



THE EFFECT OF OIL PALM FIBER/EGGSHELL POWDER LOADING ON THE MECHANICAL PROPERTIES OF NATURAL RUBBER COMPOSITES

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ABSTRACT

Oil palm fibre (OPF) and eggshell powder (ESP) reinforced natural rubber was developed in this project. The effects of OPF/ ESP loading on the curing characteristics, mechanical properties and morphological properties of OPF/ ESP reinforced rubber were investigated. For these purposes, five different natural rubber compounds were produced. Three of the rubber compounds were OPF/ ESP natural rubber composites with various loadings of OPF and ESP. The other two rubber compounds were unfilled natural rubber and carbon black reinforced rubber used to benchmark the hybrid bio-filled natural rubber composites. The ESP was prepared from eggshell waste and underwent heat treatment to enhance its properties. For OPF, alkali treatment was conducted to reduce the lignin content on the surface of the fiber and to improve the adhesion between the rubber matrix and OPF. From the experimental results, it was found that as the ESP loading increases and OPF loading decreases, tensile strength and elongation-to-break increases. Hysteresis loss and hardness value decreases as ESP loading increases and OPF loading decreases. Curing time was independent of the OPF/ ESP loading. Scanning electron microscope results revealed that the distribution and adhesion interaction between the hybrid fillers and rubber matrix was good. The experiments had shown promising results that OPF/ ESP reinforced rubber compounds can be used to replace carbon black reinforced rubber in the future.

Keywords: oil palm fiber, eggshell, natural rubber, bio-fillers, mechanical properties.

INTRODUCTION

Rubbers are widely used in various industry applications, such as tires, seals and gaskets in automotive, aerospace and food and pharmaceutical industries, etc. credit to their highly non-linear elastic behavior. Among all the rubbers available in the market, natural rubber which is obtained from the latex of the *Hevea brasiliensis* tree has good physical properties, such as high mechanical strength, low heat build-up and resistance to impact and tear [1]. However, natural rubber has its drawback as well, such as low flame resistance, sensitivity to chemicals and solvents mainly due to its unsaturated hydrocarbon chain structure and its non-polar character, causing limitation in a variety of applications [1]. Hence, rubbers are reinforced by mixing with petroleum-based fillers, especially carbon black to enhance the mechanical properties of cross-linked rubbers. However, the petroleum reservoir is depleting due to its limited reserve and increasing demand from various industries. Furthermore, the world is facing environmental degradation due to excessive non-degradable waste rubber materials. Hence, developing alternative rubber composite materials which are cost effective, environmental friendly and biodegradable at the product end of life are amongst the most highly regarded research initiative.

The advantage of composite material is that the high strength and stiffness of the filler can be incorporated

into the soft, elastic rubber matrix. Among current biocomposites research works, food solid waste materials have been attractive bio-fillers for polymeric composites due to economic and environmental advantages. These bio-fillers are extracted from plants (e.g., oil palm, flax, jute, hemp, etc.) and animals (e.g., eggshell, shellfish shell, shrimp shell, etc.) which are abundant and can be potentially used to replace the conventional reinforcing fillers.

Among different solid waste materials available, OPF and ESP appeared to be promising materials because of the toughness of the OPF [2] and high mineral content of the ESP [3]. Several research works have been conducted to incorporate these two natural fillers separately into different polymeric composites [2, 4-7]. For OPF composites, it was found that the adhesion between OPF and rubber matrix increased on alkali treatment of the fiber [5]. The alkali treated OPF exhibited better tensile properties than untreated fibers as alkali treated fibres showed higher crosslink density and better adhesion. Researchers also found that the elongation at break for compounds with treated fibre is lower than that for compounds with untreated fibre at the similar loading due to better strength and stiffness achieved from the strong adhesion between the fibre and rubber matrix. On the other hand, higher toughness was obtained from



compounds filled with untreated fibre due to its weak interfacial adhesion as weak interfacial bonding results in bond breakage at the fibre matrix interface and fibre pullout causing higher toughness. Ismail, Rosnah, and Rozman [4] found that increasing the concentration of OPF loading in a rubber matrix resulted in a reduction of tensile strength and tear strength, but increased hardness and modulus of the composites. Jacob et al. [2] found that adhesion between OPF and rubber matrix can be improved by aqueous alkali treatment at elevated temperatures, increasing the physical properties of the compound, such as tensile strength tensile modulus, tear strength and hardness of the rubber compounds. However, processing characteristics, such as scorch and curing time were found to be independent of the fiber loading and modification of fiber surface.

