

Entylene Vinyl Acetate/Carbonized Wood Fiber Composites: The Effect of Zinc Chloride Content on Tensile Properties, Electrical Properties and Thermal Degradation

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Abstract. Challenges faced to develop conductive composites comprised of poor electro-active stability, control of the mobility, mechanical properties, presentation and concentration of bioactive molecules. Carbonized wood fiber (CWF) was successfully produced from waste wood fiber by using conventional furnace machine at 700 °C in air atmosphere for 4 hours. While, CWF coated ZnCl₂ was carried out surface modification process via ethanol solution. In this study, the effect of different ZnCl₂ content coating CWF with the fixed CWF filler and ethylene vinyl acetate (EVA) composites was studied. The samples were prepared by using Brabender Plasticoder at 160 °C and 50 rpm rotor speed. The result indicated that increasing ZnCl₂ content showed tensile strength, tensile modulus, electrical conductivity, and thermal stability compared to unmodified composites.

1. Introduction

Ethylene vinyl acetate (EVA) copolymer is an insulating material and converting it to conductive material is quite challenging. Nowadays, researcher proved that EVA material properties change when combine to another conductive filler into composites. According to Asakura et al., [1] had prepared the modelling of dielectric properties for EVA/polyaniline (PAni) composites. They found that increased of filler content will increase the electrical conductivity. The use of filler in composites creates new materials simply known as polymer composites. Though, the practice of using synthetic fibers as reinforcement filler initiated health problems issues to the manufacturers and the consumers such as skin irritations and lung cancer due to the content of hazardous ingredients [2, 3]. Hence, many researchers start to explore new alternative reinforcing filler using natural fibers due to the abundance of natural fibers and ease of processability. The use of natural fibers as reinforcing filler in thermoplastic composites offers significant disposability and positive environmental benefits. The



major advantages of natural fibers over synthetic fibers include biodegradability, recyclability, lower specific weight, high specific strength and stiffness, good thermal properties, non-corrosive nature, and lower in cost [4-6].

Converting natural fiber to carbon, carbonization is a particular form of that process in chemical technology called pyrolysis that is the breakdown of complex substances into simpler ones by heating. Khalil et al.,[7] derived from bamboo stem (BS), coconut shells (CNS) and oil palm empty fiber bunch (EFB) were obtained by pyrolysis of fiber at 700 °C to produce carbon black (CB). Generally, wood fibers are hydrophilic in nature whereas synthetic polymers are hydrophobic. The hydrophilic characteristics also known as polar molecule of natural fibers leads to a high moisture absorption, causing dimensional change in the fiber and resulting in the swelling of manufactured composites [8]. This is because water is also a polar covalent molecule, which means it has oppositely charged regions. The oppositely charged regions of the water molecule and the hydrophilic polar molecule are able to attract one another, which is why hydrophilic molecules are generally soluble in water.

Many study involving carbonized wood fiber (CWF) composites have been largely performed by researchers. While, different waste wood, method, temperature, time produces different yields and characteristics of products. Furthermore, this will affected their application at end product. Generally, some researcher aims to focus on chemical properties of elemental analysis percentages after carbonation process. The average weight percentages of the chemical elements forming wood material are about 50 wt% of carbon (C), 43 wt% of oxygen (O), 6 wt% of hydrogen (H), and 1 wt% of nitrogen (N)[9]. Furthermore, Tillman[10] has been reported that hardwood species or grade A, average C content around 47-50 wt%, and for softwood species or grade C, around 50-53 wt%, due to the varying lignin and extractives content. All wood species contain about 6 wt% of H content. The O content ranges from 40-44 wt%, sulphur (S) is less than 0.1 wt% and N ranges from 0.1-0.2 wt%.

Works concerning about the use of different modification content to improve the compatibility between fibers and matrices have been revealed. Zinc chloride ($ZnCl_2$) was used, because zinc has the tendency to donate an electron higher than iron in electrochemical series. Advantages of metal salt catalyst such as ease of volatilization, availability, non-toxicity, low price, and easy in handling, even hold in combination with the toluene precursor, which is less toxic than benzene[11]. In this research, the compatibility of EVA filled CWF using different content of $ZnCl_2$ as a surface modification agent was studied.

