CHARACTERISTICS AND PROPERTIES OF ACTIVATED CARBON FROM BAMBOO FILLED STYRENE BUTADIENE RUBBER (SBR) VULCANIZATES

by

NOR MUNIRAH BT ROHAIZAD

(1430411238)

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TABLE OF CONTENTS

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	Activated Carbon
ASTM	American Society for Testing And Materials
BCP	Bamboo Charcoal Powder
BET	Brunauer–Emmett–Teller
CB	Carbon Black
CC	Carbonized Coir
CHN	Carbon, Hydrogen, Nitrogen
CRI	Cure Rate Index
CSS	Cherry Seed Shell
DTG	Derivative Thermogravimetric
E_B	Elongation at Break
ENR	Epoxidized Natural Rubber
EPDM	Ethylene Propylene Diene Monomer
FTIR	Fourier Transform Infrared
M_{100}	Modulus at 100 % of Elongation
M_H	Maximum Torque
M_L	Minimum Torque
N330	Carbon Black
NBR	Acrylonitrile Butadiene Rubber
NR	Natural Rubber
phr	Part per hundred rubber
PKH	Palm Kernel Husk
SBR	Styrene Butadiene Rubber

SBR-AC	AC Filled SBR Vulcanizte
SBR-CGS	CB Filled SBR Vulcanizate
SBR-GV	Gum Vulcanizate
SBR-TOR	TOR Compatibilized SBR Vulcanizate
SEM	Scanning Electron Microscopy
Semi-EV	Semi-Efficient Vulcanization
t_{c90}	Cure Time
TGA	Thermogravimetric Analysis
TMTD	Tetramethyl Thiuram Disulfide
TOR	Trans-Polyoctylene Rubber
t_{s2}	Scorch Time
XRF	X-Ray Fluorescence

LIST OF NOMENCLATURES

CaO	Calcium oxide
CO_2	Carbon dioxide
CuO	Copper oxide
Fe_2O_3	Ferum (II) oxide
H_3PO_4	Phosphoric acid
K_2O	Potassium oxide
KBr	Potassium bromide
KOH	Potassium hydroxide
MnO	Manganese oxide
NaOH	Sodium hydroxide
P_2O_5	Phosphorus pentoxide
Pd	Palladium
SO_3	Sulfur trioxide
Si	Silica
SiO_2	Silica dioxide
ZnO	Zinc oxide
$ZnCl_2$	Zinc chloride

LIST OF SYMBOLS

%	Percentage
ºC	Degree Celcius
ºC/min	Degree Celcius per minute
Å	Armstrong
nm	Nanometer
µm	Micrometer
g	Gram
mg	Miligram
cm^{-1}	Per centimeter
mL/min	Milliliter per minute
Ib-in	Pound inch
mm/min	Milimeter per minute
kN	Kilo Newton
min	Minute
dN-min	Desi Newton minute
min^{-1}	Per minute
MPa	Megapascal
m^2/g	Meter square per gram
cm^3/g	Centimeter cube per gram

Pencirian dan Sifat-sifat Karbon Diaktif daripada Buluh Terisi Vulkanisat Getah Stirena Butadiena (SBR)

