Effect of oxidation agent on wood biomass in ethylene vinyl acetate conductive polymer: tensile properties, tensile fracture surface and electrical properties

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Abstract: The wood fiber (WF) type of Pulverised Wood Filler obtained by combustion process at temperature under 700 °C for 3 hours was characterized and coated with ferric chloride (FeCl₃) by ethanol solution. Both carbonized wood fiber (CWF) and carbonized wood fiber-ferric chloride (CWF-FeCl₃) were used as filler in ethylene vinyl acetate (EVA) conductive polymer. The filler was coated with FeCl₃ to enhance the properties of the CWF to achieve progressive mechanical and electrical properties. The CWF and CWF-FeCl₃ loading were varied from 2.5 to 10.0 wt%. EVA/CWF and EVA/CWF-FeCl₃ conductive polymer were processed by using Brabender Plastoder at 160 °C with 50 rpm rotor speed for 10 min. The mechanical properties were investigated by tensile testing and the tensile fractured surface of conductive polymers was analyzed by scanning electron microscopy (SEM) analysis. Then, the electrical conductivity of conductive polymer was determined by four-point probe I-V measurement system. The EVA/CWF-FeCl₃ conductive polymer showed greater electrical conductivity and tensile strength but lower elongation at break than EVA/CWF conductive polymer. SEM morphology displayed rougher surface between CWF-FeCl₃ and EVA phases compared to EVA/CWF conductive polymer.

1. Introduction
Lately, conductive polymer composite acquired from the addition of various carbon blacks to polymer matrices was reported[1-3]. Polymer electrolytes have drawn attention due to their achievable use as electrolytes in solid-state electrochemical devices, for example like super capacitors, batteries, fuel cells, electrochemical windows, sensors, etc.[4]. The possibility of applying carbon black filled composites in various electronics application as an electrode for electric double layer capacitors also had been previously reported especially particulate fillers of a carbon which are broadly used as in polymer industries[5]. This carbon black are obtained from crude oil hence, is relatively expensive. Therefore, it is important to generate other possible substitute fillers from renewable resources like agricultural wastes.
Rice husks, wood remains, nut shells, manure, and crop residues are regarded as agricultural waste, but recently such solid waste have been transformed into biochar for the purpose of carbon sequestration. In addition, transportation and handling of lignocellulosic wood biomass is often challenging as they have low bulk density, in the range of 200 to 600 kg/m³[6]. Biochar is commonly defined as charred organic matter, produced with the intent of being deliberately added to soil to improve its agronomic properties. On average, one ton of dry biomass can create 400 kg of biochar containing 80 to 90 % pure carbon, reported by Lehmann et. al., at temperature 300 to 700 °C, under low oxygen concentration[7]. The study conducted by Milla et. al. found that SEM-EDX analysis for wood biochar demonstrates high carbon content and a large degree of macro-porosity in the 1 to 10 micron scale, with contents of potassium (K), carbon (C), chlorine (Cl) and calcium (Ca)[8].

The thermoplastic polymer materials currently have been selected as matrices for bio-fibers. The most frequently used thermoplastics polymer in this area are polyethylene (PE), polypropylene (PP), polystyrene, etc.[9]. However, thermoplastic copolymer such as acrylonitrile butadiene styrene (ABS), poly vinyl chloride (PVC), ethylene vinyl acetate (EVA), etc. are used for advanced application because of customizable chemical structure. EVA copolymer is a polymer that has low temperature flexibility, toughness, good adhesion to a wide variety of materials and recognized as ‘rubber-like’ in softness. EVA copolymers are naturally polar due to the presence of vinyl acetate (VA) group which causing the polarity of EVA increases with higher VA content[10]. Moreover, an increase in VA content provides better flexibility and adhesion and low temperature performance, but increase of ethylene content promotes mechanical strength and block resistance[11].