2. Experimental

2.1. Materials

The EVA grade 2518 CO with contains 18.1% of vinyl acetate (VA) was supplied by The Polyolefin Company (Singapore) Pte Ltd. The waste wood fiber types of Pulverised Wood Filler with mixed wood grade was obtained from PolyComposite Sdn. Bhd. Kajang, Selangor. Besides that, zinc chloride ($ZnCl_2$) and ethanol were supplied from AR Alatan Sdn. Bhd. Alor Setar, Kedah.

2.2. Methodology

CWF was pyrolyzed using a small-scale reactor at 700 °C with a residence time of 3 hours in a muffle furnace by using conventional heating machine with air comprise. Then, CWF filler was modified with different content of $ZnCl_2$ in ethonal solution under room temperature. The CWF was mixed with $ZnCl_2$ by using mechanical stirred model 5430 with rotor speed of 500 rpm for 24 hours. Then, CWF_{ZnCl₂} filler was filtered and left to dry in the oven at 50°C for 24 hours to evaporate ethanol residue. The modified CWF_{ZnCl₂} were used as filler in EVA composites. The EVA/CWF_{ZnCl₂} composites with different content of $ZnCl_2$ were blended by using Brabender Plasticorder at temperature of 160 °C and rotor speed of 50 rpm for 10 minutes, respectively. Then, the hydraulic hot press machine (GT 7014A) was used form plate shape with a thickness of 1 mm. The formulations of EVA/CWF_{ZnCl₂} composites are shown in Table 1. Table 2 show mass percentages of CWF and CWF_{ZnCl₂} fillers by using energy dispersive X-ray (EDX) spectroscopy analysis.

Table 1 Formulations of EVA/CWF_{ZnCl₂} composites at different ZnCl₂ content.

Materials	Ratio
EVA (phr)	100
CWF (phr)	10
ZnCl ₂ (wt%)	0~8

Table 2 Mass percentages from EDX spectra.

Element	Mass (%)	
	CWF	CWF _{ZnCl₂}
Carbon (C)	90.66	89.32
Oxygen (O)	9.34	8.20
Chloride (Cl)	-	1.54
Zinc (Zn)	-	0.92

2.3. Characteristic

Tensile properties in which tensile strength and tensile modulus were tested based on ASTM D638 standard by using Universal Testing Machine Instron 5569 with a capacity of the 5 kN, crosshead speed 50 mm/min and gauge length of 50 mm. Electrical properties of conductive polymer were measured by four-probe measurement system model Keithley Model 4200 Semiconductor Characterization System with voltage varied from 0~10 V. The resistivity (ρ) and electrical conductivity (σ) calculated by using equation 1 and 2;

$$\rho = \left(\frac{\pi}{\ln 2} \right) t \left(\frac{V}{I} \right) \quad (1)$$

$$\sigma = \frac{1}{\rho} \quad (2)$$

where; t is sample thickness, V is voltage difference in charge between two points and I is the rate at which charge is flowing. Thermal degradation analysis was carried out by using a Perkin Elmer Pyris TGA 7 thermogravimetric analyzer (TGA) according to ASTM D3850-2000. Samples of about 10 mg were decomposed from 30~900 °C with a heating rate of 10 °C/min and 50 ml/min of nitrogen gas flow to prevent thermal oxidation process of sample.

3. Results and Discussion

3.1. Tensile Properties

Fig. 1 presents the effect of ZnCl₂ content on a tensile strength of EVA/CWF_{ZnCl₂} composites. The tensile strength increased as the ZnCl₂ content increased on EVA/CWF_{ZnCl₂} composites. During surface modification of CWF, particle size of CWF particle found to reduce compared to unmodified CWF and this was due to corrosion of ZnCl₂ on the surface of CWF filler. When the particle size of CWF was decreased, and the specific surface areas increased during chemical modification. However, this chemical modification affected the chemical bonding between EVA and CWF_{ZnCl₂} and their dispersion in the EVA matrix during compounding. These chemical bonding caused the an improvement of the interfacial interaction of filler and matrix[12]. Good interface interaction between CWF_{ZnCl₂} particles and EVA copolymer help to transfer stress from the matrix to filler, which contributed to the higher tensile strength of the composites. When content of ZnCl₂ up to 8 wt%, CWF_{ZnCl₂} particles tended to agglomerate and lead to poor distribution of CWF_{ZnCl₂} in EVA matrix and weak interface interaction between CWF_{ZnCl₂} filler and EVA matrix. Thereby, the tensile strength of CWF_{ZnCl₂} filled EVA composites decreased as the CWF_{ZnCl₂} increased up to 8 wt%[13]. This phenomenon is further explained by the nature characteristics of CWF, which are easily agglomerated in its primary and secondary structure, which has led to poor dispersion and distribution into the polymer matrix [14].

