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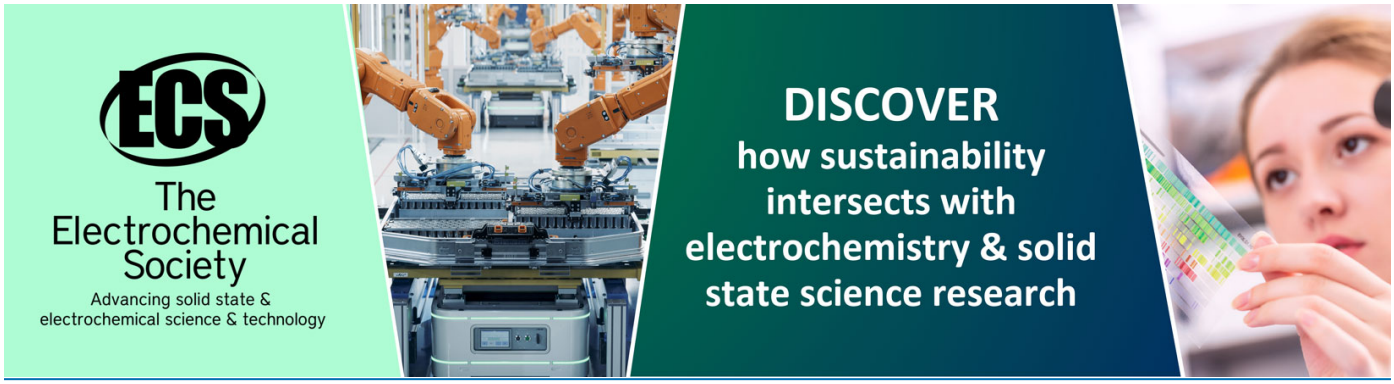

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The Potential of Oil Palm Ash and Eggshell Powder as Hybrid Biofillers in Natural Rubber Biocomposites

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Abstract. Astronomical amounts of solid biomass wastes are generated globally each day. It is imperative that the potential of conversion and utilisation of these wastes be identified and implemented, thus reducing landfill load and recovering value from this immense source of material. Natural rubber biocomposites were produced by compounding natural rubber matrix with oil palm ash and eggshell powder as hybrid fillers. The mechanical properties of the biocomposites were determined. It is observed that the biocomposites exhibit higher stiffness than the unfilled natural rubber compound. Acid treatment is found to further increase the stiffness of the biocomposites.

1. Introduction

Natural rubber (NR) is a polymer of isoprene (2-methylbuta-1,3-diene) with the chemical formula C_5H_8. NR possesses excellent physical properties such as high mechanical strength, resistance to impact and tear and low heat build-up. However, NR does have its own drawbacks such as low flame resistance and vulnerability to solvents and chemicals, subsequently limiting its applications. As such, this drawback is typically resolved by mixing the NR with petroleum-based fillers such as carbon black to enhance the mechanical properties of the rubber.

Food industries produce a substantial amount of solid waste each day. Consequently, it is becoming more and more imperative to curb this rapidly expanding issue. With this in mind, optimised systems for food waste management are turning into a necessity given the increasingly stringent constraints pertaining to the environmental issues [1]. Among the numerous solid waste materials available, eggshell powder (ESP) and oil palm ash (OPA) were chosen to be the focus of this paper as potential NR bio-fillers. In fact, these materials have yielded encouraging results when incorporated separately into the NR matrix in previous research works [2, 3, 4, 5]. OPA incorporation yielded the improved cure rate index and increased the elongation at break by 7.4% [4]. Ooi et.al [3] found that the degree of swelling decreased with OPA loading and this was further reduced with the hydrochloric acid (HCl) treatment of the OPA. Moreover, an improvement in crosslink density and improved rubber-filler interaction were observed for HCl-treated OPA in comparison to the untreated OPA composites. The

properties such as load bearing capacity, aging resistance and dynamic mechanical properties improved as well. The thermal stability of OPA-filled NR composites was maintained even for the post-treated samples. For the ESP composites, it was found that the tensile strength and elongation decrease with increase ESP filler loading. On the contrary, the modulus of elasticity and hardness increase as the ESP filler loading increases [6, 7].

As a food item, eggs are regarded as an essential ingredient in the diets of people everywhere in the world. This can be attributed to the high nutritional content and ease of preparation of the eggs as food. ES waste is often disposed of as food waste and is listed worldwide as one of the worst environmental problems [2]. Besides that, Yi et al. [8] suggests that the abundance and chemical composition of ES makes it a potential source of filler for lightweight, cost-saving and low-load bearing composites.