The CWF acted as conductive fillers that provide dramatically increment in electrical conductivity at the very low filler content. Meanwhile, salt is added into solvent such as water to form an electrolyte. Individual atomic components are split by the force applied on the solute to hold ion apart in a chemical dissociation process in which the solution applies force[12]. Ferric chloride (FeCl₃) is a chemical compound at industrial scale with iron in the oxidation state of +3. The advantages of metal salt catalyst are ease of volatilization, availability, non-toxicity, low price, and easy in handling, while hold in combination with the toluene precursor, which is less toxic than benzene[13]. In this research, the compatibility of EVA filled carbonized wood fiber using addition of oxidation agent was studied.

2. Methods

2.1 Materials

EVA grade 2518 CO contains 18.1% of vinyl acetate (VA) pellets with density of 0.94 g/cm³, processing temperature of 160 °C, and melt flow rate of 2.5 g/10 min was supplied by The Polyolefin Company (Singapore) Pte Ltd. The wood fiber with size of 199 μm (average diameter of the filler) and the types of Pulverised Wood Filler with mixed wood grade was obtained from PolyComposite Sdn. Bhd., Selangor. The metallic salt, ferric chloride (FeCl₃) with molar mass of 162.2 g/mol and density of 2.9 g/cm³) and chemical, ethanol (C₂H₅OH with molar mass of 46.07 g/mol and density of 0.79 g/cm³) was brought from AR Alatan Sdn. Bhd., Kedah.

2.2 Preparation of fillers CWF and CWF-FeCl₃

The wood fiber (WF) was ground and sieved using 150 μm and then was carbonizing using a small-scale reactor at 700 °C (3 hours) in a muffle furnace. After that, CWF with diameter size in the range of 41 to 110 μm (average is around 85 μm) were used as conductive filler in compounding A. For compounding B, CWF was coated by using 6% of ferric chloride (FeCl₃) under room temperature. Firstly, the 11 g of FeCl₃ was transferred into 500 ml of ethanol in a beaker. After the mixture was homogenous, the CWF were mixed together by using mechanical stirrer model 5430 with rotor speed of 500 rpm (24 hours). Then, filler was filtered and left to dry in the oven at 50°C (24 hours) to eliminate ethanol residue. After that, the modified CWF- FeCl₃ with diameter size in the range of 45 to 100 μm (average is around 75 μm) were used as filler in conductive polymer. The percentages of atomic mass of both filler are presented in Table 1.
Table 1. Atomic mass (%) from SEM-EDX spectra for CWF and CWF-FeCl₃.

| Element      | CWF     | CWF-FeCl₃ |
|--------------|---------|-----------|
| Carbon (C)   | 74.20   | 79.70     |
| Oxygen (O)   | 23.32   | 18.88     |
| Magnesium (Mg)| 0.55 | 0.26      |
| Silica (S)   | 0.13    | 0.07      |
| Potassium (K)| 0.60    | 0.01      |
| Platinum (Pt)| 1.20    | 0.39      |
| Chloride (Cl)| -       | 0.52      |
| Ferum (Fe)   | -       | 0.18      |

2.3 Conductive polymer composites preparation

The EVA/CWF and EVA/CWF-FeCl₃ conductive polymer with different ratio of filler loadings were carried out by using Brabender Plasticorder and was setup at temperature of 160 °C (rotor speed of 50 rpm). Firstly, the EVA pellet was loaded into the mixing chamber and preheated for 2 minutes. After that, CWF or CWF-FeCl₃ was added into the chamber and mixed for another 8 minutes. The molten conductive polymer was removed from the chamber. Then, to produce the conductive polymer in plate form, the hydraulic hot press machine (GT 7014A) was used. The hot and cool press was set at the temperature of 160 °C and 20°C. 1 mm empty mold was heated for 5 min before used. Then, the conductive polymer were put into the mold, preheated and compressed partially for 10 minutes. Once the conductive polymers started soften, they were fully compressed for 4 min. Finally, the composites were compress for 3 minutes for cooling process. The formulations of EVA/CWF and EVA/CWF-FeCl₃ conductive polymer are shown in Table 2.

