SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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CARBONISATION OF DEAD LEAVES BIOMASS AS ACTIVATED CARBON FOR POTENTIAL APPLICATION AS REINFORCEMENT FILLER IN NATURAL RUBBER COMPOSITES
By
AIMAN BIN ZULKIFLI
Supervisor : Dr Raa Khimi Bin Shuib

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Carbonisation of Dead Leaves Biomass For Potential Application as Reinforcement Filler in Rubber Composites". I also declare that it has not been previously submitted for the award of any degree of diploma or other similar tittle of this of any other examining body or university.

Name of Student: Aiman Bin Zulkifli   Signature:

Date:

Witness by   Signature:

Supervisor: Dr Raa Khimi Bin Shuib

Date:

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
FESEM	Field Emission Scanning Electron Microscope
TGA	Thermogravimetric analyzer
M100	Modulus at 100% elongation
M300	Modulus at 300% elongation
Phr	Part per hundred
NR	Natural rubber
AC	Activated carbon
DLP	Dead leaves powder
DLP AC	Dead leaves activated carbon
TMTD	Tetramethyl thiuram disulfide
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
CB	Carbon black
MDR	Moving Die Rheometer
MPa	Megapascal

LIST OF SYMBOLS

%	Percentage
dNm	deciNewton meter
MH	Maximum Torque
Ts2	Scorch time
T90	Cure time
G	Gram
µm	Micrometers
s	Second
°C	Degree celcius

KARBONISASI DAUN MATI BIOJISIM BAGI POTENSI APLIKASI SEBAGAI PENGISI PENGUKUH DALAM KOMPOSIT GETAH

ABSTRAK

Projek ini mengkaji kesan biomas daun mati untuk aplikasi yang berpotensi sebagai pengisi tetulang dalam sebatian getah asli. Karbon diaktifkan dihasilkan dari biomas daun mati oleh teknik pirolisis menggunakan gas nitrogen sebagai medium pengaktifan pada suhu yang relatif berbeza (550, 700, 900 dan 1000 ° C). Untuk menghasilkan daun mati yang diaktifkan karbon, sampel dipanaskan pada kadar pemanasan 20 ° C / min hingga suhu karbonisasi akhir. Karbon diaktifkan dicirikan oleh analisis saiz zarah, FESEM, EDX, Spektroskopi Raman dan ketumpatan karbon diaktifkan ditentukan dan dibandingkan dengan karbon hitam. EDX menunjukkan bahawa daun mati yang diaktifkan karbon yang dihasilkan pada 1000 ° C mempunyai kandungan karbon tinggi dengan kandungan oksigen rendah berbanding dengan suhu karbonisasi yang lain. Daun mati yang diaktifkan karbon kemudian digunakan sebagai pengisi dalam vulcanizate getah SMRL dan sifatnya dibandingkan dengan getah SMRL bertetulang hitam karbon. Pemuatan pengisi diubah pada 0, 5, 10 dan 15 phr. Pengiling bergulung dua bersaiz makmal digunakan untuk menghasilkan sebatian getah. Penyembuhan, sifat mekanik dan terma telah disiasat untuk menilai keberkesanan daun mati karbon diaktifkan sebagai pengisi tetulang untuk matriks getah. Telah didapati bahawa sebagai daun mati mengaktifkan peningkatan kandungan karbon dalam getah SMRL, ciri pengawetan menjadi lebih cepat. Didapati kekuatan tegangan, modulus 100%, modulus 300% dan kekerasan didapati berkurangan sebanyak 17%, 9%, 10% dan 5%. Walau bagaimanapun, pemanjangan pada rehat meningkat kira-kira 12% dengan meningkatkan daun mati kandungan karbon diaktifkan. Kestabilan termal sebatian getah diisi daun mati karbon diaktifkan adalah rendah. Kajian morfologi menggunakan SEM mendedahkan bahawa penyebaran karbon aktif dalam getah asli adalah kurang

baik. Walau bagaimanapun, interaksi antara matriks pengisi dan getah meningkat apabila kandungan karbon diaktifkan meningkat.