As one of the leading palm oil producers in the world, Malaysia generates a substantial amount of oil palm wastes, leading to an alarming excess of biomass waste. Consequently, the oil palm biomass waste significantly raises the expenditures required for its transport and disposal [9]. The oil palm biomass primarily comprises of empty fruit bunches, oil palm fibres & shells, trunks and fronds [10]. These are combusted as an additional source of fuel to operate the steam boilers within the vicinity of the oil palm mills. In this manner, the burned waste post-combustion coined as OPA is obtained. Afterwards, the OPA is typically disposed as landfill [4]. In a particulate-filled NR system, the interfacial adhesion between the OPA and the NR matrix holds a vital role in the enhancement of the desirable mechanical properties [3].

The incorporation of OPA-ESP hybrid fillers in NR matrix has not been explored in previous research works and studies. Nevertheless, the objectives of this project are to develop NR biocomposites and to identify the mechanical properties of the biocomposites. Furthermore, the properties of the biocomposites were compared with unfilled NR and conventional NR filled with carbon black.

2. Materials and experimental methods

2.1. Bio-fillers preparation and characteristic

The raw eggshell was washed thoroughly. Next, the cleaned eggshell was crushed and the pieces were stirred in beaker containing distilled water using mechanical stirrer at an agitation speed of 1100 rpm for an hour to eliminate the unwanted eggshell membrane. The eggshell was then rinsed to remove the residue membrane and dried for 18 hours in a furnace at 100° C. Next, the dried eggshell was milled using an ultra-centrifugal mill with a 500 μm mesh sieve at 6000 rpm. The milled eggshell obtained was then heat-treated at 600° C for 2 hours in a furnace to produce the ESP [5].

The raw OPA was milled into fine powder using the ultra-centrifugal mill with 500 μm sieve at 6000 rpm. The milled OPA was then dried in a vacuum oven at 80º C and 200 millibar for 24 hours to expel moisture [4]. Next, acid-treated OPA was prepared by mixing the powdered OPA in 10% aqueous HCl solution and stirring it with a glass rod for two hours at room temperature. Next, the soaked OPA particles were filtered and washed thoroughly with distilled water. The acid-treated OPA was then dried for 24 hours at 80° C, followed by activation at 105° C in an oven for an hour [3]. Lastly, the HCl-treated OPA was cooled to room temperature and sieved prior to being kept in desiccator.

The crystalline phase and chemical composition of the fillers were identified using the PANalytical X-Ray Diffraction (XRD) instrument with the 2θ range being set between 10° and 90°, with step size and step time of 0.02° (2θ) and 0.5 seconds respectively.

2.2. Biocomposite samples preparation

Seven different rubber compounds were mixed and prepared using the conventional laboratory-sized two roll mill. 500 gram slabs of SMR L rubber were used for the formulation of each of the seven NR compounds. Each ingredient was weighed using digital mass balance according to the rubber formulations indicated in Table 1. The total mixing time was set to be less than 40 minutes in order to

prevent the occurrence of pre-mature vulcanisation as a result of the generated excess heat during the compounding process. The nip gap, mill roll speed ratio, time and temperature of mixing, number of passes and sequence of ingredient addition were retained for each mixing to ensure consistency of the process flow for each rubber compound produced.

Table 1. Formulation table for the rubber compounds.

Ingredients added (phr)	NR Gum	A	B	C	CB	D	E
NR (SMR L)	100	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5	5
Stearic Acid	1	1	1	1	1	1	1
CB N550	-	-	-	-	30	-	-
Eggshell powder	-	10	20	30	-	10	30
OPA	-	1	1	1	-	-	-
Acid-treated OPA	-	-	-	-	-	1	1
Permanax TQ (TMQ)	1	1	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS	0.5	0.5	0.5	0.5	0.5	0.5	0.5

2.3. Measurement of mechanical properties

Strip cutouts (width of 6 mm) of the rubber samples for each rubber composite sample were tested using the Instron 5582 Universal Testing Machine. The cross-head speed was set at 500 mm/minute. The gauge length was 25 mm.

3. Results and discussion

3.1. Characterization of fillers

The XRD pattern of ESP was presented in Figure 1. It was found that these XRD patterns exhibit similar crystalline peaks as that of commercial calcium carbonate (CaCO3). The standout peak is found to be around 30° (2θ) which is a common characteristic of crystalline calcite by the reference code 98-007-8903. Hence, this was identified as a structure dominated by crystalline calcite content. The result from XRD was highly consistent with previous works [5, 11]. The XRD pattern of the OPA shown in Figure 2 exhibits a sharp peak with the greatest height at 26.5295° (2θ), which is identified as the compound of graphite 2H matched by the reference code 98-005-2916.

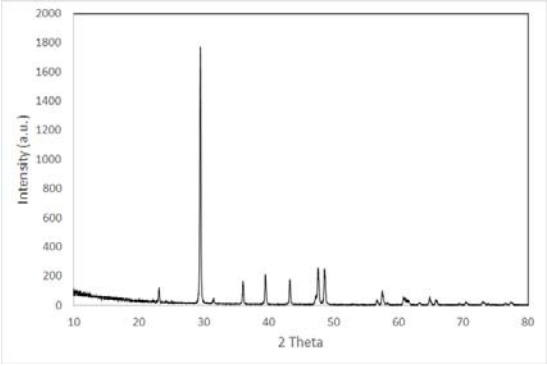

Figure 1. XRD pattern of the ESP sample.

