HARDNESS AND MICROSTRUCTURE OF COCKLE SHELL POWDER FILLED RECYCLED POLYETHYELENE-TEREPHTHALATE/POLYCARBONATE BLENDS

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory committee is as follows:

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DR. MOHD EDEEROZEY BIN ABD MANAF

ABSTRACT

The aim of this study is to evaluate the hardness property and study the morphology of cockle shell powder (CSP) filled recycled polyethylene-terephthalate (PET)/polycarbonate (PC) blends. Firstly, all three materials were crushed into powder and pellet sizes before going into internal mixer for melt mixing and compounding process which will finally be pressed in the hot press mould. The hardness property of the composite was measured using Vickers Hardness Tester. The morphology of the composite was observed using OM and SEM to determine the failure behavior that occurred. The addition of 5 wt.% CSP showed increase in HV hardness value by 9.48 %. It was observed that an increase in composition of CSP increased the HV hardness value while decreasing the amount of porosity. From the SEM micrograph obtained, failures were caused by brittle properties of the composite with the abundant number of porosity.

ABSTRAK

Tujuan kajian ini dijalankan adalah untuk menilai sifat-sifat kekerasan dan mempelajari morfologi bagi komposit serbuk kulit kerang (CSP) yang dipenuhi dengan campuran polyethylene-terephthalate (PET)/polycarbonate (PC) yang telah dikitar semula. Pertama sekali, ketiga-tiga bahan telah dihancurkan sehingga menjadi bentuk serbuk dan saiz pelet sebelum dimasukkan ke dalam pengadun dalaman untuk menjalani proses pencampuran secara cair dan mengkompaun yang akhirnya akan ditekan dalam tekan acuan panas. Sifat-sifat kekerasan komposit tersebut telah diuji menggunakan Vickers Hardness Tester. Morfologi komposit itu telah diperhatikan melalui OM dan SEM untuk menentukan kegagalan yang berlaku. Penambahan CSP sebanyak 5 wt.% telah menunjukkan kenaikan nilai kekerasan sebanyak 9.48 %. Kajian membuktikan bahawa penambahan dalam komposisi CSP akan menaikkan nilai kekerasan sambil menurunkan bilangan keliangan. Melalui mikrograf yang diperoleh dari SEM, kegagalan telah berpunca dari sifat kerapuhan dan jumlah keliangan yang banyak dalam komposit tersebut.

DEDICATION

Every obstacle was faced with self efforts along with the guidance of elders especially those who are very close to my heart.

My humble effort I dedicate to my supervisor, Dr. Mohd Edeerozey bin Abd Manaf, for his infinite guidance and support in completing this research.

Along with my sweet and loving mother, Putiah binti Karmin, and my father, Mahmod bin Basar, whose affection, love, encouragement and prays of day and night made me able to obtain such success and honor.

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LIST OF ABBREVIATIONS

ABS	-	Acrylonitrile Butadiene Styrene
ABS-*g*-MA	-	Maleic Anhydride Grafted ABS
ASTM	-	American Society for Testing and Materials
CaO	-	Calcium Oxide
$CaCO_3$	-	Calcium Carbonate
CD	-	Compact Disc
CDM	-	Clean Development Mechanism
CNT	-	Carbon Nanotube
CS	-	Cockle Shell
CSA	-	Cockle Shell Ash
CSP	-	Cockle Shell Powder
DSC	-	Differential Scanning Calorimetry
E-EA-GMA	-	Ethylene-Ethyl Acrylate-Glycidyl Methacrylate
EFB	-	Empty Fruit Bunch
HDPE	-	High Density Polyethylene
HIPS	-	High Impact Polystyrene
IR	-	Infrared
JI	-	Joint Implementation
LOI	-	Limiting Oxygen Index
MF	-	Mesocarp Fiber
MOP	-	Molded Oil Palm
OM	-	Optical Microscopy
OPC	-	Ordinary Portland Cement
PC	-	Polycarbonate
PET	-	Polyethylene Terephthalate
PMMA	-	Poly(methyl methacrylate)
PP	-	Polypropylene

PVC	-	Poly(vinyl chloride)
SEBS	-	Poly(Styrene-b-Ethylene-b-Butylene-b-Styrene)
SEM	-	Scanning Electron Microscopy
SiO_2	-	Silicon Dioxide
TiO_2	-	Titanium Dioxide
UPR	-	Unsaturated Polyester Resin

LIST OF SYMBOLS

%	-	Percentage
wt. %	-	Weight
°	-	Degree
°C	-	Degree Celcius
mm	-	Milimeter
g/cm^3	-	Density
kJ/m^2	-	Charpy Impact Strength
MPa	-	Mega Pascal
GPa	-	Giga Pascal
ε	-	Elongation at Break
σ_t	-	Tensile Strength
E	-	Tensile Modulus

