Effect of Uncarbonized and Carbonized Eggshell Powder on Mechanical and Thermal Properties of Recycled High Density Polyethylene/ Ethylene Vinyl Acetate Blend Composites

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Abstract. The blend composites of recycled high density polyethylene (rHDPE)/ethylene vinyl acetate (EVA) were prepared by melt blending technique at 160 °C with rotor speed of 50 rpm within 10 minutes. Based on Fatimah et al. study[1], the optimum ratio rHDPE/EVA at 70/30 were studied and prepared for different loading of uncarbonized (fresh) and carbonized eggshell powder (5 to 25 wt%). The ESP was collected, washed, crushed, and sieved to obtain size 63 μm by method Farahana et al.,[2]. But she found that, the mechanical properties reduced with incorporation of ESP filler. Nowadays, carbonized natural filler are the focus of some researchers and the CESP was undergoing a combustion process for 3 hours at 700 °C with air combustion via muffle furnace. The result showed tensile properties decreased with increasing filler loading for both fillers. Then, the mass swell percentage after 46 hours soaked in dichloromethane, the results showed an increment of both fillers were increased the mass swell caused by the hydrophilic nature of fillers. The intensity ratio, interlayer spacing, and crystallinity percentage value decrease with increasing filler loading for both filler give better interaction between matrix and filler. The thermal stability increase for both filler with increasing filler loading. Overall, rHDPE/EVA/CESP blend composites had excellent properties with the addition of carbonized filler.

1. Introduction
Composite materials are known as the combination of two or more constituent materials to form a new polymer with better properties [3,13]. Over the last decades, polymer have replaced numerous conventional materials such as wood and metal in various appliance due to their unique properties such good mechanical properties, thermal stability, low cost. These properties make polymer become highly demanded in industry.

High density polyethylene HDPE is one of the most manufactured plastic throughout the world having excellent properties as regular chain structure, low energy demand on processing, low cost and good mechanical properties [4]. HDPE is stronger and harder than any typical standard polyethylene that make it suitable to be used in packaging and manufacturing industries because it had good barrier properties and also better rigid characteristics than low density polyethylene (LDPE) [5]. Other than
that, the addition of stiff and strong reinforcements, referred to micron-sized fillers into the HDPE polymer may produce polymer composites with enhanced mechanical properties [6,7].

Ethylene vinyl acetate (EVA) is a random copolymer that consists of partially crystalline polyethylene blocks and recognize as ‘rubber-like’ in softness, which makes it suitable for inorganic filler polymer. In addition, EVA is polar in nature as the vinyl acetate (VA) group and polarity of EVA increases with increase in VA content [8]. Good transparency and good flexibility can be obtained as the VA content increases in EVA. In that case, different properties of EVA can be produced. Polymerizing VA with ethylene will change the state of EVA to amorphous material as the disruption in the crystal structures occurs in polyethylene [9]. EVA exhibits potential polymer for blending with PE to improve toughness, flexibility and transparency of the PE properties [10].

The addition of carbonized ESP (CESP) as a filler into the rHDPE/EVA blend composites can give good mechanical properties and good thermal properties. Also, it is suitable for the production of insulator products.

2. Methodology

2.1. Material

rHDPE with a density of 0.94–0.97 g/cm³ has melting temperature at 120–150 °C and the value of shrinkage and absorption percentage is 1.7 and 0.01 % respectively. EVA with 18.1 % of vinyl acetate (VA) copolymer had a density of 0.92–0.95 g/cm³ and a melting temperature of 80–120 °C. The value of shrinkage and water absorption percentage of EVA is 1.55 and 0.013 %, respectively. The rHDPE was purchased from Zarm Scientific & Supplies Sdn. Bhd., Pulau Pinang, while EVA was purchased from AR Alatan Sdn. Bhd., Kedah. ESP was used as reinforcement filler in the rHDPE/EVA matrix and were obtained from local food industry in Perlis. The chemical was used for testing mass swell is dichloromethane with density is 46.07 g/mol and were purchased from AR Alatan Sdn. Bhd., Kedah.

2.2. Preparation of ESP and CESP

The eggshell was washed cleanly before crushed into small pieces. They were dried in the oven at 80 °C in conventional oven until the weight is constant to evaporate all water as to make it free from moisture. The dried eggshells were grinded into a powder form using planetary ball mills and kitchen blender. The planetary ball mill was set at 300 rpm for 60 minutes. In order to obtain filler sizes of 63 μm, the sieve was used to remove coarse particle of the powder. Next, the CESP were prepared using a combustion process using a muffle furnace. The size of CESP after sieve was 63 μm, then the filler was calcined in muffle furnace at 700 °C for about 3 hours [11]. Both ESP and CESP were used as a fillers in rHDPE and EVA components and the formulations are shown in table 1.