In an egg, the eggshell contributes around 11% of the overall weight of the egg. Calcium carbonate is abundant in the eggshell and considered to be one of the major constituent present in it. With the addition of eggshell waste as filler into the natural rubber, studies were carried out to study the effect of eggshells filler on mechanical and physical properties of natural rubber [1, 3, 6]. It was found that the tensile strength and elongation were decreased with increased of ESP filler loading [6]. However, the modulus of elasticity and hardness were increased with increased ESP filler loading [7]. ESP that underwent heat treatment at 600°C exhibited better tensile strength, tear strength, hardness, tension set and swelling resistance were greater compared to those untreated eggshell as filler due to better filler-rubber interaction through high surface area.

Despite of incorporating the plant based and animal based natural fillers separately into rubber matrix, there were studies conducted to produce hybrid natural fillers reinforced rubbers [8, 9]. For example, Prodpran et al. [9] incorporated palm oil and chitosan into protein-based film from round scads and found that addition of palm oil improved the film's water vapour barrier property while addition of chitosan into the natural rubber enhances the mechanical properties of the films. However, chitosan decreased the water vapour barrier property of the films due to its hydrophilic nature. Furthermore, cross-linked chitosan/oil palm ash composite beads were found to be an excellent adsorbent for removal of dye [10].

However, incorporation of OPF and ESP as fillers in natural rubber has not been previously explored. Hence, this project is conducted to study the effect of incorporating eggshell waste and OPF as fillers in natural rubber composites. For this purpose, five different rubber compounds were produced. One of the compounds was natural rubber, while the other three were reinforced natural rubber with various loading of eggshell powder and oil palm fiber, and the last compound was carbon black reinforced natural rubber. The curing characteristics, mechanical properties and morphological properties of the compounds were investigated.

MATERIALS AND METHODS

Materials

Standard Malaysian natural rubber grade L (SMR L) supplied by Malaysian Rubber Board was used as the rubber matrix. The oil palm fiber was purchased from SzeTech Engineering Sdn. Bhd. while the eggshell powder was produced from chicken eggshell wastes collected from various hawkker stores around Broga and used as the biofillers. The Fast Extrusion Furnace (FEF) carbon black-N550 was used as the conventional filler. The other compounding ingredients used were zinc oxide, stearic acid, Permanax 1, 2-dihydro.2, 2, 4-trimethyl quinoline (TMQ), N-cyclohexyl-2-benzothiazole sulphonamide (CBS), and sulphur, which were supplied by Malaysian Rubber Board and used as received. Sodium hydroxide was purchased from EOS Scientific Ltd.

Preparation of materials

Eggshell powder

The eggshell wastes collected were washed thoroughly with water several times and crushed into smaller pieces, as shown in Figure-1. The pieces of eggshell wastes were then stirred mechanically to separate the eggshell and its membranes [1]. The membranes were removed and the eggshell pieces were dried in the furnace for 2 hours at 105°C [3]. After the drying process, the eggshell pieces were grounded into powder form using ultra centrifugal mill as shown in Figure-2.



Figure-1. Crushed eggshell.



Figure-2. Eggshell powder.

A porcelain dish is filled with ESP and placed in a box furnace for 2 hours at 600°C [3]. Heat treatment was done onto the ESP to enhance the properties of the eggshell powder. Figure-3 (a) and (b) show the eggshell powder before and after heat treatment respectively.

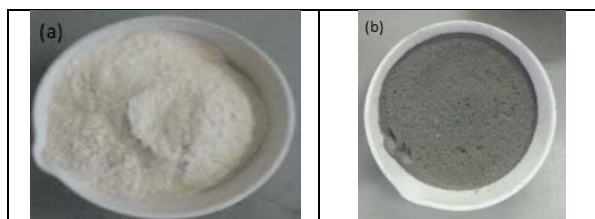


Figure-3. Eggshell powder before (a) and after (b) heat treatment.