CHAPTER 1
INTRODUCTION

1.1 Background of Study

The trend nowadays in the industry is the increasing production of thermosets and thermoplastics globally. These plastic types are made in industrial factories, that have been running industrial activities for more than 150 years. Although the products are beneficial and are seen fit in the modern world with modern technology, the amount of greenhouse gas emitted by the factories are worrying. At the same time, pollution, whether it is air, land, or water pollution, has also been the main topic discussed around the world along with the global warming. However, many steps have been taken in order to preserve the environment while reaping benefits.

One of the many steps taken as a path to save the environment is called Kyoto Protocol. The Kyoto Protocol is an international agreement that sets emission reduction targets by the United Nations Framework Convention on Climate Change. Besides measuring the emission rate nationally, the Kyoto mechanisms include International Emissions Trading, Clean Development Mechanism (CDM), and Joint Implementation (JI). Every country will report the actual emissions with accurate recordings to the Protocol. Relating with the Kyoto Protocol is the Carbon Credit which is a financial instrument that provides a quota of one ton of carbon dioxide per company. Those who managed to reduce their greenhouse gases under the quota are awarded credits that can be traded legally.

Cockle shell (blood cockle) or its scientifically known as *anadara granosa* is one of the contributor in the aquaculture industry in Malaysia. The high demand from consumers in using the cockle in the food industry led to mass production of cockle factories that focuses on suckling processes (Othman et al., 2013). However, the unused shells are thrown away, possibly to landfills, and will pollute the environment due to its long decaying time. The shells, that are made mostly of calcium carbonate ($CaCO_3$), are seen as green technology that may replace the vast usage of plastics (Shafiu Kamba et al., 2013). In fact, many researchers have studied the effect of $CaCO_3$ obtained from the shells as replacement of certain materials such as partial coarse aggregate replacement in concrete (Muthusamy et. al, 2012).

The dominance of plastics worldwide is increasing in the last few decades and most products nowadays are made of plastics that will eventually goes to waste in landfills which then resulting in pollution. An increasing abundance of polyethylene-terephthalate (PET) and polycarbonate (PC) has led to displeasure in conserving the environment. Therefore, waste management is needed as a solution which includes recycling.

However, although the process of recycling would solve disposal problems and at the same time use natural resources which is cost-effective, recycled materials that are reprocessed into new products tend to provide lower properties than its origin. Hence, various materials are mixed in order to produce a product with better mechanical and thermal properties which is even comparable with its origin.

In this research, cockle shell is mixed altogether with recycled PET/PC through internal mixing. The effects of various cockle shell powder (CSP) composition on the mechanical properties of the composite such as tensile, impact, flexural, water absorption and thickness swelling is studied. SEM is used to analyze the fracture surface of the composite. At the same time, the effect of recycled PET/PC blend ratio on the thermal properties of the CSP/PET/PC composite is observed through DSC.

1.2 Problem Statement

The excessive amount of shell wastes that are made through shellfish agriculture will mostly be sent to be disposed in the landfills. These unused resources may lead to pollution that acts as a burden to the environments along the seashore. Hence, (Bugallo *et*. al, 2013) states that the shell wastes should be recycled where it could solve the disposal problems and allow the reuse of natural resources which results in benefits to the marine company.

The problem in the industry would be to find a better composite material that is to improve the properties of the cockle shell and reuse it as a recycled product. The mixing of cockle shell powder and recycled PET/PC blends would in some way show improvement of the thermal and mechanical properties when compared to the original materials according to its composition.

1.3 Objectives

This research is done to investigate the mechanical and thermal properties of cockle shell powder filled recycled PET/PC blends. The objectives of the research are as follows:

i. To evaluate the hardness properties of cockle shell powder filled recycled PET/PC blends at various cockle shell powder compositions.
ii. To study the microstructure properties of cockle shell powder filled recycled PET/PC composite.

1.4 Scope

The research concentrates on the effect of mixing cockle shell powder (CSP) with recycled PET/PC blends on the hardness property. CSP of composition 0%, 5%, 10%, and 15% are used as filler in the composite. PET/PC blend with constant percentage of composition weight is used as the polymer matrix. The CSP is first ground and cleaned before compounded in internal mixer with PET/PC blend. The research involves laboratory works that includes hardness test, and microstructure analysis through optical microscope (OM) and scanning electron microscopy (SEM).

