[5] Tay, J.H. & Show, K.Y. (1997) Resource recovery of sludge as a building and construction material – a future trend in sludge management. *Water Science & Technology*, 36(11), 259–266.

[6] Abdul G. L., Azni I., Calvin H. K. W., Abdul A. S., Megat Johari M. M. Noor and Aminuddin M. B. (2004). Incorporation of Sewage Sludge in Clay Brick and its Characterization. *Waste Management. Res*. 22 (4), 226-233.

[7] Craig, R.F. (1992): Soil Mechanics, pp. 1–36. Chapman & Hall, London. ILO/UNIDO (International Labor Office & the United Nations Industrial Development Organization). (1984): Small-scale Brickmaking – Technical Memorandum No. 6. 210 pp

[8] Slim, J.A. & Wakefield, R.W. (1991): The utilisation of sewage sludge in the manufacture of clay bricks. *Water* SA, 17, 197–202.

[9] Alleman, J.E., Bryan, E.H., Stumm, T.A., Marlow, W.W. & Hocevar, R.C. (1990): Sludge-amended brick production: applicability for metalladen residues. *Water Science & Technology*, 22(12), 309–317.

[10] Craig, R.F. (1992): *Soil Mechanics*, pp. 1–36. Chapman & Hall, London. ILO/UNIDO (International Labor Office & the United Nations Industrial Development Organization). (1984): Small-scale Brickmaking – Technical Memorandum No. 6. 210 pp

[11] Fadel Elseed, A. M. A. 2005. Effect of supplemental protein feeding frequency on ruminal characteristics and microbial production in sheep fed treated rice straw. Small Rumin. Res.57:11-17.

Study of Cocoa Pod Husk / Polyvinyl Alcohol (PVA) as A New Biodegradable Composite Film

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ABSTRACT

This paper present the possibility for the use of cocoa pod husk in composite with poly(vinyl alcohol) (PVA). In this study, we preparad a new green composite film from cocoa pod husk (CPH) and poly(vinyl) alcohol (PVA) and to characterize the morphology and mechanical properties of the composite film. The effect of fiber loading, plasticizer (glycerol) and effect of alkaline treatment were investigated. Poly (vinyl acohol) (PVA) with 5, 10, 15wt% cocoa pod husk (CPH) powder were prepared by aqueous mixing. The mixture was casted as composite film prior characterizations. The effect of plasticizer (glycerol) was investigated in the study and it was found that the film showed some good mechanical properties with addition of glycerol and increasing fiber loading. The effect of alkaline treatment on fiber was investigated.

Keywords: *Cocoa pod husk; Poly (vinyl) alcohol; Biodegradable polymer; alkaline treatment; Composite*

INTRODUCTION

Nowadays, thermoplastic composites produced from synthetic polymers filled with renewable natural resources start to gain the attention from world as they are considered as one of the environmental friendly biomaterials. Most of the researches focus on the use or the potential of inexpensive polymeric raw materials such as cellulose, starch, cellulosic resources and other. It is predicted and expected the resulting products are eco friendly and cost effective. Those biodegradable materials can be completely degraded into our ecosystem [1-2]. Moreover, the application of biodegradable polymers and renewable agro wastes as packaging materials is one of the alternatives to solve the problem of solid waste from inert polymers. There are several of synthetic aliphatic polyesters and natural resources are being used as biodegradable materials [3-4]. According to [5-6], most of the organic materials have the natural tendency to decompose or degrade. In our current century, the needs of degradable disposable containers or packaging materials are high. More and more researches and investigations are now being applied to produce plastic materials high biodegradability by involves abundant agro wastes, plant carbon hydrates, vegetables oils and etc. in their countries respectively.

Polyvinyl alcohol (PVA)-starch blend plastics are one of the most popular of the biodegradable plastics, and are widely used in packaging and agricultural mulch films [7-8]. However, according to [7,9], an amylose-PVA composite (PVA-starch blend) was biodegraded slower which was ~75% weight loss required 300 days in a degradation test with activated sludge [3]. PVA is non-toxic, water soluble, highly polar and synthetic polymer which has been used vastly in biomaterial technology. It has excellent film forming, emulsifying and adhesion properties. Degree of hydrolysis can affect properties of PVA and its film quality [10].

Cocoa pod husk (CPH) is a by product of the cocoa harvesting industry whereby it forms about 80% of the cocoa fruit and it is a waste product which can be utilized fully [11]. Besides, it can be used as filler in biodegradable mulch films as the high cellulose fiber content of CPH will provide reinforcing effect in the mulch films [12]. Besides that, the use of CPH as fertilizer can increase the soil macronutrients content because of high Na, P, K, Mg and Ca concentrations of CPH when it degrade in the soil [13]. Natural fibers with good biocompatibility, which can act as green filler in composites have gained interest to replace synthetic fiber. Natural fibers in composites are low cost, good thermal and low density. Combination of natural fiber and biopolymers where both are derived from natural has the potential to provide materials with enhanced mechanical properties. At present time, many studies have investigated the biodegradable polymers filled with natural fibres [14].

