When treated CWF were stretched, these amorphous regions resulted in poor sharing of loads and hence increased stress in the fiber. Thus, fiber treated gives lower tensile strength and modulus. Elongation at break of untreated CWF filled blend film is lowest compared to alkali and acid treated CWF. Virgin CWF film shown rigid film due to the presence of higher crystalline phase and it tends to break easily. Crystallinity in chain act as hindrance for turning into compact structure as existed in more ordered structure. Treated CWF are less crystalline blend films, when induced to stress chain form regularity and its structure turn into a compact form and degree of freedom for the molecular chains to move is higher. Amorphous regions provide higher chain mobility and prevent chain slipping [9].
3.5 Surface Morphology

Figure 6 present SEM surface morphology of blend films filled with untreated CWF and treated CWF on PEO/Chitosan blend films. Figure 6 (a) shows the virgin CWF filler is distributed evenly but it also shows rough and agglomeration of filler in the blend film. Homogeneous dispersion was difficult to attain by hydrophilic or polar filler causes of poor adhesion between filler and matrix. The morphology of PEO/Chitosan blend film with treated CWF using alkali and acid are shown in the figure 6 (b) and (c). Both micrograph revealed that less rough surface, less agglomeration of filler morphology with well dispersion and distribution compared to untreated CWF filler. After the treatment, content of lignin and semi-cellulose partially removed [10]. Thus, cellulose content of fiber is exposed more and interact with matrix phase. The irregular structure of filler is found on the surface morphology of blend film indicating transform to amorphous region. This supported result by XRD analysis when percentage crystallinity decrease. Thus, electrical conductivity shows a significant increase with incorporation in treatment medium.

4. Conclusions

Solution casting method were used to produce polyethylene oxide/chitosan with 30/70 filled with 25wt% of treated CWF using different chemical treatment such as acid and alkali medium. The study focused on the effect of different treatment medium on CWF filled blend film on the electrical properties, presence of functional groups, crystal orientation, tensile properties, and morphology. The electrical conductivity test, higher electrical conductivity properties achieved by blend film when CWF-Acid compared with other blend films. Significant removal of hydroxyl group in CWF-Acid filled blend film compared to CWF-Alkali filled film has been proved by FTIR analysis. Next, for XRD analysis, the crystallinity of blend film filled with CWF-Acid shows lowest crystallinity (%) compared to untreated and CWF-Alkali. The tensile properties of the films show that the films filled CWF-Acid have lower tensile strength, tensile modulus and higher elongation at break compared to CWF-Alkali filled film. Lastly, the morphology smooth surface and less agglomeration when incorporation of treatment on CWF filler.
References
[1] Parameswaranpillai I, Thomas S and Grohens Y 2014 Charac. Poly. Blends 13 1-6
[2] Ardeshirzadeh B, Anaraki N A, Irani M, Rad L R and Shamshiri S 2015 Mat. Sci. Eng. 48 384-390
[3] Fernández-de Castro L, Mengibar M, Sánchez Â, Arroyo L, Villarán M C, Diaz de A E and Heras Â 2016 LWT 73 368-374
[4] Kadir M F Z, Aspautz T, Majid S R and Arof A K Spectrochim. A. 2011 78 1068–1074.
[5] Hanif M P M, Rozyanty A R, Kahar A W M, Tan S J and Supri A G 2019 Mat. Today 16 2016--2022
[6] Pusch J and Wohlmann B 2018 Inorg. Com. Fib. 4 31–51
[7] Zawawi I, Mansur A, Astimar A A, Ridzuan R, Kamarudin H and Aisyah H A 2019 J. Adv. Research Fluid Mech. Therm. Sci. 57 57-68
[8] Hajar M D, Supri A G, Hanif M P and Yazid M I 2017 J. Phy. Conf. Series 908 012020
[9] Iqbal M Z, Abdala A A, Mittal V, Seifert S, Herring A M and Liberatore M W 2016 Polymer 98 143–155
[10] Yazid M I, Osman A F, Ghani S A, Leng T P and Din S H 2018 J. Vinyl Add. Tech. 24 21629
[11] Cui Y, Lee S, Noruziaan B, Cheung M and Tao J 2008 Comp. Part A: App. Sci. Manufact.39 655-661
[12] Mwaikambo L Y and Ansell M P 2002 J. App. Poly. Sci. 84 2222–2234
[13] Sawpan M A, Pickering K L and Fernyhough A 2011 Comp. Part A: App. Sci. Manufact. 42 888–895
[14] Kaczmar J W, Pach J and Burgstaller C 2011 Polimery 56 817–822
[15] Benyahia A, Merrouche A, Rokbi M and Kouadri Z 2013 Cong. Francais de Mecan. 26 1–6
[16] Tengku F Z H, Faisal A, Salmah H and Iqmal T 2010 Indo. J. Chem. 2010 10 334 -340
[17] Hashim M Y, Roslan M N, Omar M 2014 Intern. Integ. Eng. Sum. Universiti Tun Hussein Onn Malaysia Johor
[18] Righetti M C, Aliotta L, Mallegni N, Gazzano M, Passaglia, Cinelli P and Lazzer A 2019 Front. Chem. 7 00790
[19] Sari N H, Wardana I N G, Irawan Y S and Siswanto E 2017 Orient. J. Chem. 33 3037-3042