CARBONISATION OF DEAD LEAVES BIOMASS AS ACTIVATED CARBON FOR POTENTIAL APPLICATION AS REINFORCEMENT FILLER IN RUBBER COMPOSITES

ABSTRACT

This project studies the effect of the dead leaves biomass as activated carbon (DLAC) for potential application as reinforcement filler in SMRL rubber. The DLAC was produced from dead leaves biomass by pyrolysis technique using nitrogen gas as the activation medium at different temperatures (550, 700, 900 and 1000 °C). The dead leaves activated carbon were prepared by heating at a heating rate 20 °C/min to the final carbonization temperature. The activated carbon were characterized by particle size analysis, FESEM, EDX, Raman Spectroscopy and density and compared with carbon black. EDX showed that the dead leaves activated carbon produced at 1000 °C have high carbon content with low oxygen content compared to other carbonization temperatures. DLAC at 1000 °C was then used as filler in SMRL rubber vulcanizate and the properties were compared with carbon black filler. The filler loading was varied at 0, 5, 10 and 15 phr. The two roll mill was used to produce the rubber compound. Curing, mechanical and thermal properties were investigated to assess the effectiveness of the dead leaves activated carbon as reinforcement filler for rubber matrix. The curing characteristics become faster, the tensile strength, modulus 100%, modulus 300% and hardness were found to decrease and elongation at break increased about 12% with increasing the dead leaves activated carbon content. The thermal stability of rubber compound filled dead leaves activated carbon was low. Morphological studies using SEM revealed that the dispersion of activated carbon in natural rubber was poor. However, interaction between filler and rubber matrix increased as the activated carbon content increased.

CHAPTER ONE

INTRODUCTION

1.1   Overview

Biomass resources can be derived from various natural sources such as wood and herbaceous species, agricultural and industrial residues, municipal solid waste, sawdust, bio solids, grass, animal wastes, aquatic plants and algae (Özçimen and Ersoy-Meriçboyu, 2010).Nowadays , there a lots of abundant dead leaves on the ground. Qin Li, (2013) stated that, the plant biomass is the most abundant organic materials on earth which has enormous potential as a feedstock for the production of activated carbon. The attractiveness of plant biomass has increased in recent years due to rapid depletion of conventional fossil fuels and growing concerns of environmental pollution and climate change.

Activated carbon is a microcrystalline form of carbon with high porosity and surface area. It may be visualized as foam solid that has a large surface within a rigid granule or particle structure of relatively small volume. Its chemical structure allows it to preferentially adsorb organic materials and other nonpolar compounds from gas or liquid streams (Lumadede, 2002).

Activated carbon is obtained from a carefully controlled process of carbonization of organic substances. It can be prepared for research in the laboratory from a large number of materials. However, the most commonly used ones in commercial practices are peat, coal, lignite, wood and agricultural by-products such as coconut shell, almond shell, rice husks, etc. (Balcı, 1992).

The pyrolysis of starting material with the exclusion of air and without addition of chemical agent usually results in an inactive material with a specific surface area and low adsorption capacity. One can prepare a carbon with a large adsorption capacity by activating the carbonized products with a reactive gas. The majority of activated carbon used throughout the world is produced by steam activation (physical activation).

Based on research conducted by Zhang *et al*, (2015), the activated carbon from the dead leaves biomass can be used as a partial replacement for carbon black in synthetic rubber. Moreover, McDonald-Wharry *et al.* (2015) said, the activated carbon have a lots of potential when it is blended with rubber . The activated carbon based filler increases the thermal and resistance to biological degradation. It also increases the electric conductivity, stiffness and hardness of the rubber composites. This potential can be achieved if the char being completely carbonize to produce high purity carbon based products.

The production of activated carbon from plant biomass are preferable as it is cheap and renewable natural. The natural rubber (NR) is known to exhibit numerous outstanding properties, such as high tensile strength and the ability to crystallize under strain and high resilience when reinforcing fillers are added. Activated carbon may become suitable substitute as filler for rubber composite where carbon black are currently dominant or combine with them to produce hybrid reinforcement for NR.

The main objective on this research was to produce the activated carbon made from dead leaves biomass by using carbonization process and to assess the potential of dead leaves activated carbon as reinforcing filler for rubber composites.

1.2   Problem Statement

The petroleum industry is one of the areas which has great effects on the environment through the consumption of fossil fuels in the manufacturing of fuel, chemicals and materials. The production of carbon black from petroleum is in billions of tons and has been depended on for decades. It can be found in rubber tire industry which consume lots of carbon black. Therefore, it is necessary for a transition from the use of carbon black filler to more renewable, sustainable and environmentally friendly filler to take place in order to help reduce the consumption of petroleum and reduce the emission of greenhouse gases. This holistic approach will help to protect the environment at the long run.