In this study, we present the preparation of a new green composite film from cocoa pod husk (CPH) and poly (vinyl) alcohol (PVA) and to characterize the composite film. The effect of chemical modification, fiber loading and effect of plasticizer (glycerol) were investigated. Tensile properties and functional groups of this new composite film were studied. Biodegradability of the films was studied via soil burial test.

EXPERIMENTAL

Materials

Poly (vinyl alcohol) (PVA) and glycerol used were supplied by Innovative Pultrusion Sdn.Bhd, Negeri Sembilan. Cocoa pod husk (CPH) was collected from a rural cocoa farm located in Kluang, Johor Darul Takzim, Malaysia. The collected CPH was dried under sun for one week after collected from the farm. Sun-dried CPH is crushed into smaller pieces of cocoa pod husk for easier processing via strong plastic crusher. Then, crushed CPH was oven-dried in Memmert model oven at 80°C for 24 hours to remove all the moisture and kills living bacteria or microorganism in the cocoa pod husk. Oven-dried CPH was pulverized and sieved into 250 µm.

Alkalisation of Cocoa Pod Husk Powder

The CPH powder was treated with alkaline solution to remove the impurities , waxy substances and lignin covering the surface of the fibers. CPH powder was mixed with 5 wt% aqueous solution of sodium hydroxide (NaOH) and stirred for 24 hours, rinsed , and washed with distilled wáter until the wáter becomes neutral. After washed and filtred, chemically treated CPH powder was oven-dried at 105°C for further use.

Preparation of Composite

The calculated amounts of CPH aggregate suspension was added to 10 wt% PVA solutions and stirred at room temperature with magnetic stirrer. The mixtures were homogenized in water bath via magnetic stirrer at 70-80°C for ~45-60 minutes. Glycerol was used as plasticizer in the experiments. Glycerol was added and the mixtures were stirred at 80°C until got a homogenous mixture. Mixture was distributed into glass plate. Each solution was dried at ~45°C for 24 hours to form the desired films. According to [4], complete drying was avoided because the composite film required some moisture to remain flexible and to avoid any cracking on the film surface. The formed films were then peeled off carefully from the glass plates and placed into sealed containers to avoid any moisture exchange.

Characterizations

Moisture content of the CPH powder and composite film were determined by drying the film in an oven at 60°C for 24 hours. American Standards Testing and Machine (ASTM), D638 was used to carry out mechanical testing on each sample. ASTM D638 was used to determine the tensile properties of unreinforced and reinforced plastics in dumbbell shape of specimens. The samples were cut according to the specification size to be tested on the mechanical properties. Tensile strength (TS) and elongation at break (%E) were evaluated for each sample using the INSTRON 3365 testing machine. Fourier transform infrared studies of the samples were performed with a Perkin Elmer spectrometer. The samples were prepared in transparent film for analysis by FTIR spectroscopy. Soil burial test for the composite film deterioration in soil was conducted by referred to the similar test on composite film in previous studies [2,15,16]. The small pieces of film (2 x 2 cm) was cut and completely covered by the test soil from all sides. The soils were exposed to atmospheric conditions for 7 and 15 days. After the soil test period, the samples were removed, washed with distilled water and dried to their constant weight in oven. The weight of the samples before and after soil burial test was recorded.

RESULTS AND DISCUSSIONS

Moisture content

Table 1 shows the moisture content of the composite films after oven dry for 24 hours. It found that the moisture content of composite film increase significantly after the addition of glycerol. The composite film made from 10wt% PVA solution without any fibres achieved 6.60% moisture content, however moisture content of composite film increased after the addition of plasticizer. Glycerol has strong hydrophilic character, it is expected the film with glycerol has higher moisture content with those without addition of glycerol.

Table 1 Moisture Content of NaOH Treated CPH/PVA Composite Film

CPH Loading	Moisture	Content (%)
	Content (%)	With Glycerol
0%	6.60	26.37
5%	3.40	12.31
10%	5.94	11.86
15%	8.11	11.72

Tensile properties

Tensile properties were measured for the CPH/PVA composite film containing 5, 10, and 15 wt% of CPH powder. The results of tensile properties (elongation rate, tensile strength) are shown in Figure 1 and 2. Figure 1 shows the effect of fibre medication on the percentage of elongation on composite film. The overall composite films made from NaOH modified CPH achieved higher percentage of elongation. The composite film prepared from 5wt% NaOH-modified CPH powder plasticized with glycerol exhibited the greater percentage of ~864% , which may be due to better cross linking between modified CPH powder and glycerol. Figure 2 shows the tensile strength of alkaline treated CPH/PVA film with and without addition of plasticizer. From Figure 2, tensile strength was decreasing gradually with the increasing fibre loading. It might due to the inability of fibre and the irregularity shape of fibre to support stress which moved from the polymer to fibre. Besides, the decrease of tensile strength also might due to the bubble formation which results in weal interfacial adhesion. The existence of partially spaces between fibre and polymer will results in weak structure of the composite film [3].