Oil palm fiber

The oil palm fiber was grounded into approximately 10mm long using the ultra-centrifugal mill. The grounded oil palm fiber was then immersed in 10% aqueous sodium hydroxide solution at room temperature for 12 hours as shown in Figure-4 [11]. After that, the OPF was washed several times with water to remove unwanted impurities and dried. The immersion of OPF in aqueous sodium hydroxide solution was done as a treatment process to reduce the lignin content on the surface of the fiber and also improve the adhesion between the rubber matrix and OPF [11].



Figure-4. Treatment process for oil palm fiber.

Rubber compounds

The formulation of the rubbers is given in Table-1. The mixing of the rubber compounds were carried out at Malaysian Rubber Board using a laboratory two roll open mixing mill. The nip gap, mill roll speed ratio, time, temperature of mixing, number of passes, and sequence of addition of ingredients during mixing were keep the same for all compounds.

Table-1. Rubber compounds formulation table.

Ingredients added (phr ^a)	NR ^b	A	B	C	CB ^c
SMR L ^d	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	1	1	1	1	1
FEF ^e CB, N550	-	-	-	-	40
Eggshell powder	-	10	20	30	-
Oil palm fibre	-	30	20	10	-
Permanax TMQ ^f	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5
CBS ^g	0.5	0.5	0.5	0.5	0.5

^aparts per hundred rubber.

^bNatural rubber.

^cCarbon black.

^dStandard Malaysian Rubber Grade L.

^eFast Extrusion Furnace.

^f1,2-dihydro-2,2,4-trimethyl quinolone.

^gN-cyclohexyl-2-benzothiazole sulphonamide.

Methods

Rheometer

At the end of the mixing cycle, the materials were collected and conditioned at a temperature of 25 ± 1 °C for 24 h before cure assessment. The curing characteristics of the rubber compounds were then obtained using the

rheometer (MDR2000P). The temperature was set at a constant temperature of 150 ± 1 °C, according to ASTM D2084. The test time was set to run for 30 minutes. Curing characteristics, such as minimum torque (ML), maximum torque (MH), scorch time (TS2) and optimum cure time (T90) were obtained.



Hardness test

The hardness test was carried out using shore A type durometer (REED HT-6510A) according to ASTM D2240. Readings were taken at three different points distributed over the sample and an average was taken from the three readings.

Tensile test

The rubber compounds were cut into dumbbell shape according to ASTM D638 type V. Tensile test is carried out using the Instron 5582 Universal Testing Machine. The cross-head speed is set at 500 mm/min. Before the testing was carried out, the dumbbell samples were conditioned at ambient temperature ($25^{\circ}\text{C} \pm 3^{\circ}\text{C}$) and relative humidity ($30\% \pm 2\%$). An average reading was taken from five different dumbbell samples extracted from the same compound.

Cyclic loading test

Cyclic loading test was carried out to obtain the hysteresis loop of the rubber compounds. Instron 5582, along with Merlin software was used to run the experiment. The experiment was carried out in room temperature of 24°C . The rubber samples were set to run for 3 cycles with a max extension limit of 150%, at a cross-head speed of 150 mm/min, according to ASTM D3479.

Scanning Electron Microscope

Small cubic shaped samples were cut from the rubber compounds with a sharp blade and the morphological properties of the rubber compounds were observed with a scanning electronic microscope. The samples' surfaces were coated with thin layers of palladium to prevent electron charging of the samples when the experiment is running.