Commercially available carbon blacks are obtained from thermal cracking of natural gas and furnace black produced by incomplete combustion of oil filled stocks. This carbon black is relatively expensive due to its dependence on dwindling supply of crude oil. Therefore it is essential to develop viable alternative source of fillers from renewable resources such as agricultural waste, bamboo stem, dead leaves and coconut shells which are carbonaceous in nature and rich in organic materials. This biomass can be converted into carbon thereby reducing unwanted, low value agricultural reduces and underutilized crop into useful, high value materials. Activated carbon from dead leaves biomass are biodegradable and non-toxic They are an abundant resource, highly available, renewable, and can lead to cost effective production.

In addition, the properties of the fillers is mainly dependent on the particle size and surface chemistry of the filling agents. Carbon black, silica, clay, whitings (chalk), calcium carbonate (Brostow et al., 2016; Medalia, 1978; Poh et al., 2002) are some of the commonly used fillers. Among these carbon black is dominant due to the smaller

particle size wide range of grades, and specific level of structures (Vojislav et al., 2010). Nowadays, the use of carbon black in rubber industry is restricted since they have been classified as Group 2B carcinogenic agent, which is possibly carcinogenic to human beings (Baan, 2007; Sorahan and Harrington, 2007). This is mainly due to their poor solubility, which extends the retention time thereby increasing the negative impact. Many inorganic and organic types of filler have been reported to replace the toxic effect of carbon black without compromising the quality (Rattanasom et al., 2007). In this study, dead leaves biomass has been taken as source for the preparation of activated carbon. However, the use of dead leaves to derive a commercially important product has not been explored much.

1.3   Research Objective

This study embarks on the following objectives ,

- To identify the methods to carbonize the dead leaves biomass into a activated carbon as reinforcing filler.
- To investigate the effect of the dead leaves activated carbon as a reinforcing filler on the mechanical and thermal properties of natural rubber composites.

CHAPTER TWO

LITERATURE REVIEW

2.1   Biomass

Biomass is a complex biological organic solid products derived from living or recently living organism and available naturally. Various types of wastes such as animal manure, waste paper, sludge and many industrial wastes are also treated as biomass that can be processed to get energy. Biomass materials are traditionally used as resource materials to extract valuable chemicals, but more recently they have been considered as a sustainable substitute for fossil fuels in the energy sector. Sustainability in energy recovery from biomass is becoming attractive because biomass to energy conversion adds no additional greenhouse gases effect to the atmosphere (Strezov *et al.*, 2007).

The biomass is one of the most promising sources of alternative energy which can solve the problem of the energy crisis in the world up to some extent due to its potential availability. Moreover, the use of biomass can reduce the problem of global warming and pollution. It is the only renewable energy source which can be converted into three different forms: solid fuel, liquid fuel and gaseous fuel (Tripathi *et al.*,2016)

Özçimen and Ersoy-Meriçboyu (2010) said, the renewable energy is a kind of energy produced from any source that can be maintained in a constant supply over time. The most important renewable energy sources can be classified as solar, wind, hydro, geothermal, wave and biomass. Among these sources, the biomass is considered as an important one since it could be a suitable alternative for conventional fossil fuels. Unlike solar, wind and hydroelectric systems, modern biomass energy

systems could be set up in virtually any location where plants can be grown or domestic animals are reared. This is one of the most important properties of the biomass energy in which it differs from other renewable energy systems and it offers an opportunity for sustainable energy. Among renewable energy sources, biomass is the only energy source that can be used without any energy storage systems. Plants use and store CO_2 when they grow. CO_2 stored in the plant is released when the plant material is burned or decays. By replanting the crops, the new plants can use the CO_2 produced by the burned plants. Therefore using biomass and replanting helps to close the carbon dioxide cycle. However, if the crops are not replanted, then excessive release of carbon from biomass resulting in global warming issue

Lignocellulosic biomass is the most abundant organic materials on earth, which has enormous potential as a feedstock for the production of fuel, heat and electrical power. The attractiveness of lignocellulosic biomass has increased in recent years due to the rapid depletion of conventional fossil fuels and growing concerns about environmental pollution and climate change (Liu and Balasubramanian, 2012).

The conversion of biomass into the energy can be made mainly by two methods. One is biochemical conversion and the other is thermochemical conversion. In the biochemical conversion, biological catalysts and organisms are used to get the energy-rich products from the biomass and produce the ethanol. Is thermochemical conversion technique, heat and chemical catalysts are used to produce the energy. The product obtained from the thermochemical conversion are bi-oil, biochar and gases. One of the major challenges in biochemical technique is the rapid conversion of biomass into the energy efficiently. The limitation of biochemical technique such as has diverted the researchers towards the thermochemical techniques (Tripathi *et al.*,2016).