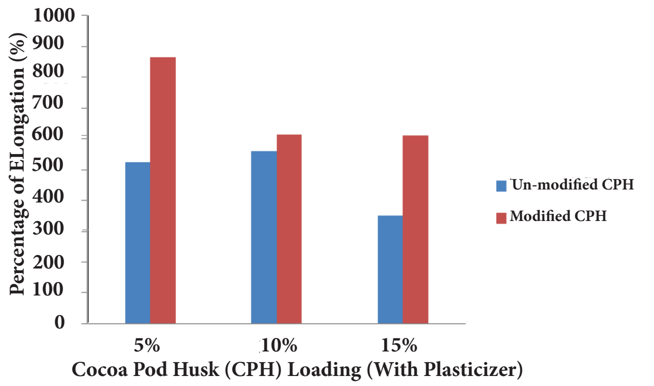

Figure 1: Elongation Percentage of CPH/PVA film (modified & unmodified CPH)

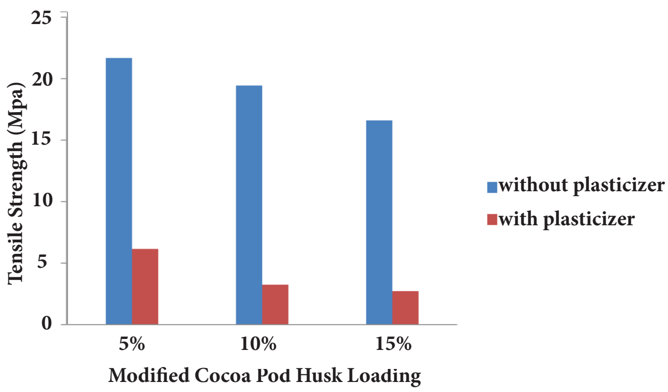

Figure 2: Tensile Strength of Alkaline Treated CPH/PVA film (with & without plasticizer)

FTIR analysis

The FTIR spectrum for 15 wt% NaOH modified CPH/PVA composite film after plasticized with glycerol. The spectrum exhibited a broad peak at around ~3677 -3100 cm^{-1} which can assighed to hydrogen bonded O-H group or due to –OH stretching. The peaks betwen ~2700 cm-1 and 2900 cm-1 corresponded to C-H stretching. The absorptions near ~1250 to 1300 cm-1 maybe due to the carboxylic acids and its derivatives which may corresponded to the organic components from cocoa pod husk fibres.

Soil burial test

Biodegradability of the composite was studied by soil burial test. It revealed that the CPH/PVA composite films are biodegradable in nature environment. It achieved the highest ~53.77% reduction after 15 days exposed to environmental condition. The size of composite films had significantly diminished after 7-15 days of exposure in soil as shown in Figure 5 and 6. The films appeared in fragile and brittle after soil burial test. The degradation of composite film was examined by measuring its weight loss which can refers to the erosion of molecules from solid phase [2]. From Figue 4, it is clear that samples with higher fibre loading had the higher weight changes after both 7 and 15 days. This may due to the higher filler loading than the polymer content make it easier to degrade in soil. However, the weight changes were probably undersestimated as there was some soil debris strongly adhered to the film surface which unable to rinse off. Meanwhile, Table 2 presented the effect of fibre modification on the degradation rate of composite film. It founds that the film formed by modified CPH fibre has a better weight changes compare with the film withou any chemical modification.

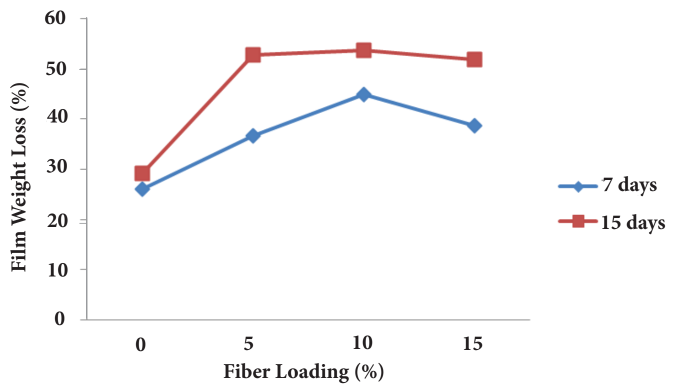

Figure 3: Film Weight Loss (%) of Modified CPH/PVA Films After 7 & 15 Days Soil Burial Test