ABSTRAK

Dalam kajian ini, karbon buluh dan karbon diaktif (AC) buluh telah disediakan melalui proses karbonisasi dan proses pengaktifan kimia menggunakan kalium hidroksida (KOH) sebagai ejen pengaktifan. Proses karbonisasi dijalankan pada suhu karbonisasi yang berbeza (250, 450 dan 650 °C) pada kadar pemanasan 5 dan 15 º C / min. Semakin meningkat suhu karbonisasi, peratusan hasil menurun, walaubagaimanapon kandungan karbon meningkat. Luas permukaan BET karbon buluh meningkat dengan peningkatan suhu karbonisasi dan lebih banyak liang terbentuk seperti yang ditunjukkan dalam mikrograf SEM. Karbon buluh yang dihasilkan pada suhu 650 ºC dengan kadar pemanasan 15 ºC / min menunjukkan potensi yang paling tinggi untuk menghasilkan AC buluh, dan kemudiannya digunakan sebagai pengisi dalam sebatian SBR disebabkan oleh kandungan karbon yang lebih tinggi dengan luas permukaan BET lebih besar. Seterusnya, karbon buluh dan karbon diaktif buluh terisi sebatian SBR (SBR-CGS dan SBR-AC) dengan pelbagai kandungan pengisi dari 10 hingga 50 bahagian per ratus getah (bsg) telah disediakan. Kesan kandungan pengisi terhadap ciri-ciri pematangan, sifat fizikal dan tegangan ditentukan. Hasil kajian menunjukkan penambahbaikan dalam ciri-ciri pematangan bagi kedua-dua vulkanisat SBR-CGS dan SBR-AC. Ciri-ciri fizikal bagi kedua-dua vulkanisat terisi SBR bertambah baik dari segi kenaikan dalam kekerasan dan susutan dalam daya tahan dengan kandungan pengisi yang meningkat. Selain itu, sifat tegangan untuk kedua-dua vulkanisat SBR-CGS dan SBR-AC juga meningkat di mana kekuatan tegangan dan modulus tegangan serta pemanjangan pada takat putus (E_B) meningkat. Kajian morfologi menunjukkan bahawa kedua-dua pengisi tersebar secara homogen dalam SBR vulkanisat, menyebabkan interaksi pengisi-getah yang baik dan seterusnya meningkatkan sifat tegangan. Perbandingan antara kedua-dua vulkanisat terisi SBR menunjukkan bahawa vulkanisat SBR-AC mempunyai sifat-sifat yang lebih baik daripada vulkanisat SBR-CGS disebabkan oleh keliangan pengisi AC buluh. Vulkanisat SBR-AC yang mengandungi 50 bsg AC buluh mempamerkan sifat-sifat optimum dan sebatian tersebut dipilih untuk ditambah dengan *trans-polyoctylene rubber* (TOR) sebagai bahan penyerasian. Kemasukan TOR ke dalam vulkanisat SBR-AC menunjukkan sedikit kenaikan dalam kekuatan tegangan dan pengurangan dalam kekerasan dan modulus tegangan dengan peningkatan kandungan bahan penyerasian dari 2 hingga 8 bsg.

Characteristics and Properties of Activated Carbon from Bamboo Filled Styrene Butadiene Rubber (SBR) Vulcanizates

ABSTRACT

In this study, carbonized bamboo and bamboo activated carbon (AC) were prepared via carbonization process and chemical activation process using potassium hydroxide (KOH) as activating agent. Carbonization process was conducted at different carbonization temperature (250, 450 and 650 ºC) with heating rate of 5 and 15 ºC/min. As carbonization temperature increased, the percentage of char yield decreased, however the carbon content increased. The BET surface area of carbonized bamboo increased with increasing carbonization temperature and more pores were created as shown in SEM micrographs. Carbonized bamboo produced at 650 ºC with heating rate 15 ºC/min showed the highest potential to produce bamboo AC, subsequently used as filler in SBR compounds owing to its higher carbon content with higher BET surface area. Next, carbonized bamboo and bamboo activated carbon filled SBR (SBR-CGS and SBR-AC) compounds with varying filler loading from 10 to 50 part per hundred rubber (phr) were prepared. The effects of filler loading on the cure characteristics, physical and tensile properties were determined. Results showed that the improvement in cure characteristics for both SBR-CGS and SBR-AC vulcanizates. The physical properties of both filled SBR vulcanizates improved in terms of increment in hardness and decrement in resilience as the filler loading increased. Besides, the tensile properties for both SBR-CGS and SBR-AC vulcanizates also enhanced which the tensile strength and tensile modulus as well as elongation at break (E_B) increased. The morphology studies showed that both filler dispersed homogeneously in SBR compounds, resulted in good filler-rubber interaction and consequently improved the tensile properties. Comparing both filled SBR vulcanizates, it showed that SBR-AC vulcanizates have better properties than SBR-CGS vulcanizates due to the porosity of bamboo AC filler. SBR-AC vulcanizate with 50 phr of bamboo AC exhibited optimum properties and was selected to be added with trans-polyoctylene (TOR) as compatibilizer. Incorporation of TOR into SBR-AC vulcanizates showed slightly increment in tensile strength and reduction in hardness and tensile modulus as the compatibilizer loading increased from 2 to 8 phr.