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2.2   Activated Carbon

Activated carbon can be produced by a variety of raw materials from animals, vegetables, and minerals. There are two main sources in the production of activated carbon namely coal and agricultural wastes or lignocellulosic materials. Commercially, activated carbon is derived from non-renewable resources starting material such as petroleum residues, wood, coal, peat and lignite which are very expensive . Therefore, agricultural waste are preferable as a starting material for activated carbon production . This is because the use of agricultural by-products as activated carbon precursors has also been found to be renewable and relatively less expensive which can give a lots of advantages in future .

Activated carbon also known as activated charcoal which basically refer to a carbon-based material that has been processed and is widely used as adsorption media or adsorbent in water technology. It is used to remove diverse, dissolved contaminants from water and process gas-phase streams and widely used as adsorbent due to its high porosity with the extremely large surface area, high physicochemical stability, high adsorptive, high mechanical strength and a high degree of surface reactivity (Yahya et al. 2015).

There are several factors that would influence the performance of the activated carbon. Some of the factors include the type of starting materials or precursors , carbonization methods for the preparation of activated carbon and treatment conditions such as temperature and time of its activation. Although type of precursors is known to be the most important thing in influencing the quality, characteristics and properties of activated carbon, other factor like methods used for the preparation of activated carbon and treatment conditions also need to be consider as it plays an important role in affecting the properties and quality of the activated carbon. The performance and pore

characteristic of activated carbon are greatly depends on the physical and chemical properties of precursors as well as on the activation technique (Ahmed , 2016).

Agricultural by-products offer an inexpensive and renewable additional source of activated carbon. These by-products have less or no economic value and often present a disposal problem. Therefore, there is a need to restraint these low cost by products. Thus, conversion of agricultural by-products into activated carbon would add considerable economic value and help to reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbon (Demibras, 2009). In another word, it could ultimately utilize the waste effectively into wealth. Therefore, in recent years, the production of activated carbon have been focusing by using agricultural by-products such as corncob, hazelnut shell, olive stone, coconut shell, wood, bamboo, rice husk, coconut husk and sugarcane bagasse.

Producing activated carbon from plant biomass offer many advantages, for example, the precursors are diverse, abundant, and renewable, the synthesis is a process relatively simple due to the high reactivity of the biomass and it contributes to decreasing costs of waste disposal and the negative impact to the environment. Nonetheless, one of the most significant advantages of using renewable and waste materials derived from agro-industrial crops waste lies on the possibility of obtaining functional materials such as electrodes, catalysts, fertilizers, liming and neutralizing agents, and adsorbents of certain elements and compounds from water and air (González-García, 2018).

Low yield of activated carbon derived from agricultural by products is expected due to its low carbon contents available as compared with coal or peat. However, due to its low cost, it gives significant impact more than its lower yield (Yahya et al. 2015).

2.3 Char, Biochar and Hydrochar

Chars and carbonized chars produced from lignocellulosic biomass also known as ''biocarbons'' are being investigate for a wide range of applications and potential applications (Jenkins GM and Kawamura K, 1976). Based on (Mcdonald-wharry, 2014), the term "biochar" is said to have been coined by Peter Read of the Centre of Energy Research at Massey University, Palmerston North. Peter Read has been trying to replace the commonly miss used term "charcoal "with "biochar" for the carbonaceous materials made from recent biomass, probably to avoid confusion with coals. In some circles the term "biochar" is only used for biomass-derived carbonaceous materials that are applied to soil or used to sequester carbon, specifically excluding those biomass-derived chars used for fuel or metallurgy and a story goes that the term "agrichar" is going to be commonly used until it was found to have been trademarked.

The bio-chars and carbonized biomass are black solid materials produced through thermal conversion of biomass (wood, leaves, and a range of mostly plant materials) usually in a low oxygen or anoxic environment. This heating removes most of the mass and preferentially removes hydrogen and oxygen content as various liquid and gaseous pyrolysis products. Özçimen and Ersoy-Meriçboyu, (2010) characterized the biochar products into carbon-rich, high heating value and relatively pollution-free potential solid biofuels.

Hydrochar is define as the solid product of hydrothermal carbonization (HTC) or liquefaction. It is distinct from biochar due to its production process and properties, and typically has higher hydrogen to carbon ratios and lower aromaticity than biochar as well as little or no fused aromatic ring structures.

