Characterization of Raw Egg Shell Powder (ESP) as A Good Bio-filler

Amal S.M. Bashir[1], Yamuna Manusamy[2]

[1] *Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, amaal_989@hotmail.com*

[2] *Associat Professor- Universiti Tunku Abdul Rahman, yamunam@utar.edu.my*

Abstract—Chicken eggshell (ES) is an aviculture byproduct that has been listed worldwide as one of the worst environmental problems. It constituted by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer. The chemical composition (by weight) of by-product eggshell consists of calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) such as type X-collagen, sulfated polysaccharides, and other proteins. This study was conducted to investigate the various characteristics of ESP including scaning electron microscopy (SEM), particle size, surface morphology, FTIR and X-ray fluorescence (XRF), and thermo gravimetric analyzer (TGA). Based on its unique characteristics, the potential use of ESP as a natural filler prepared from food waste incorporated with natural rubber latex foam (NRLF) was investigated.

Index Terms—Composit, eggshell waste, natural filler, characterization.

I INTRODUCTION

Chicken eggshell (ES) is an aviculture byproduct that has been listed worldwide as one of the worst environmental problems. It constituted by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer [1]. The chemical composition (by weight) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) such as type X-collagen, sulfated polysaccharides, and other proteins [2]. Yi et al. [3] reported that ES chemical composition and availability makes ES a potential source of filler for bulk quantity, inexpensive, lightweight and low load-bearing composite applications. There have been several attempts to use eggshell components for different applications; adding ES into food supplements for people and animals, art projects galore include egg shells as an ingredient, Mosaics, paints, paper making, dying and carving [4]. Moreover ES are reused as a fertilizer or soil conditioner because of their high nutrition contents such as calcium, magnesium and phosphorus [5].

ES can be used as natural filler for making lightweight polymer composites which provides an effective means.

Various researchers have investigated the potential use of natural filler (NF) from ES wastes. Egg shell is popular to be used as bio-filler in materials especially in plastics and polymers. Studies has shown that egg shell able to replace up to 75 % of commercial $CaCO_3$ and talc as new bio-filler into polypropylene composites. Study of egg shell as bio-filler also proved that it performs better than all different types of particle size of $CaCO_3$ fillers used [6].

In rubber production, egg shell is used as bio-filler in epoxidized natural rubber (ENR) composites. It was indicated thet ES filled materials showed superior vulcanization characteristics by the increasing of maximum torque and cure rate index (CRI) with the reducing of cure time and scorch time. Morphological property revealed that ES was greater interfacial adhesion than those of others [7].

Consequently, this study was carried out to investigate the various characteristics of ESP including particle size, surface morphology, FTIR and X-ray fluorescence (XRF), area and thermal behaviour. Based on its characteristics, the potential use of ESP as a natural filler incorporated with natural rubber latex foam (NRLF) was highlighted

II Material and Methods

Sample Preparation

The raw ES used in this study was collected from cafeteria located at university Tunku Abdul Rahman (UTAR) Kampar, Perak, Malaysia.

The samples were rinsed with clean water to remove the residue egg contains that attached on the egg shells. The water content was removed by drying under hot sun. The membrane was removed, and then grounded using grinder model Retsch ZM 200. Then ESP was sieved. The Mastersizer 2000 particle size analyzer was used to detect the particle size for ESP.

Particle Size Distribution

Particle size distribution (PSD) is an indication of different sizes of particle which are presented as proportions. Measurement was caridout by referring relative particle amount as a percentage where the total amount of particles is 100 % in the sample particle group. In PSD test, various kinds of standards such as volume, area length and quantity are normally used to determine particle amount [8]. Frequency distribution shows in percentage of the particles amounts appear in respective particle size intervals after the range of target particle sizes was divided into separate intervals.

The cumulative distribution, particles passing the sieve, expresses the percentage of the particles amount from specific particles sizes or below. In this study, Mastersizer 2000, Hydro2000 MU (A) was used to determine the particle size distribution.

Field Emission Scanning Electron Microscope (FESEM)

FESEM- JEOL 6701-F scanning electron microscope was used to investigate the surface morphology and textur of the ESP. The test sample was cut and placed onto the specimen stub with double- sided carbon tape. The specimen was then prepared for examination by coated with platinum.