Table 2. Formulations of EVA/CWF and EVA/CWF-FeCl₃ conductive polymer composites at different fiber loading.

| Materials | EVA/CWF (wt%) | EVA/CWF-FeCl₃ (wt%) |
|-----------|---------------|---------------------|
| EVA       | 100           | 100                 |
| CWF       | 2.5, 5.0, 7.5, 10 | -                   |
| CWF-FeCl₃ | -             | 2.5, 5.0, 7.5, 10    |

2.4 Characterization and measurements

Tensile properties in which tensile strength and percentage elongation at break were conducted based on ASTM D638 using Universal Testing Machine Instron 5569 at a capacity of the machine was 5kN, crosshead speed 50 mm/min and gauge length 50 mm. An average of five dumbbell shaped type four were used and the shaped specimens were conditioned at room temperature before the testing is conducted. Then, tensile fracture surface of conductive polymer were carried out using a Scanning Electron Microscopy (SEM) model JOEL JSM-6460LA, where, surface of the samples were coated with a thin platinum layer of about 20 µm in thickness using Auto Fine Coater to avoid electrostatic charges during examination. The elemental composition of CWF and CWF-FeCl₃ was determined using an Energy Dispersive X-Ray Spectroscopy (EDX). Similar specimen for microstructural analysis was used for elemental composition analysis. Finally, the electrical properties of conductive polymer were measured using four-probe I-V measurement system model Keithley Model 4200 Semiconductor Characterization System with voltage varied from 0 until 10 V. The resistivity (ρ) and electrical conductivity (σ) can be calculated using the equation 1 and 2 below:

\[ \rho = \left( \frac{\pi}{\ln 2} \right) \left( \frac{V}{I} \right) \]  \hspace{1cm} (1)

\[ \sigma = \frac{1}{\rho} \]  \hspace{1cm} (2)
Where; \( t \) is sample thickness, \( V \) is voltage difference in charge between two points and \( I \) is the rate at which charge is flowing.

3. Results and Discussion

3.1 Tensile properties

Fig 1 presents the effect of CWF loading on the tensile strength of the EVA/CWF and EVA/CWF-FeCl\(_3\) conductive polymer at different fiber loading. The results showed that the tensile strength of the EVA/CWF conductive polymer decreased slightly as the fiber loading increased due to the incompatibility of the CWF in the EVA phases. This incompatibility reduced the tensile strength because fractures were initiated at the weak interface between the composites. It can be seen from Fig 1 that under a similar fiber loading, the EVA/CWF-FeCl\(_3\) conductive polymer had a greater tensile strength than the EVA/CWF conductive polymer. This can be explained that incorporating of FeCl\(_3\) into EVA/CWF conductive polymer had improved the interfacial interaction or van der waal’s forces between CWF and EVA phases. This was due to CWF-FeCl\(_3\) induced carbonyl group of vinyl acetate in EVA to form temporary induced dipole molecules which provide good interfacial interaction between CWF-FeCl\(_3\) and EVA matrix. Hence, good interfacial interaction allows applied load to be transfer from EVA matrix to CWF-FeCl\(_3\) and dissipated throughout the matrix. The morphology of tensile fracture surface by using SEM proved the enhancement in mechanical properties was due to the improvement in the interfacial bonding between CWF and EVA matrix as presented in Figure 3.

![Figure 1](image_url)  
**Figure 1.** Tensile strength vs. conductive filler loading of EVA/CWF-FeCl\(_3\) conductive polymer.

Figure 2 illustrates the effect of CWF loading on elongation at break of EVA/CWF and EVA/CWF-FeCl\(_3\) conductive polymer. Both of the elongation at break of EVA/CWF and EVA/CWF-FeCl\(_3\) conductive polymer decreased with increasing of filler loading. The addition of greater CWF loading into the conductive polymer tended to cause failure to occur earlier than lower CWF loading. This was due to the plasticity of the polymer matrix, which decreased the chain mobility as the conductive polymer become stiffer. Besides that, weaker interfacial region between the EVA copolymer and CWF were formed when CWF loading increased. Thus, cracks could travel more easily through these weak interfacial regions and caused the elongation at break of EVA/CWF conductive polymer to reduce. At the similar CWF loading, the EVA/CWF-FeCl\(_3\) conductive polymer exhibited lower elongation at break compared to EVA/CWF conductive polymer. This was due to good interfacial interaction between the filler and matrix had increased the stiffness of the conductive polymer and thus reduced the elongation at break of the conductive polymer[14].
Figure 2. Elongation at break vs. conductive filler loading of EVA/CWF-FeCl$_3$ conductive polymer.