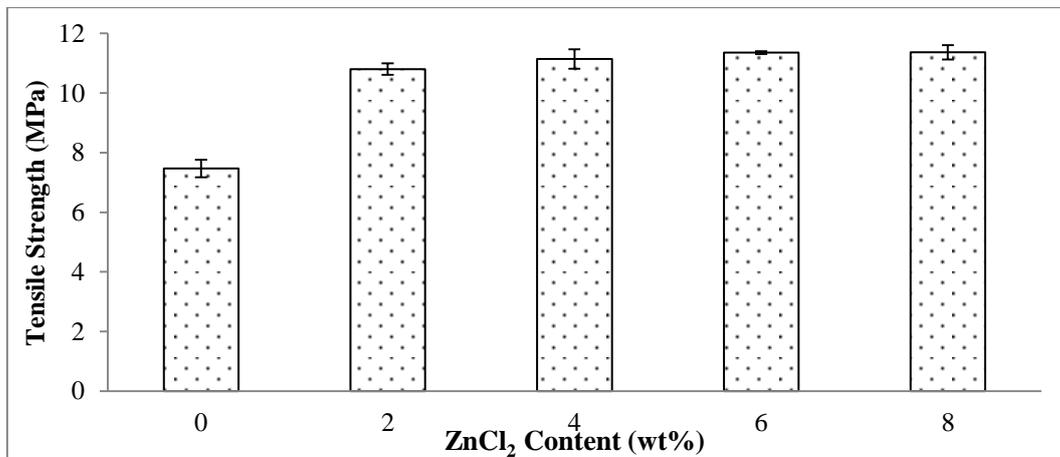


Fig. 1 Effect of ZnCl₂ content on tensile strength of EVA/CWF_{ZnCl₂} composites.

Fig. 2 shows the effect ZnCl₂ content on a tensile modulus EVA/CWF_{ZnCl₂} composites. The increment in tensile modulus with respect to ZnCl₂ content was due to the incorporation of rigid ZnCl₂ particle into the composites and hence imparted greater stiffness to the EVA/CWF_{ZnCl₂} composites[15]. This was due to the stiffening effect caused by the good interaction between the ZnCl₂ coated CWF and the EVA matrix thus improved the stiffness of the composites. Besides, the polymer chain mobility was restricted by the addition of ZnCl₂ resulted from the improvement in rigidity of the composites[16]. It is suggested that the percolated network of CWF can help to improve the tensile modulus in the ternary composites and to stabilize the improvement with the introduction of ZnCl₂[17].

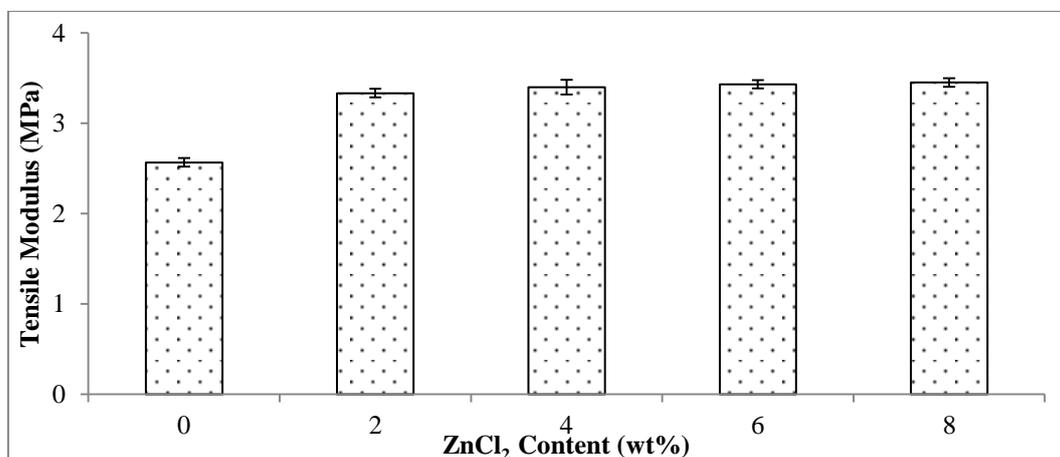


Fig. 2 Effect of ZnCl₂ content on tensile modulus of EVA/CWF_{ZnCl₂} composites.