Table 1. Formulation of rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading

| Composite Code | rHDPE | EVA | ESP (g) | CESP (g) |
|----------------|--------|-----|--------|---------|
| rHDPE/EVA      | 70     | 30  | -      | -       |
| rHDPE/EVA/ESP  | 70     | 30  | 5–25   | -       |
| rHDPE/EVA/CESP | 70     | 30  | -      | 5–25    |

2.3. Preparation of composites

Preparation of blend composites was carried out by melt blending technique in brabender plasticoder at temperature of 160 °C with rotor speed of 50 rpm within 10 minutes. The rHDPE pellets were first loaded into the chamber of the mixer and preheated for 2 minutes. Then, EVA pallets were added into the chamber of the mixer to be mixed with melted rHDPE for another 5 minutes until rHDPE/EVA homogeneously blended together. In contrast, rHDPE/EVA/ESP and rHDPE/EVA/CESP, the filler were added into the blend after 7 minutes of mixing and left to be mixed for 3 minutes. Then, the
blend composites will be put into compression machine with 7 minutes preheat, 3 minutes hot compress, and 5 minutes cool press.

2.4. Testing and characterization
Tensile properties were determined according to ASTM D638 by using the Instron 5569 with a cross-head speed for 50 mm/min. Five dumb-bell shaped samples were used and the mean values of tensile strength, modulus of elasticity, and elongation at break of each composite were obtained from the test. The mass swell test was carried out according to ASTM D543 with dimension 20×10×1 mm for each composite composition. The samples were fully immersed into the test tube containing dichloromethane for 46 hours. After the immersion period, the samples were removed from the test tubes and blotted with tissue paper before weighing by using an analytical balance with 0.1 mg resolution. The percentage mass swell (the weight increase) was calculated as follows:

\[
\text{Mass Swell} = \frac{W_2 - W_1 \times 100}{W_1} \quad (1)
\]

Thermal stability of the composites was investigated by thermogravimetric analysis (TGA) by using a Perkin Elmer Pyris TGA7 instrument from 50~650 °C at a programmed heating rate of 10 °C/min in nitrogen. A sample weight of approximately ±10 mg was taken for all the measurements. The weight loss against temperature was recorded.

The interlayer spacing of the filler was determined by using a Shimadzu XRD-6000 Analyzer at an acceleration voltage of 35 kV and 25 mA with CuKα (λ= 0.15406 nm) radiation source. The scans were carried out in the range of 10~80° (2θ). This analysis was performed at ambient temperature with scan speed of 10 °C/min. The crystal orientation ratio equation (Equation 2) was used for the first time to explain the X-ray interference through crystals and also to study the structures of different materials, while the interlayer distance was determined by the diffraction peak, using Bragg’s Law equation (Equation 3).

\[
I = \frac{I_2}{I_1}; \quad (2)
\]

where is the intensity ratios I of these two peak are identified as crystallization degree of the orientation of the crystal paleness, I2 is the intensity peak number 2, and I1 is the intensity peak number 1.

\[
n\lambda = 2d \sin \theta \quad (3)
\]

where d is the distance between atoms, n is the number of lengthways (n=1), λ is the wavelength of the incident radiation, and θ is the incidence angle.

3. Results and Discussion

3.1. Tensile Properties
Tensile properties of rHDPE/EVA, rHDPE/EVA/ESP and rHDPE/EVA/CESP blend composites which is tensile strength, tensile modulus and elongation at break are shown in figure 1. From figure 1 (a) indicate that the addition of ESP and CESP filler decreased the tensile strength in the rHDPE/EVA blend composites same result reported by [3]. This was due to the poor distribution and low interaction of filler within the matrix. The increased in filler concentration impeded good stress transfer between the matrix and the reinforcement filler when external stress applied. A superior property was recorded while testing rHDPE/EVA reinforced with CESP filler this is due to the removal of spongy portion and subsequent elimination of volatile matters during carbonization [12]. Moreover, the large particle of
ESP filler and the presence of organic content become lower tensile strength of the blend composites [14].

Meanwhile, the effect of filler loading on tensile modulus of rHDPE/EVA/ESP and rHDPE/EVA/CESP composites shown that the tensile modulus has increased for both series of composites when the amount of filler is increased. The increased of tensile modulus with incorporation of both filler was predicted due to the presence of small and rigid filler particles gave better reinforcement structure in composites which can improve the stiffness and reduced the ductility of the blend composites. Similar reported with incorporation of basalt fiber by Wu et al.,[15] and sisal fiber by Zhao et al.,[16] Based on result tensile modulus, CESP had higher compared to ESP filler. Means that CESP filler more wetting filler would increase the contact area between rHDPE/EVA at the interface, reduced the void, and offered a better stress transfer within the composites which increased the stiffness of the composites hence improved their tensile modulus.

The elongation at break decreased for both compositions as the filler loading is increased but at the same time the CESP had higher value than ESP filler. Based on studied by [19], the decrement of elongation at break at higher filler loading could be attributed to the poor interfacial adhesion between the rHDPE/EVA matrix and filler. Increased in the amount of filler would increase the rigidity of whole composites which causing reduction in toughness and ductility of the blend composites. The flexibility of the composites had been restrained by the incorporation of ESP or CESP filler and the early deformation of filler forced the matrix to deform more than the overall deformation of the blend composites, hence decreased the elongation at break value. The rHDPE/EVA/CESP composites have better filler particle dispersion and tend to form smaller agglomerates than the rHDPE/EVA/ESP composites. This is because any separation in the ESP filler as a result of loose particles is removed when carbonizing the ESP to obtain carbonized particles [19].