CHAPTER 1

INTRODUCTION

1.1 General Background

Carbon black (CB) is mainly used in rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs and improvement in processing (Pal et al., 2011). Meanwhile, for thermoplastics products, CB are used as ultraviolet stabilizer, electrical conductor and also used to increase weather resistance and improve mechanical properties of the composites.

It was expected that the global carbon black market was projected to reach 12.2 million metric tons in 2015 according to the "Carbon Black: A Global Strategic Business Report". The largest consumer was Asia-Pacific which contributes 37% of total production of carbon black. About 90% of carbon black is used in the rubber industry as reinforcing filler in a variety of products including tires, tubes, cables and other rubber goods ("Carbon Black - World Consumption," n.d).

In rubber technology, the mixing of filler is extremely important especially for the synthetic rubber such as styrene butadiene rubber (SBR), ethylene propylene diene monomer rubber (EPDM) and others. The addition of filler produces improvements in mechanical properties such as tensile strength, tear resistance, abrasion resistance and modulus (Long, 1985). Reinforcing fillers like CB must be added to the SBR to develop the best properties because SBR has low strength due to the fact that SBR does not crystallize on stretching unlike NR (Schwartz, 2002). For example, the strength of vulcanized unfilled styrene butadiene rubber (SBR) is about 2.0–3.0MPa. But when reinforcing carbon black is added (40–60 pphr) into the rubber, the tensile strength increases by a factor of 10 to 27–30 MPa (Azemi, 2013).

It is well known that CB is the most effective reinforcing filler for the rubber composites (Mai & Yu, 2006). It is available in a variety of grades, each grade having different physical and chemical characteristics and therefore affording a different property profile to rubber. The highly reinforcing carbon black fillers are generally small in particle size, chemically active and have surfaces which are both porous and very irregular in shape (Hewitt & Ciullo, 2007). These characteristics are desirable to maximize the surface area of contact between rubber and filler.

In many years, a lot of researchers have gained interest in using natural fibers or biomass as to replace commercial filler that is CB in rubber compound. Numerous studies have been done to produce alternative CB from inexpensive, obtainable and renewable raw materials such as bagasse (Osarenmwinda & Abode, 2010), coconut shell (Egwaikhide et al., 2008), coir (Aguele & Madufor, 2012), kernel husk (Egwaikhide et al., 2013) and others. The reason of using natural fibers is because they have high carbon content and low ash content. Though, there are not many reports on the utilization of activated carbon (AC) as filler in rubber compounding which might have potential in replacing commercial carbon black. This is due to the fact that most of the applications of AC are employed as adsorbent since AC is well-known as porous materials with high surface area. Therefore, in this study, AC from *Gigantochloa Scortechiini* (bamboo) is produced by carbonization and chemical activation process and acts as bio-based filler in rubber.

1.2 Problem Statement

Carbon black (CB) may contribute greenhouse gas emission which is harmful to the environment. Besides, CB is relatively expensive since the main source of CB is petroleum which is limited and non-renewable resource. Therefore, biomass is used as cheaper alternative replacing commercial CB due to its availability and environmental friendly. There is a limited number of works that are concerned with the utilization of activated carbon from natural fibers or agricultural wastes especially *Gigantochloa Scortechiini* (bamboo) as bio-based filler for rubber compounding. It is needed to put additional effort to clarify the influences of activated carbon in rubber. For making better use of char obtained to produce activated carbon, the composition, surface area and pore structure should be investigated. Those char characteristics were influenced by carbonization conditions. Thus, the bivariate analysis was carried out to investigate the combined effect of carbonization temperature and heating rate on the char characteristic.

Due to the fact that the unfilled SBR has low strength, SBR needs filler for better properties. The performance of filled synthetic rubber may affect either by the rubber matrix itself or the filler that being incorporated into the matrix. The effects of filler may attribute to the particle size, structure and loading of the filler. Hence, the effects of filler loading on the cure characteristics and physical and tensile properties of SBR vulcanizates will be investigated in order to determine the optimum filler loading which gives better properties.

Nevertheless, the compatibility between natural fiber and rubber matrix might be not so good due to high moisture content in fiber that lead to agglomeration of filler, thus affect the properties of rubber vulcanizate. Therefore, incorporation of compatibilizer may improve the interaction between filler and rubber.