RESULTS AND DISCUSSIONS

Cure characteristic

The effects of different loading of ESP and OPF on vulcanized properties were determined by the relationship of torque and time and the data is summarized in Table-2. The scorch time (T_{s2}) or time to initiate cure was determined from the increase of the minimum torque (M_L) value by two units while the optimum cure time (T_{c90}) was determined from the time at the torque which reached to 90% of M_H . From Table-2, it can be seen that the OPF/ ESP reinforced rubber compounds has lower T_{s2} and T_{c90} compared to unfilled natural rubber. This is probably due to the presence of the protein and metal oxide in eggshell powder filler that aids in the curing process of the rubber compounds, improving the curing time [3]. However, T_{c90} was found to be independent of OPF/ ESP loading but the unfilled compound exhibited higher cure time. The reduction in cure time of the filled composites was attributed to the higher time the rubber compounds remain on the mill during mixing. As the fillers loading increases, the time of incorporation also increases and consequently generates more heat due to friction [2]. As for the maximum torque (M_H), it is shown that carbon black reinforced rubber has the highest maximum torque, followed by the OPF/ ESP reinforced rubber compounds and lastly unfilled natural rubber. With the addition of fillers, the natural rubber composites are stronger than unfilled natural rubber. Comparing the OPF/ ESP reinforced rubber compounds, the maximum torque decreases from compound A to compound C. This is due to the decreasing oil palm fiber loading in the compounds. The presence of oil palm fiber restricts deformation from occurring, increasing the compound's stiffness and hardness, thus increasing the maximum torque [11].

Table-2. Curing characteristics of the rubber compounds.

	M_H (dNm)	M_L (dNm)	T_{s2} (min)	T_{c90} (min)
NR	7.50	0.69	7.37	13.75
A	12.47	1.19	3.62	8.78
B	11.28	0.98	4.37	10.12
C	10.97	1.28	4.45	9.92
CB	13.81	1.20	3.42	10.22

Mechanical properties

Figure-5 shows the variation of hardness value of unfilled natural rubber, carbon black filled natural rubber and natural rubber composites with different loading of ESP and OPF. From Figure-5, it can be seen that OPF/ ESP reinforced rubber compounds has the highest hardness value, followed by carbon black reinforced rubber and lastly unfilled natural rubber. As the ESP filler loading increases and OPF filler loading decreases from

compound A to compound C, it can be seen that the hardness value decreases as well. The presence of OPF helps increase the hardness of the rubber compounds as the compounds become stiffer and harder [5]. While in ESP, presence of rigid calcium carbonate particles are found, which contributes to the brittleness and hardness of the rubber compounds [3]. The contribution of OPF filler towards the hardness value is more significant than that of ESP.

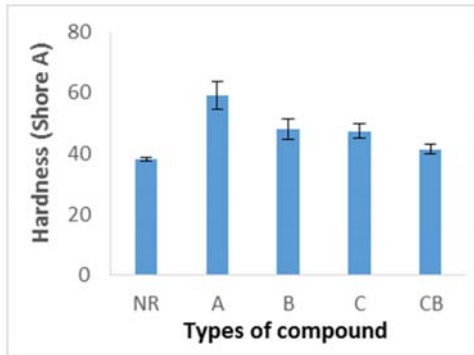


Figure-5. Hardness value of rubber compounds.

Figure-6 and Figure-7 represent the tensile strength and elongation at break of the natural rubber composites. According to Figure-6, natural rubber has the highest elongation-to-break, followed by OPF/ ESP reinforced rubber compounds and lastly carbon black reinforced natural rubber. As for the OPF/ ESP reinforced rubber compounds, it can be deduced that as the ESP loading increases and OPF loading decreases from compound A to compound C, the elongation at break also increases gradually. When the OPF loading increases, the rubber compound become stiffer and harder, thus reducing its toughness and leading to lower resistance to break [4]. In addition, there are strong adhesion bond between the eggshell powder and the natural rubber matrix [1]. This contributes to the increasing elongation to break of the rubber compounds when the ESP loading increases.

As for tensile strength shown in Figure-7, carbon black reinforced rubber has the highest tensile strength, followed by natural rubber and lastly OPF/ ESP reinforced rubber compounds? For the OPF/ ESP rubber compounds, tensile strength increases as ESP loading increases and OPF loading decreases. Oil palm fiber helps restrict any deformation from occurring in the rubber compounds. Eggshell powder had also shown good interfacial adhesion with the rubber matrix, aiding in the increase of tensile strength as well [3].