Fourier Transform Infra-red Spectroscopy (FT-IR)

The infrared spectra were measured using Spectrum-RX1 to determine the content and impurity of ESP.

X-Ray Diffraction Studies (XRD)

X-Ray Diffraction (XRD) is a fast analytical method mainly applied for identification of a crystalline material. Besides, it is also able to provide information on unit cell [9]. The analysed material which finely ground, homogenized, and average bulk composition was tested via XRD.

XRD spectra were recorded with Shidmazu XRD-600 in step scan mode using Ni-filtered Cu Kα radiation, which has 0.1542 nm in wavelength. ESP samples were scanned in reflection, whereas the moulded composites in transmission mode in the angle interval of 2θ = 1-12 º. The interlaying spacing (d-spacing) of the powder form ESP was derived from the peak position (d001 – reflection) in the XRD diffractograms according to the Bragg equation, Equation 1.

$$\lambda = 2d \sin \theta \quad (1)$$

Where λ is the X-ray wavelength, d is the interlayer spacing and θ is the angle of diffraction [10].

X-ray fluorescence (XRF)

The chemical composition of the eggshell waste powder sample was determined by X-ray fluorescence machine.

Thermogravimetric Analyses (TGA)

The Thermogravimetric analyses of the ESP sample was measured using a Mettler-Toledo Thermogravimetric Analyzer TGA/SDTA851e. ESP sample was tested at a heating rate of 20ºC/ min from 30ºC to 800 º C under nitrogen gas flow.

III. RESULT AND DISCUSSION

Particle Size Analysis

Fig. 1 demonesrates the particle size distributions curve of ESP. The particle size of ESP powder at peaks $d_{0.5}$, $d_{0.1}$, and $d_{0.9}$ were obtained as 7 µm, 1.106 µm, and 24.019 µ, respectively. It can be indicated that with finely grounded of egg shell powder, it is predicted to appear the similar reaction of commercial calcium carbonate to strengthen the physical strength of rubber composites with same loading and same particle size. In summary, the egg shell powder as bio-filler is feasible to test since the particle size of egg shell powder is highly similar to the commercial calcium carbonates.

Field Emission Scanning Electron Microscope (FESEM)

The morphology of ESP is illustrated in Fig. 2 (a) and Fig. 2 (b). From the figures, it can be observed that the ESP does not have an exact shape resulting of the grinded process used, size and length. In addition, a wide particle size range was detectd, which is in accordance with the results obtained of the particle size analysis (Fig.1). The scanning electron micrograph of Fig. 2 (b) shows the high porosity of the eggshell powder particles. In fact, the eggshell contains a significant amount of gas exchange pores [11].

Fourier Transform Infra-red Spectroscopy (FT-IR)

Fig. 3 shows the FT-IR spectra graph for ESP with numer-

ous bands from 4000 cm^{-1} to 400 cm^{-1}. By observing the graph, it appears that a prominent absorption peak of carbonate was observed at 1431 cm^{-1}, respectively, attributed to alkyl group. Besides, the FT-IR result also showed the absorption peak of calcite at 876 cm^{-1} of CO_3^{2-} . This agrees well with the result reported by Islam et al. [12] in which they observed the absorption peak of calcite at 875 cm^{-1} of CO_3^{2-}.

X-Ray Diffraction Studies (XRD)

X-ray diffraction patterns of the ESP sample are shown in Fig. 4. The sample presented all diffraction peaks that are characteristics of calcite ($CaCO_3$). Calcite is the thermodynamically most stable form of $CaCO_3$ at room temperature [13].

X-ray fluorescence (XRF)

As presented in Table 1, the chemical composition of the ESP shows that calcium oxide (CaO) was the most abundant component. The high amount of calcium oxide is associated to the presence of calcium carbonate, which is the main component of avian eggshell [14]. Thus, the eggshell waste sample can be considered from a chemical viewpoint a pure relatively natural carbonate-based material, as well as its composition is very similar to the calcitic calcareous [14].