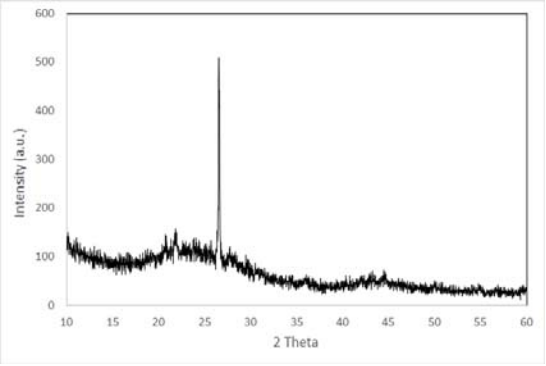

Figure 2. XRD pattern of the OPA sample.

Similarly, the XRD pattern of the acid-treated OPA exhibits the highest peak at 26.4792° (2θ), with several other sharp peaks with lower heights at around 20°, 50°, 67° and 84°. The main compound identified from both sample is quartz as indicated by the highest peak [12]. Both of these samples are

near 100% crystallinity based on the absence of 'broad' peaks, with the XRD patterns exhibiting only 'sharp' peaks.

3.2. Mechanical properties

The mechanical properties such as the tensile strength and elongation at break measured from tensile test are illustrated in Figures 3 and 4 respectively. Overall, the observation suggested that the tensile strength for the biocomposites decreases with increasing ESP. This observation can be attributed to the poor interfacial adhesion between the elastomeric matrix and the bio-fillers. The interfacial adhesion serves as an important medium that enable a portion of stress to be transferred from the filler particles during deformation [13]. In addition, filler particles may form aggregates as the amount increases, leading to poorer interfacial adhesion and thus lower tensile strength.

Similarly, the elongation at break decreases with increasing filler content. The addition of filler particles increases the stiffness and hardness of the biocomposites. Subsequently, this results in a reduction of the biocomposites' resilience and toughness and therefore lower elongation at break [14]. As indicated by the reduction, the poor interfacial adhesion reduces the capability of the filler to support possible stress transfer from the bio-fillers to the elastomeric matrix. Therefore, the stress distribution is not uniform and resulting in the biocomposites having poor mechanical properties. This observation found similarities in some other previous works [6, 7, 14] for other combination of matrix-filler systems.

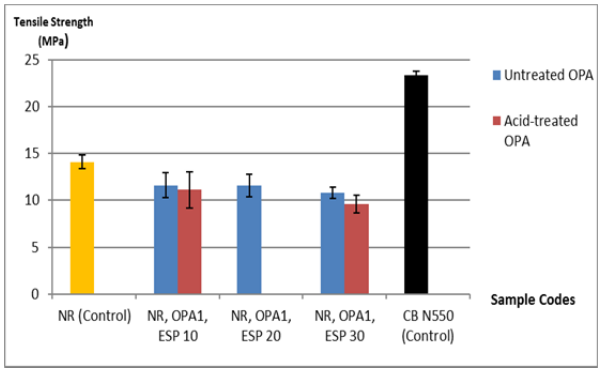

Figure 3. Tensile strengths of the specimens.

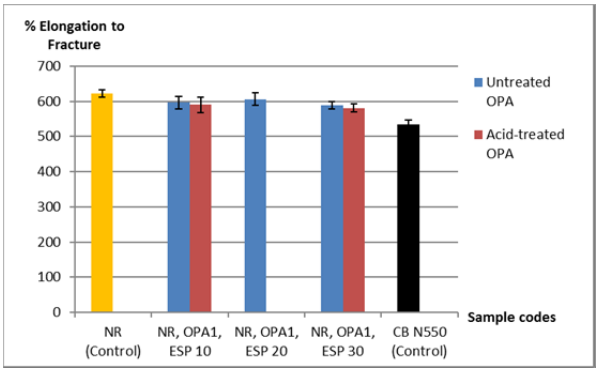

Figure 4. Elongation at break of the specimens.

4. Conclusion

OPA and ESP were incorporated as hybrid bio-fillers to successfully formulate and produce the NR biocomposites. The cure characteristics, mechanical and morphological properties were studied. It was observed that the biocomposites generally show lower tensile strength and lower elongation at break. On contrary, the biocomposites show slightly higher tensile modulus (M100) and higher hardness values. The main factor that affect the mechanical properties is attributed to the interfacial adhesion between the bio-fillers and NR matrix. It was expected that the interfacial adhension could be improved by refining the size of the bio-fillers. These observations indicated that there is a potential to utilize bio-fillers to produce biocomposites in the future.

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