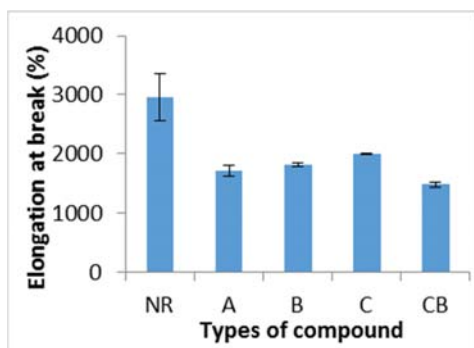


Figure-6. Elongation of break of rubber compounds.

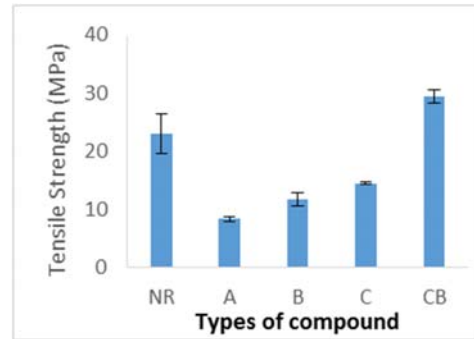


Figure-7. Tensile strength of rubber compounds.

Figure-8 depicts the loading and unloading curve of the compounds under cyclic loading at stabilized hysteresis (the 3rd cycle). In order to investigate the effect of different filler loadings on hysteresis of natural rubber biocomposites, the amount of hysteresis loss ratio at different ESP and OPF is investigated. Following [12], the hysteresis loss ratio is calculated from the stabilized hysteresis. In the following, the hysteresis loss ratio is defined by:

$$\text{Hysteresis loss ratio} = \frac{H}{E} \quad (1)$$

where H is the amount of hysteresis (dissipated energy, given by the difference of the area under the uploading and the unloading path of stress-strain curve) and E is the supplied energy during uploading (given by the area under the uploading path of the stress-strain curve) as depicted in Figure-9.

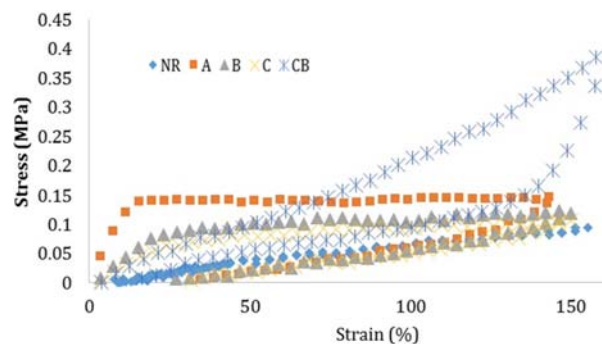


Figure-8. Stress strain curve of rubber compounds.

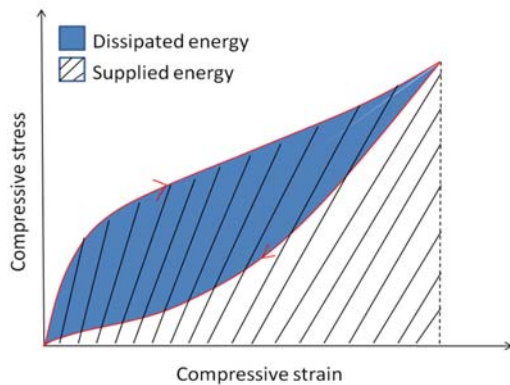


Figure-9. Definition of hysteresis loss ratio.

Figure-10 shows the hysteresis loss ratio in compounds filled with different fillers. From Figure-10, it can be seen that carbon black reinforced rubber has the highest energy loss, followed by OPF/ ESP reinforced rubber compounds and lastly unfilled natural rubber. As the ESP filler loading increases and OPF filler loading decreases, the energy loss within the rubber compound decreases. The presence of oil palm fiber resulted to stiffer compound, thus decreasing its elasticity [4]. Hence, more energy loss occurs as the OPF loading increases.

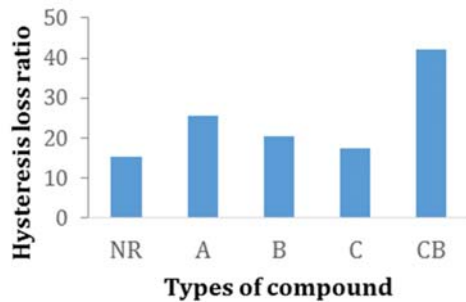


Figure-10. Hysteresis loss ratio of rubber compounds.