3.2. Electrical conductivity

The electrical conductivity of EVA/CWF composites at with different content of ZnCl₂ is shown in Fig. 3. The electrical conductivity of composites are increased with increasing of ZnCl₂ content. At low ZnCl₂ content, the electrical conductivity of the EVA/CWF_{ZnCl₂} composites is slightly higher than that EVA/CWF composites due to the CWF coated ZnCl₂ particles are isolated from each other by the insulating matrix. As the content of CWF_{ZnCl₂} into EVA matrix increased, the CWF_{ZnCl₂} particles begin to contact with each other, and a continuous conductive pathway is formed throughout the entire volume of the composites which allowed the electron to travel. Furthermore, introduced ZnCl₂ into CWF filler through surface modification caused particle size of filler reduced. Thus, reduction particle

size will increase the surface area of filler in matrix and electron can easily jump from one orbital to another orbital[18].

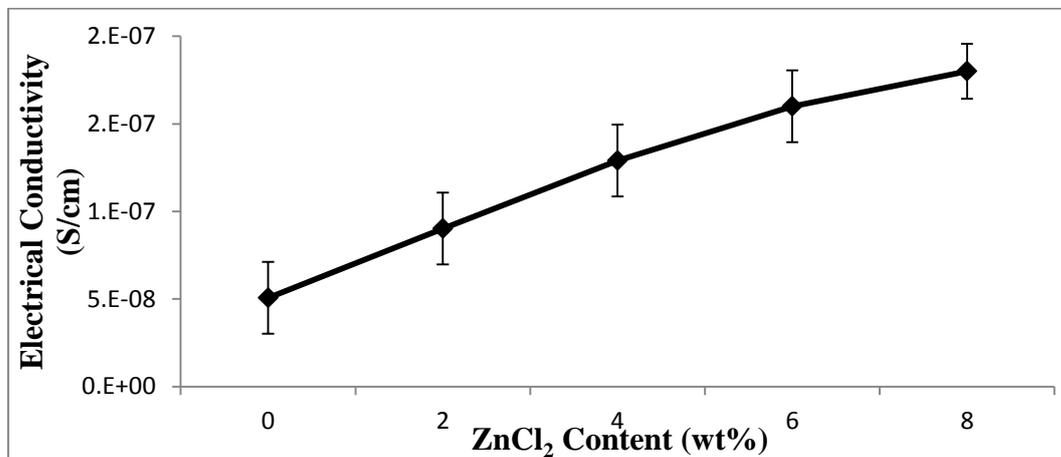


Fig. 3 Effect of ZnCl₂ content on electrical conductivity of EVA/CWF_{ZnCl₂} composites.

3.3. Thermal degradation

The thermogram analysis (TGA) and differential thermogravimetric (DTG) curve of selected EVA/CWF_{ZnCl₂} composites at different content of ZnCl₂ are presented in Fig. 4, meanwhile Table 3 recorded the initial decomposition temperature (IDT), final decomposition temperature ($T_{\text{Max}\%wt}$) and residual mass of the composites. Addition of various ZnCl₂ content demonstrated weight loss through two-stage decomposition process at temperature around 315 to 390 °C and main stage decomposition at temperature 410 to 500 °C due to EVA phase and similar to demonstrated weight loss EVA/CWF composites. The IDT reduced with incorporation ZnCl₂ content and similar decrement with thermal stability at $T_{\text{Max}\%wt}$ and residual mass compared to without surface modification. This was due to different particle size of CWF and CWF_{ZnCl₂} filler[19]. With a smaller particle size, the CWF_{ZnCl₂} fillers were well distributed and dispersed within the EVA matrix, this will form a good interfacial bonding between the filler and matrix. The CWF_{ZnCl₂} fillers with the high aspect ratio increased the surface contact area and formed good interfacial bonding with the matrix [20].

Work by Yue[21] reported that weight loss of pure ZnCl₂ started at about 400 °C and had a maximum weight loss rate at 587 °C with a heating rate of 30 °C/min in N₂. Based on Table 3, increasing content of ZnCl₂ into EVA/CWF_{ZnCl₂} composites, the IDT, $T_{\text{Max}\%wt}$ and residual mass increased compared to unmodified composites. These results suggested that additions of ZnCl₂ contents will improve the thermal stability and residual mass of the EVA/CWF_{ZnCl₂} composites because ZnCl₂ acts as a dehydrating agent, eliminating water and inducing the aromatization of carbon[21]. This higher thermal stability of polyacrylonitrile (PAN) owing to the metal powder of ZnCl₂ will affect the physical bonding which enhanced the interaction between filler to the matrix, thus created a barrier that slowed down the volatilization of the EVA/CWF_{ZnCl₂} composites during thermal decomposition process[13]. Supported by Rusu[22], vicat softening temperature increases with the increase zinc powder content in high density polyethylene (HDPE) composites.