Nowadays, the world is more concerned about the use of hydrochar as a fertilizer and sequestrate carbon to prevent the climate change. The advantages of hydrochar to elevate soil fertility include: rise in pH, buffer capacity, and cation exchange capacity (CEC). It also helps in increasing soil nutrients and ameliorates the physical structure of the soil. Relatively high carbon content in hydrochar is responsible for mitigating climate change, which slows down the release of carbon dioxide into the atmosphere. The use of hydrochar depends upon its immanent properties. For example, adsorption power highly depends on the surface area of hydrochar. The hydrochar with high pH, CEC, and water holding capacity are suitable to use as a soil amendment to increase fertility (Saqib *et al.*, 2017) .

2.4   Carbonization Process

Carbonization consists of two basic steps to produce activated carbon from lignocellulosic biomass. The first step is carried out by pyrolysis of the precursors in an inert atmosphere at elevated temperatures to produce a solid known as char and then proceed to activation process with N_2 and CO_2 gas to produce activated carbon (Lua et al., 2006). The purpose of activation is basically to develop further porosity and creating some ordering of the structure which results in a highly porous solid of the activated carbon. The carbonization is a phase to increase the carbon content in the carbonaceous material by eliminating non-carbon species using thermal decomposition (Daud et al., 2000). Normally, higher temperatures (600–700 ◦C) reduced the yield (Houache1 et al., 2008). Higher temperatures also increases ash and fixed carbon contents and reduce the amount of volatile matter (Putun et al., 2005). During the carbonization process, the feedstock will experiences a diversity of molecular changes, including mass loss, change in structure, increase in pH and alkalinity.(Vassilev, Vassileva and Vassilev, 2015)

Based on Saqib et al., (2017) , converting the lignocellulosic biomass into biochar is the technique to produce reasonable energy. There are three different processes to convert lignocellulosic feedstock into biochar. They are a biochemical process, hydrothermal process, and thermochemical process.

The biochemical process, in which cellulosic and hemicellulosic sugar is converted into alcohol with the help of enzyme and microorganism. Next, the hydrothermal carbonization is a process that converts lignocellulosic feedstock into a useful product. Municipal solid waste components and biomass are converted into a carbon-rich product termed as hydrochar . The carbon-rich product was achieved by hydrothermal carbonization (HTC) of dead leaves at different treatment temperatures of 200–250 °C (Saqib *et al.*, 2017).

Furthermore , hydrothermal treatment offers significant advantages for biomass conversion including the lack of an energy extensive drying process, high conversion efficiency and relatively low process temperature among thermal methods. In Liu & Balasubramanian, (2012) previous study, the hydrochar has high energy density and its fuel quality was similar to that of lignite. Application of hydrochar provides some advantages and a possible option for biomass energy recovery. When lignocellulosic biomass and other carbohydrate-based or oxygen-rich precursors are carbonized, the materials properties will increase drastically such as electrical conductivity, hardness, and elastic modulus typically occur between HTTs of 300 and 1000 °C (McDonald-Wharry et al., 2013).

Pyrolysis is one of the thermochemical technologies used to convert the biomass into energy and chemical products consisting of liquid bio-oil, solid biochar, and pyrolytic gas. Depending on the heating rate and residence time, biomass pyrolysis can be divided into three main categories which slow conventional, fast and

flash pyrolysis which mainly aiming at maximizing the bio-oil and biochar yields. Various parameters influence the biomass pyrolysis process , these include the biomass type, biomass pre-treatment (physical, chemical, and biological), reaction atmosphere, temperature, heating rate and vapor residence time. Biomass pyrolysis with a long history of use, initially for the production of charcoal (biochar), has emerged as a frontier research domain.

Biomass pyrolysis is generally defined as the thermal decomposition of the biomass organic matrix in non-oxidizing atmospheres resulting in liquid bio-oil, solid biochar, and non-condensable gas products. Slow pyrolysis, termed carbonization, has been conventionally applied for the production of charcoal (Kan et al., 2016). Slow pyrolysis is having a long history of being used for the production of charcoal. It is the conventional type of pyrolysis which is characterized by slow heating rate and long residence time. In slow pyrolysis the biomass is pyrolyzed up to a temperature of the order of 400–500 °C with a heating rate of about 0.1 to1 °C/s for a time ranging between 5 and 30 min. Slow pyrolysis favours the formation of char but liquid and gaseous products are also formed in a small quantity. In slow pyrolysis, lower heating rate and longer vapour residence time provides a suitable ambiance and sufficient time for the secondary reactions to complete. Moreover, longer vapour residence time allows those vapours to be removed which are produced during the secondary reaction. This ultimately results is the formation of solid carbonaceous biochar (Tripathi et al., 2016).