1.5 Organization of Thesis

The thesis includes five chapters. The introduction and background of research is explained briefly in chapter 1, while the literature reviews are presented in chapter 2. Next is the chapter 3, which describes everything about the materials, fabrication, and characterization methods. Chapter 4 consists of results after the project is done including the discussions. Finally, chapter 5, states the conclusion obtained from the thesis along with suggestions for future works.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter consists of reviews on recycling of polymers and agricultural wastes. Previous studies obtained from journal are used as reference in explaining the production of recycled materials including its results. Processing of blending of polymers is also explained in this chapter. Different application of materials with different mixing is further elaborated.

2.2 Agricultural Wastes in Malaysia

Agricultural operations result in the production of wastes. These wastes are called agricultural wastes and it includes both organic and non-organic wastes. Agricultural wastes commonly exported by companies in Malaysia are palm-based products, fertilizers, coconut fibers and shells, wood saw dusts, and empty fruit bunch due to the geographical factors in Southeast Asia that consists of mainly tropical rainforests.

Among the primary agricultural crops in Malaysia that consists of oil palm, rubber, cocoa, rice, and coconut, only two resources that is mostly used which are oil palm and rubber (Mekhilef et. al, 2011). Oil palm biomass is contributed by empty fruit bunch (EFB) and mesocarp fiber (MF) that went through a process of heat and pressure in order to make molded oil palm (MOP). As a bio-based material, MOP is tremendously practical in industries that provide furniture, electronics, packaging, building, and also automobile applications. The amount of oil palm remains that could possibly generate energy is shown in Table 2.1.

Table 2.1: Types of biomass and quantity produced (Mekhilef et al., 2011)

Types of biomass	**Quantity/annum (MT)**
Empty fruit bunch (EFB)	15.8
Fronds	12.9
Mesocarp fiber (MF)	9.6
Trunk	8.2
Shell	4.7

Crops and manure as agricultural wastes that undergo anaerobic digestion are applied vastly in waste managing, energy production, energy recovery and decreasing greenhouse gas emission and pollution (Sadeghi *et.* al, 2015). Pig, poultry, and cow are the major wildlife fertilizers currently utilized for generating of energy. In order to prevent solid forms of animal manures causing harmful environmental effects, anaerobic digestion is done in fluid form.

2.2.1 Agricultural Wastes Recycling

The significance of biomass to be used as energy and material resources is affected by the increasing in expense of petroleum oil. Therefore, the benefits and also the probability of rice husk ask in conserving the environment are presently being focused as it represents high ash biomass wastes. Agricultural biomass waste has proved useful with better properties such as rate of adsorption, preventing wastewaters pollution at low price over the globe. Although the downside and problems have been met, there seems no sign of stopping this magnificent advance in this topic in the coming times (Foo & Hameed, 2009).

Nanosized calcium carbonate powder is prepared using shell wastes by a mechanochemical method which is through the process of high energy ball-milling in sodium hypochlorite solutions (Lu *et.* al, 2015). The study aims to recycle shell wastes as an eco-friendly high value-added products for industrial applications. From the results obtained, the solution used revealed the mineralizing role of high alkalinity during the milling process.

However, ball-stirring mills used in the powder engineering could be utilized to scale up the production of nanosized $CaCO_3$ powders from shell wastes.

2.2.2 Cockle Shell Wastes in Composite Material

A study was carried out to develop a composite material from agricultural wastes consisting of cockle shell ash (CSA) as replacement for cement and filler in concrete (Othman et al., 2013). Cockle shell should be contemplated as a biodegradable material in the steps of reduce, reuse, and recycle. Examples from previous studies are shown in Table 2.2. Type I Ordinary Portland Cement (OPC) that act as the primary binder is partially replaced with CSA in the composition of 5%, 10%, 15%, 25%, and 50%. Table 2.3 shows the mixture of proportions. From the results of tensile test as in Figure 2.1, it can be concluded that the percentage of increment in strength with high content of CaO in the CSA is the result of long curing period.

Table 2.2: Types of shells as a replacement material in concrete in Malaysia (Othman et al., 2013)

Type of shells	Replacement material in concrete	References
Clam	Fine aggregate	(Yusof et. al, 2011)
Cockle	Coarse aggregate	(Muthusamy et al., 2012)

Table 2.3: Concrete mix proportions (Othman et al., 2013)

Materials (kg/m^3)	OPC	CSA5	CSA10	CSA15	CSA25	CSA50
OPC	432	410.4	388.8	367.2	324	216
Cockle shell ash	0	21.6	43.2	64.8	108	216
Coarse aggregate	586	586	586	586	586	586
Fine aggregate	1089	1089	1089	1089	1089	1089
Water	233	233	233	233	233	233