3.2 Tensile fracture surface

The influence of the CWF loading of EVA/CWF and EVA/CWF-FeCl$_3$ conductive polymer was observed in Fig 3(A)-(G) from the tensile fracture surface of conductive polymer. The micrograph of the tensile fracture surface of EVA is presented in Fig 3(A).

![SEM micrographs of tensile fracture surface of EVA/CWF and EVA/CWF-FeCl$_3$ conductive polymer at different fiber loading](image)

Figure 3. The SEM micrographs of tensile fracture surface of EVA/CWF and EVA/CWF-FeCl$_3$ conductive polymer at different fiber loading.

It can be seen that the micrograph exhibited a smooth surface. As the filler loading increases, the micrographs show weak interfacial adhesion by the presence of voids from the matrix surface. According to Danyadi et. al., the small numbers of holes which related to debonding or fiber pull out
from the matrix indicated weak adhesion between WF and PP matrix\[15\]. It can be seen that, Fig 3(E)-(G) EVA/CWF-FeCl$_3$ conductive polymer indicated that tear line, good interfacial interaction and less pull out of CWF-FeCl$_3$ in the EVA phases compared to Fig 3(B)-(D) EVA/CWF conductive polymer. This was due to the presence of FeCl$_3$, which acted as surface modifier that enhanced the interfacial interaction between the fillers and the matrix. A similar observation was reported by Supri et. al., the addition of benzyl urea in recycled high density polyethylene/natural rubber blend composites showed rough surface and good interfacial adhesion of chicken feather fiber compared to composites without coupling agent\[16\].

3.3 Electrical conductivity

Fig 4 shows the electrical conductivity of EVA/CWF and EVA/CWF-FeCl$_3$ conductive polymer with different filler loadings. It can be observed that the electrical conductivity of both conductive polymers increased when the addition of filler loading increased. This was due to the gap between the conducting particles become closer hence increased the conductivity of the conductive polymer. When filler loading increased, the electrons are able to flow throughout filler and matrix because of CWF which having role as networks for the electron to flow. Das et al., reported that the addition of more polyaniline/dodecylbenzene sulfonic acid (PAni/DBSA) in EVA matrix contributed to the increasing of conductivity\[17\]. However, at lower content of conductive fillers, the distance of conductive fillers particles is very broad, and the conducting pathways are discontinuous within EVA matrix which may bring to low conductivity. Low amount of conductive filler dispersed to homogeneous matrix would not enhance the conductivity until the conductive films was highly loaded with CWF so that the aggregates would be interacted with each other. For EVA/CWF-FeCl$_3$ conductive polymer, the principle of electric conduction occurred when the incorporation of FeCl$_3$ as oxidation agent filler that will be coated onto CWF. This was due to the metal iron particles allowed the ease of electron transfer via conduction. The FeCl$_3$ acts as a medium to transfer the electron in conductive polymer composite due to their formation. Supported research by Suherman et al. stated that the effect of graphite loading on the conductivity of graphite/epoxy nanocomposites will increase the electrical conductivity\[18\].

![Figure 4. Electrical conductivity vs. conductive filler loading of EVA/CWF-FeCl$_3$ conductive polymer.](image)

4. Conclusion

The results show an increment in tensile strength but decrement in ductility of EVA/CWF-FeCl$_3$ conductive polymer in comparison with EVA/CWF conductive polymer. The tensile fracture studies
proved better filler distribution on the surface of EVA/CWF-FeCl$_3$ conductive polymer when compared to EVA/CWF conductive polymer. However, the electrical conductivity increased progressively with the addition of FeCl$_3$ in EVA/CWF-FeCl$_3$ conductive polymer than the electrical conductivity in EVA/CWF conductive polymer.

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6. References
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