![Figure 1](image)

(a) Tensile strength  (b) Tensile modulus  (c) Elongation at break

**Figure 1.** Tensile properties for rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading

### 3.2. Swelling Behaviour

Figure 2 presents the percentage mass swell of rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading after submersion in dichloromethane at the room temperature for 46 hours. Based on the observation, by additional of ESP and CESP filler in the rHDPE/EVA blends shows the increasing in number of the mass swell percentage for both blend composites. This can be described by relating to the hydrophilic nature of filler which tended to absorb the dichloromethane after certain exposure time. CESP filled rHDPE/EVA blend composites is less absorption compared to ESP filler. The decreased percentage mass swell may be due to the promoted dispersion of the CESP filler particles in the rHDPE/EVA matrix due to greater reinforcement effect that may cause higher resistance to the chemical absorption by the composites, besides the almost non-diffusivity properties of CESP. Similar observations have been reported by other researchers [20].
3.3. Thermal Analysis

The data of temperature of 50% weight loss ($T_{50\%}$wt) and residual mass for the rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading are listed in table 2. According to table 2, incorporation of filler in net rHDPE/EVA blend composites were improve the thermal stability due to ESP or CESP filler decomposed in the early stage and produced ash that would absorb heat generated during degradation thereby delayed the thermal degradation process of polymer matrix [17,21]. The increased of filler loading for both filler had increased the thermal stability due to the degradation of ESP or CESP filler constructed barrier to the gas exhausted from the rHDPE/EVA matrix through heating, thus thermal stability of the blend composites. Besides that, it was evidenced that the residual mass of each blend composite showed an ascending trend with addition of filler in the blend composites. Thus, CESP filler is more thermal stability than ESP filler due to carbonization process of CESP filler, where contain of CESP filler is content of carbon or ash and this filler were withstand with high temperatures.

Table 2. Temperature of 50% weight loss and residual mass for rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading

| Composite Code   | $T_{50\%}$wt (°C) | Residual Mass (%wt) |
|------------------|--------------------|---------------------|
| rHDPE/EVA        | 442.44             | 4.67                |
| rHDPE/EVA/ESP-5  | 446.73             | 1.04                |
| rHDPE/EVA/ESP-20 | 452.76             | 5.63                |
| rHDPE/EVA/CESP-5 | 452.83             | 1.13                |
| rHDPE/EVA/CESP-20| 462.67             | 6.06                |

3.4. X-ray Diffraction (XRD)

Table 3 shows XRD diffractograms of rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading. From the data of table 3 shows that the crystal orientation ratio and d-spacing increased and crystallinity percentage reduced with incorporation of filler compared to net rHDPE/EVA blend composites. This indicating that the higher crystallization structure due to the presence of crystalline ethylene group in rHDPE and EVA matrix. Further with addition of both filler, the result exhibited decreasing value. This was due to the addition of filler hindered the ordered arrangement of crystalline phase for ethylene of rHDPE and EVA matrix resulted in lower crystallinity...
of rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites [22]. While CESP filler showed lower the crystal orientation ratio, d-spacing and crystallinity percentage than ESP filler. This was due to content of CESP filler are carbon or ash and shown less agglomeration between filler-filler and give good distribution of filler in rHDPE/EVA blend composite.

Table 3. Data of intensity ratio, interlayer spacing, and crystallinity percentage for rHDPE/EVA, rHDPE/EVA/ESP, and rHDPE/EVA/CESP blend composites with different filler loading

| Composite Code            | Intensity (counts) | d spacing (nm) | C (%) |
|---------------------------|--------------------|----------------|-------|
| rHDPE/EVA                 | 12732              | 3736           | 0.2934| 3.94  | 83.8 |
| rHDPE/EVA/ESP-5           | 10799              | 3453           | 0.3197| 5.56  | 74.7 |
| rHDPE/EVA/ESP-20          | 6307               | 1840           | 0.2917| 4.96  | 72.2 |
| rHDPE/EVA/CESP-5          | 9557               | 2811           | 0.2941| 5.12  | 66.8 |
| rHDPE/EVA/CESP-20         | 4581               | 1280           | 0.2794| 3.49  | 62.2 |

4. Conclusion

Tensile strength and elongation at break reduce while modulus of elasticity increase with increasing both ESP and CESP. rHDPE/EVA/CESP blend composites is higher tensile properties compare to rHDPE/EVA/ESP blend composites. The swelling percentage reduce in increasing of filler loading for both composites. rHDPE/EVA/CESP blend composites has lower swelling percentage compared to rHDPE/EVA/ESP blend composites. Thermal stability will increase by increasing both filler and CESP filler show higher thermal stability than ESP filler. The reduced intensity of the peaks reflects the smaller PE fraction and smaller crystal size in the composites in the X-ray diffraction analysis. The increase in CESP filler has reduced the crystal orientation ratio values, and a hence lower degree of crystallization of the composites was achieved. The crystallinity percentage will decrease as the higher loading filler in the blend composites.

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