Table 1: Chemical composition of the ESP

Chemical compostion	Wt.%
C	21.1286
Na_2O	0.1046
MgO	0.9261
P_2O_5	0.4149
SO_3	0.3264
K_2O	0.0542
CaO	76.9922
Fe_2O_3	0.0132
SrO	0.0396

Thermogravimetric Analyses (TGA)

The thermal behaviour of the eggshell waste sample was analyzed by TGA test. The results show the presence of three thermal events. As shown in Fig. 5, the first stage at (~ 65 ºC) is endothermic and is attributed to the removal of physically adsorbed water on the particles of the waste powder. The second stage (~ 544.73ºC) is exothermic, and related to decomposition of organic matter. The third stage (~ 699.14 ºC) is endothermic, and was caused by decomposition of calcium [14].

IV CONCLUSION

In this study, the chemical, physical, and morphological characteristics of ES waste were investigated using particle size analayser, SEM, FTIR, XRD, XRF, and TGA. It can be indicated that ES charcterisics (similar to commercial calcium carbonate" and availability makes ES a potential source of filler for bulk quantity, inexpensive, lightweight and low load-bearing composite applications.
)

REFERENCES

[1] D.J. Kang, K. Pal, S.J. Park, D.S. Bang, J.K. Kim, " Effect of eggshell and silk fibroin on styrene–ethylene/butylene–styrene as bio-filler". Materials and Design, 31, 2216–2219, 2010.

[2] W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin, C.W. Yeh, "Characterization and adsorption properties of eggshells and eggshell membrane". Bioresource Technology. 97 488–493, 2006.

[3] F.Yi, Z.X. Guo, L.X. Zhang, H. Yu, Q. Li, "Soluble eggshell membrane protein: preparation, characterization and biocompatibility". Biomaterials. 25, 4591–4599, 2004.

[4] Squidoo. The Very Many Uses for Eggshells http://www.squidoo.com/using-egg-shells, 2013.

[5] A.G.J. Tacon, "Utilisation of chick hatchery waste: The nutritional characteristics of day-old chicks and egg shells. Agric". Wastes 4 335–343,1982.

[6] P. Toro, R. Quijada, M. Yazdani-Pedram, J. Luis Arias. Mater. Lett. 61, 4347-4350, 2007.

[7] P. Intharapat, A. Kongnoo, K. Kateungngan, "The Potential of Chicken Eggshell Waste as a Bio-fillee Epozidized Natural Rubber (ENR) Composite and its Properties". Journal of polymer material, 21, 245-258, 2013.

[8] Shimadsu Corporation, "Particle Size Distribution Dependent on Principle of Measurement". [Online] Available from: http://www.shimadzu.com/an/powder/support/practice/p01/lesson02.html [Accessed 3rd April 2013].

[9] B. Engin, H. Demirtas, M. Eken, "Temperature effects on egg shells investigated by XRD, IR and ESR techniques, Radiation Physics and Chemistry. 75, 268-277, 2006.

[10] Y. Munasamy, H. Ismail, M. Mariatti, C.T. Ratnam. "EthyleneVinyl Acetate/ Natural Rubber/ Organoclay Nanocomposites: Effect of Sulfur and Peroxide Vulcanization". Journal of Reinforced Plastics and Composites, 27, 1925-1945, 2008.

[11] A. C. Fraser, M. Cusak, The Am. Microsc. and Anal. 53, 23-24, 2002.

[12] M.S. Islam, S.R Hamdan., M.D Rahman, I. Jusoh, A. Ahmed,"treated light tropical hardwoods". BioResources 6, 737-750, 2011.
[13] C.S. Gopinath, S.G. Hegde, A.V. Ramaswany, S. Mahapatra, Mater. Res. Bull. 37, 1324, 2002.
[14] M.N Freire, J.N.F. Holanda, "Characterization of avian eggshell waste aiming its use in a ceramic wall tile paste". Cerâmica, 52, 240-244, 200