Morphological properties

Morphological characteristics of rubber composites coming from unfilled vulcanizate, carbon black filled, ESP/ OPF filled SMRL with various fillers loading were investigated. The micrographs obtained from the Scanning Electron Microscope given in Figures-10 to 12 show the black section is the natural rubber matrix, while the white segments are the eggshell powder filler. From Figures-11 to 13, it can be seen that eggshell powder is most abundant in Figure-13 compared to Figure-11 and 12. This is due to the increasing filler loading for eggshell powder. The distribution of the eggshell particles throughout the rubber matrix for all the rubber compounds was generally well dispersed. The well dispersed order of the eggshell particles is due to the small particle size and large surface area of the eggshell particles after undergoing heat treatment.

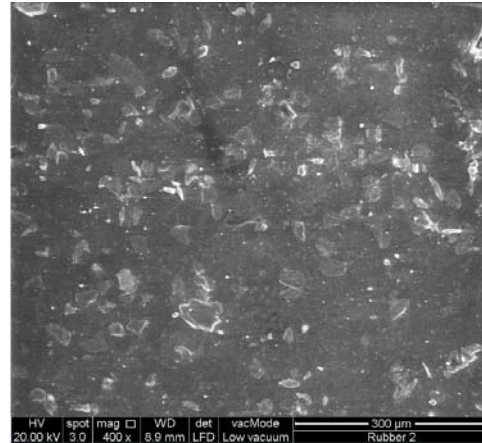


Figure-11. SEM pictures at 400x magnification for compound A.

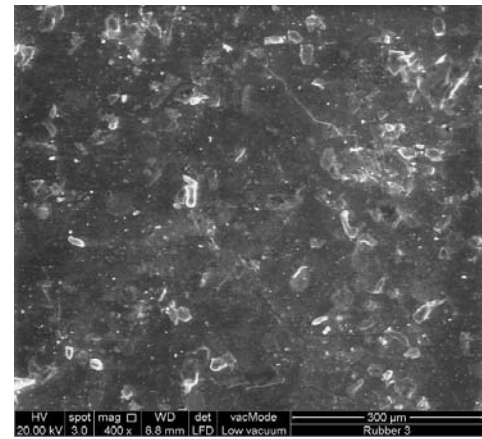


Figure-12. SEM pictures at 400x magnification for compound B.

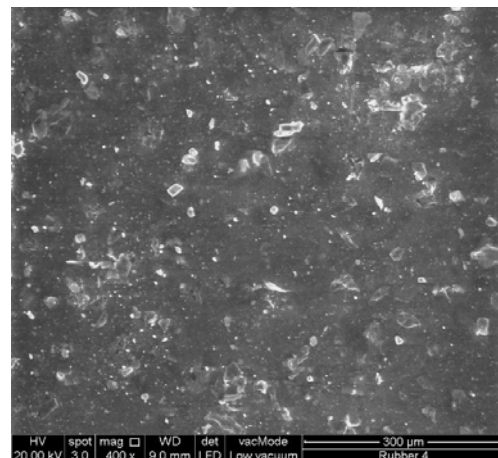


Figure-13. SEM pictures at 400x magnification for compound C,



CONCLUSIONS

Oil palm fiber (OPF) and eggshell powder (ESP) were incorporated as bio fillers in natural rubber composites. The curing characteristic, mechanical properties and morphological properties of oil palm fiber (OPF)/ eggshell powder (ESP) reinforced natural rubber composites have been investigated. It is concluded that curing times for OPF/ ESP reinforced natural rubbers were found to be independent of the fillers loading. However, the maximum torque decreases as the ESP loading increases and OPF loading decreases due to restricted movement contributed by the presence of OPF. As for the mechanical properties, it is concluded that as the ESP loading increases and OPF loading decreases, the hardness and hysteresis loss of the OPF/ ESP reinforced natural rubber decreases contributed by the brittleness of the ESP. However, the tensile strength and elongation at break of the OPF/ ESP reinforced natural rubber compounds increases as the OPF loading decreases and ESP loading increases due to increase in elasticity of the composites.

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