Table 2 Effect of NaOH Fibre Modification on Biodegradability of Films

CPH Loading(%)	Weight Loss After 15 Days (%)	
	Without Modification	NaOH Modification
5	30.46	52.86
10	35.93	53.77
15	33.62	51.81

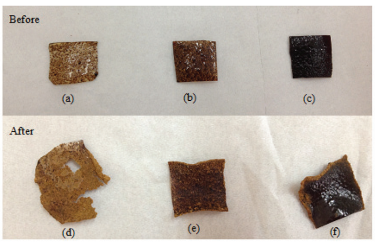

Figure 4: Modified CPH/PVA composite films after soil burial test for 7 days: Before test (a) 5% CPH, with glycerol; (b) 10% CPH, with glycerol; (c) 15% CPH, with glycerol; After test (d) 5% CPH, with glycerol; (e) 5%CPH, with glycerol; (f) 10% CPH, with glycerol

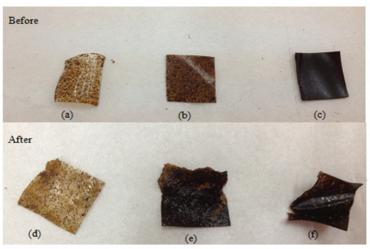

Figure 5: Modified CPH/PVA composite films after soil burial test for 15 days: Before test (a) 5% CPH, with glycerol; (b) 10% CPH, with glycerol; (c) 15% CPH, with glycerol; After test (d) 5% CPH, with glycerol; (e) 5%CPH, with glycerol; (f) 10% CPH, with glycerol.

CONCLUSIONS

A simple route to study the potential uses of the waste cocoa pod husk from cocoa form was carried out. Composite film prepared from 5 wt% CPH powder plasticized with 10wt% glycerol achieved the excellent elongation percentage. However, the overall tensile strength of the composite films decreased after addition of glycerol. Weight loss after soil burial test revealed that the potential of CPH/PVA composite film to degrade in nature environmental condition. The basic advantage of this product is its good elongation for packaging purpose and its biodegradability which can ensures a safe disposal of waste plastic to our environment.

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REFERENCES

[1] H-S. Kim, H-J, Kim, J-W. Lee and I-G, Choi: Polym.Degrad. Stab Vol. 91(2006), p.117
[2] B.Ramaraj, P.Poomalai: J.Apply.Polym.Sci. Vol.102(2006), p.3862
[3] T.Ishigaki, Y.Kawagoshi, M.Ike and M.Fujita: World. J. Microb. Biot. Vol.15(1999), p.321
[4] R.Jayasekara, I.Harding.,I. Bowater., G.B.Y., Christie and G.T.Lonergan: Polym.Test. Vol. 23(2004),p.17
[5] S.Kalpajiam and S.R. Schmid: Manufacturing engineering and technology, 4th Ed. Prentice-Hall, Englewood Cliffs, NJ (2001), p.195
[6] W-L. Dai: Mater.Lett. Vol.57 (2003), p.3128
[7] C.Bastioli, V.Bellotti, L.D.Giudice, G.Gilli: J.Environ.Polym. Degr. (1993), p.1181
[8] T.Iwanami and T.Uemura: Jpn. J.Polym.Sc.Technol. Vol.50 (1993), p.767
[9] C.Bastioli, V.Bellotti, L.D.Giudice and G.Gilli: The Roy.Soc.Chem (1992), p.101
[10] G.G.D.Silva, P.J.A.Sobral, R.A.Carvalho, P.V.A.Bergo, O.Mendieta-Taboada and A.M.Q.B. Habitante: J.Polym.Environ Vol. 16 (2008), p.276.
[11] O.U.Eghosa, A.H.Rasheed, O.Martha and A.A.Luqman: Int. J. Sci. Natura Vol 1(2010),p.272
[12] F.Alemawor, V.P.Dzogbefia, E.O.J, Oddoye, J.H.Oldham: Sci.Rec. Ess Vol.4 (2009), p.555
[13] N.A.Adamafio, I.K.Afeke, J.Wepeba, E.K.Ali and F.O.Quaye: J.Sci. Vol.44 (2004), p.29
[14] A.A.Yussuf, I.Massoumi and A.Hassan: J.Polym.Environ. Vol.18(2010), p.422
[15] B.N.Dash, M.Sarkar, A.K.Rana, M.Mishra, A.K.Mohanty and S.S.Tripathy: J.Reinf. Plast. Comps. Vol 21(2002), p.1493
[16] A.K. Behera, S.Avancha, R.K.Basak, R.Sen and B.Adhilari: Carbohd Poly. Vol.88 (2012), p.329