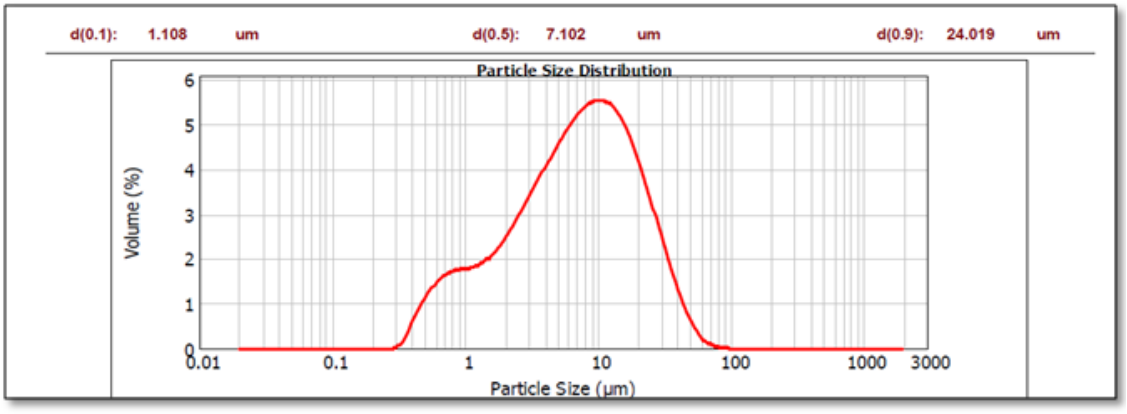
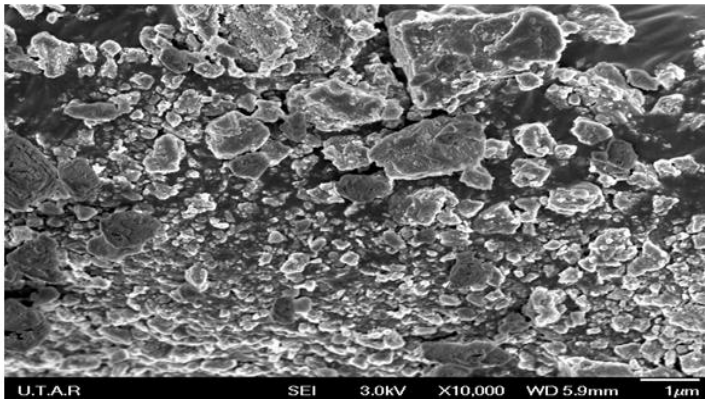


Fig.1: Particle size distribution of the ESP

(a)



(b)

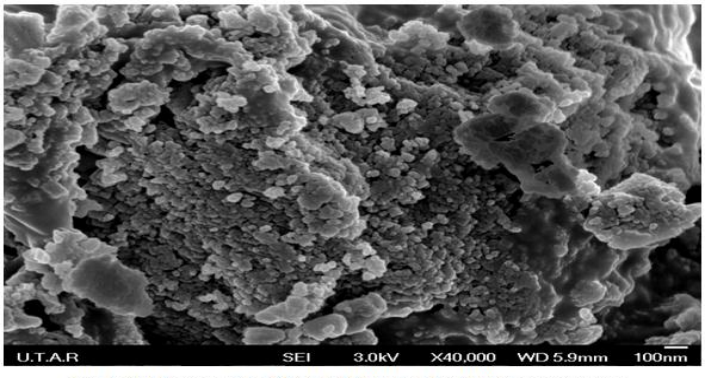


Fig.2: SEM micrograph of ESP at 10,000X and 40,000 X magnification.