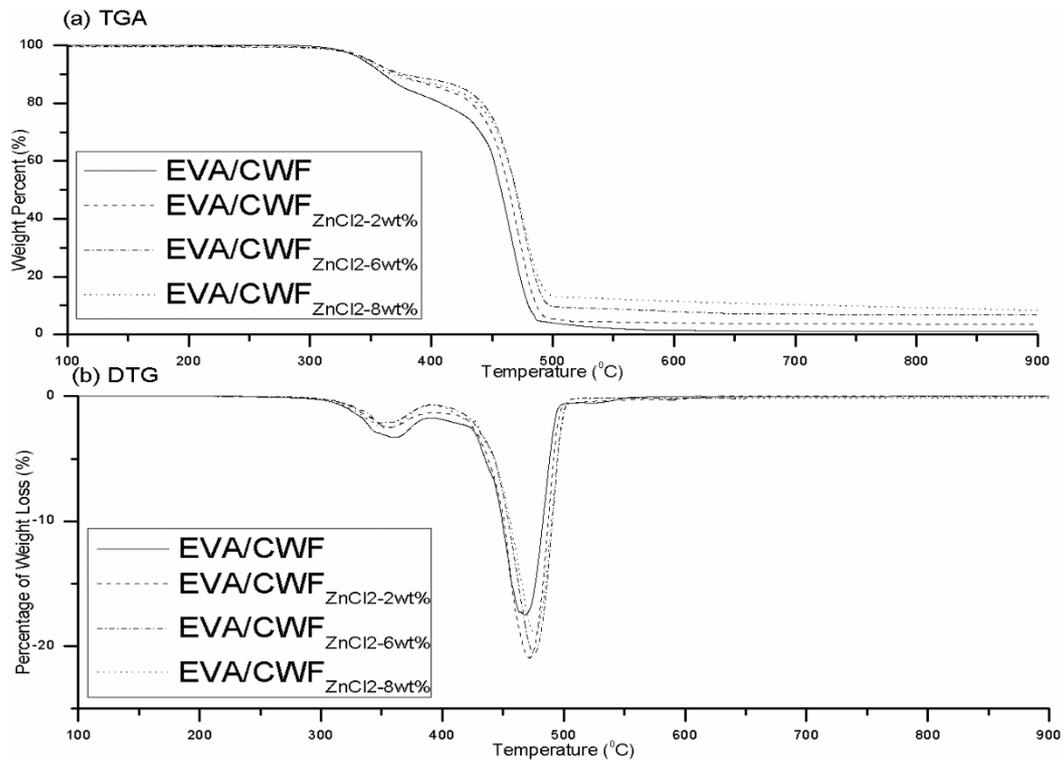


Fig. 4 Effect of ZnCl₂ content on Thermogravimetric of EVA/CWF_{ZnCl₂} composites.

Table 3 Data of IDT, T_{-Max%wt} and residual mass of EVA/CWF_{ZnCl₂} composites at different ZnCl₂ content.

Composite Codes	IDT (°C)	T _{-Max%wt} (°C)	Residual mass (%)
EVA/CWF	348.12	475.59	4.55
EVA/CWF _{ZnCl₂-2wt%}	346.18	474.75	3.53
EVA/CWF _{ZnCl₂-6wt%}	346.81	475.13	4.15
EVA/CWF _{ZnCl₂-8wt%}	347.14	476.61	4.34

4. Conclusion

The effect of ZnCl₂ content as surface modifier in terms of mechanical, electrical, and thermal properties at 10 phr of filler loading coated ZnCl₂ at different contents was investigated. The incorporation of CWF coated with ZnCl₂ in EVA matrix increased tensile strength, tensile modulus, electrical conductivity, thermal stability, and residual mass of the composites. The percolation threshold was achieved at 6 wt% of CWF_{ZnCl₂} in EVA composites showed improvement in conductivity range from the insulator to semi-conductor properties.

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