1.3 Objectives

The aims of the study were:

1. To determine the characteristics and properties of carbonized bamboo and activated carbon from *Gigantochloa Scortechiini* (bamboo) at different parameters of carbonization; carbonization temperature and heating rate using CHN, BET, XRF, and FTIR analysis.
2. To examine the effects of filler loading on the cure characteristics, physical and tensile properties and morphology of carbonized bamboo and bamboo activated carbon filled SBR vulcanizates.
3. To evaluate the effects of trans-polyoctylene rubber (TOR) as a compatibilizer on the cure characteristics, physical and tensile properties and morphology of compatibilized SBR vulcanizates.

1.4 Scope of Study

In this research, the production of bamboo activated carbon (AC) was carried out via chemical activation method. The process involved the carbonization and activation. The raw materials underwent the carbonization process by varying the carbonization temperature (250, 450 and 650 °C) and heating rate (5 and 15 °C/min). Several analyses were carried out to analyze the carbonized bamboo. The characterizations performed includes physical characteristics like surface area; chemical characteristics such as elemental analysis and thermal analysis and also morphology.

Based on the characteristics of the carbonized bamboo, carbonized bamboo produced at 650 °C and 15 °C/min was selected to be activated. The carbonized materials were impregnated with activating agents. Potassium hydroxide (KOH) was used as activating agent. Then, the activation process took place which the carbonized materials burnt in furnace at operating parameters of 700 °C and 15 °C/min.

The next stage involves the compounding of the filled SBR vulcanizates using carbonized bamboo and bamboo AC as fillers. The optimum loading of filler for the filled SBR vulcanizates was identified by considering the best properties exhibited and then trans-polyoctylene rubber (TOR) was added as a compatibilizer. The incorporation of TOR is to improve the filler-rubber interaction, yet enhance the properties of the vulcanizates.

1.5 Structure of Thesis

This thesis is divided into eight chapters.

Chapter 1 included a brief introduction on carbon black and its reinforcement effect in rubber. The issues of production of CB commercially and its drawbacks generate the ideas and energies to this research work were stated. The main objectives and the general flow of the whole study were also carefully outlined.

Chapter 2 comprised literature review on the reinforcement of CB and bio-based filler in both natural and synthetic rubbers. A literature survey was done on various published works on commercial CB and carbonized agricultural wastes filled in rubbers.

Chapter 3 covered the methodology of the experimental employed in this study, including characterization of materials, testing on the vucanizates as well as any other processing techniques involved in generating data that were presented in the study.

Chapter 4 presented the characteristics of raw bamboo (*Gigantochloa Scortechiini*), carbonized bamboo and bamboo activated carbon. All the characteristics including physical, chemical characteristics and surface morphology were reported.

Chapter 5 reported the effects of carbonized bamboo filler loading on the cure characteristics, physical and tensile properties and morphology of the filled SBR vulcanizates.

Chapter 6 encompassed the effects of bamboo activated carbon filler loading on the cure characteristics, physical and tensile properties and morphology of the filled SBR vulcanizates.

Chapter 7 reported the effects of trans-polyoctylene rubber (TOR) as a compatibilizer on the cure characteristics, physical and tensile properties and morphology of the filled SBR vulcanizates.

Chapter 8 obtained some concluding remarks on the present work as well as several suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Gigantochloa Scortechiini (Bamboo)

In peninsular Malaysia, there are about 7 genera including 44 species in total. Common genera that can be obtained are *Bambusa, Chusquea, Dendrocalamus, Dinicloa, Gigantochloa, Phyllostachys, Racemobambos, Schizostachyum* and *Thyrosostachys*. Bamboo is kind of biomass material which is widely cultivated and can be easily obtained in rural area in Malaysia.

Gigantochloa Scortechiini (see Fig. 2.1) also known as *buluh semantan* is one of the wild species that is most widespread and useful. It can be obtained in the foothills of the peninsular’s mountain ranges and often spreads into disturbed lowland areas. It can be commonly found in the northern parts of the peninsular such as the Nami and Baling areas (Kedah), Slim and Grik areas (Perak) and also at Ulu Langat, Kanching and Ulu Gombak in Selangor (Wong, 1989).

Commonly bamboo is used to produce furniture, flooring and interior decoration materials. Unnoticeably, bamboo had potential to be a worth products in rubber composite industry. Therefore, this study on pyrolysis of bamboo would be very helpful in designation of manufacturing bamboo filled rubber composite.