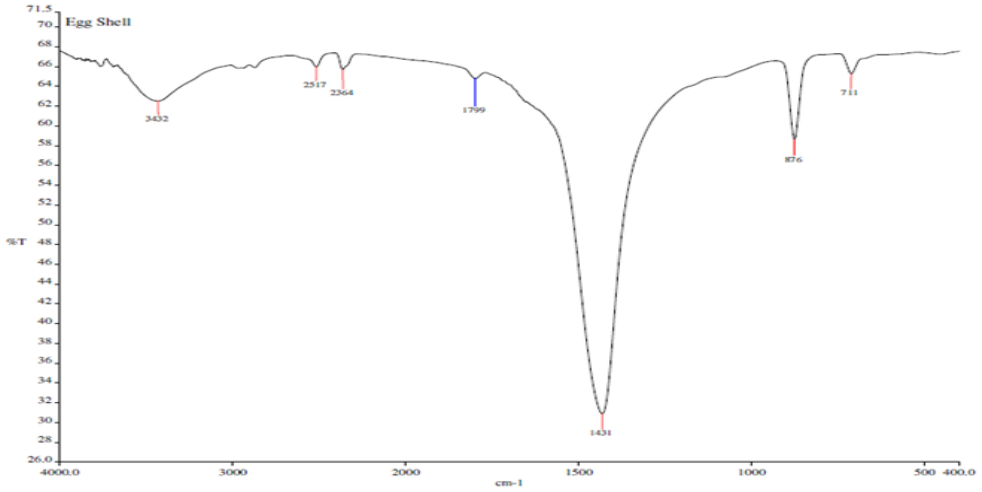


Fig. 3: FT-IR Spectra graph of ESP.

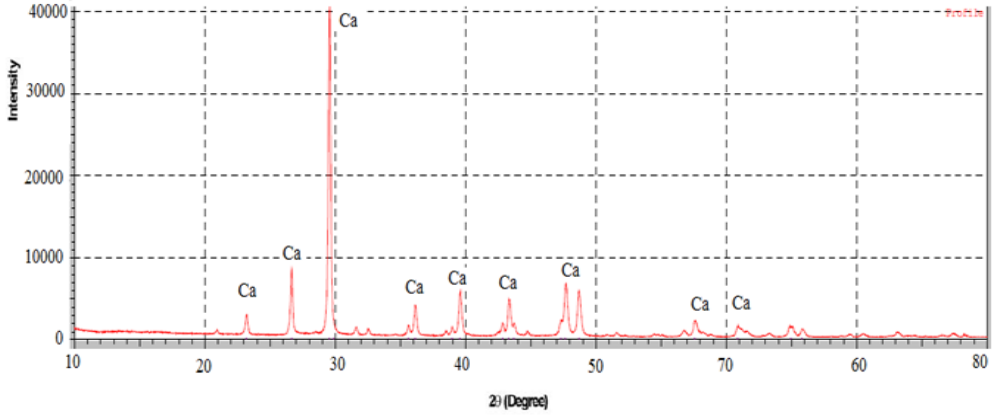


Fig. 4: X-ray diffraction pattern for the ESP

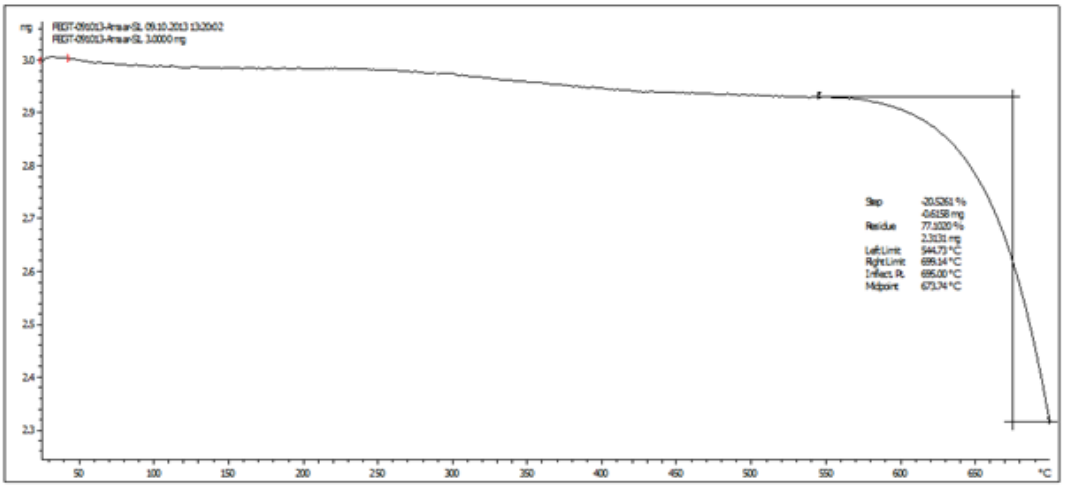


Fig. 5: TGA analysis of ESP sample