In fast pyrolysis the biomass is heated up to a temperature of 850–1250 °C with a heating rate of 10–200 °C for a short span of time varying between 1 and 10 s. Fast pyrolysis is used for the production of bio-oil as the oil product yield in fast pyrolysis dominates to the char and gaseous product yield. A typical fast pyrolysis produces 60–75% of the liquid product, 15–25% of biochar and 10–20% of non-condensable

gaseous products. The main idea in fast pyrolysis is to take the biomass up to a temperature at which thermal cracking can take place as well as minimize the exposure time which favors the char formation. The high heating rate involved in the fast pyrolysis converts the input biomass to the liquid product before it could react to form the undesired char. The bio-oil produced by the fast pyrolysis is highly corrosive because of its low pH value. High heating value of this oil is approximately half of that of crude oil, which makes the upgrading of bio-oil necessary before using it. Fast pyrolysis process nowadays is being employed in few other applications like the production of food flavors or for the production of certain chemicals (Tripathi et al., 2016).

Flash pyrolysis can be considered as an improved and modified form of fast pyrolysis. In fast pyrolysis, the temperature required for the degradation of the components of biomass is achieved by heating it with a very high rate of the order of 1000 °C/s or sometimes even higher than that. The temperature achieved in the flash pyrolysis is between 900 and 1200 °C and the heat pulse is given to the biomass lasts for a very short amount of time which is 0.1– 1s. Heat and mass transfer process along with chemical kinetics of the reactions and phase transition behaviour of the biomass plays a crucial role in the product distribution in flash pyrolysis. The rapid heating rate combined with high temperature and low vapour residence time leads to high liquid yield but the char yield gets decreased. The biggest challenge to use flash pyrolysis on the industry scale is to configure a reactor for flash pyrolysis in which the input biomass can reside for a very short amount of time under the extremely high heating rate. The problem in flash pyrolysis reactors is of the stability and quality of the bio-oil as it is strongly affected by the ash present in the product. Not only this, the char present in the bio-oil can catalyze the polymerization reaction inside the liquid product causing an increase in the viscosity of the oil .

Table 2.1 shows the carbonization temperature range used to produce product from biomass by several researchers.

Table 2.1: Temperature used to covert dead leaves biomass into char

Temperature (°C)	Product	References
200 – 250	Hydrochar	(Saqib *et al.*, 2017)
150 - 375	Hydrochar	(Liu and Balasubramanian, 2012)
700 - 1000	Non-graphitisable carbons	(McDonald-Wharry et al., 2013)
400 - 850	Activated carbon	(Adekunle & Farid, 2015)
400	Black charred	(Mcdonald-wharry, 2014)
1000	Well-carbonized black charred	(Mcdonald-wharry, 2014)

2.4.1 Physical Activation

In general, there are two different methods in the production of activated carbon. According to the Kazmierczak-Razna *et al* (2015), it can be either by physical activation or chemical activation. Both these methods have its own advantages and disadvantages and are responsible for the production of good quality activated carbon. In physical activation, basically there are two-stage processes which are carbonization of precursors in neutral gas atmosphere followed by activation by steam or carbon dioxide of carbonized obtained. According to Yahya et al (2015), it is basically reffered to dry oxidation which involves the reaction between the samples and gaseous (CO_2 and air), steam or mixture of gaseous and steam at a temperature reaching above 700

°C. CO_2 is the most commonly used because of the associated ease of handled and the activation process can be easily controlled at temperature around 800 °C. In addition , a greater uniformity of pore can be achieved with the activation using CO_2 as compared to steam. Based on Ioannidou and Zabaniotou (2007), carbonization temperature usually in the range between 400 – 850 °C while activation temperature generally around 600 – 900 ° C.

Yang et al. (2003) produced activated carbons from pistachio-nut shells, which are one type of lignocellulosic material, by a two-step physical methods. They investigated the optimization variables of operating parameters (temperature, activation time, soaking time, heating rate, gas flow rate) on the activated carbon pore structure. They found that the activation temperature, soaking time, CO_2 flow rate and heating rate during activation are the important parameters that affect the characteristics of the activated carbons obtained. Next, Yang et al. (2003) identified the optimum conditions to prepare the activated carbons with high surface area and pore volume. They examined the microstructure of the activated carbons by scanning electron microscopy while the Fourier transform infrared spectra showed the changes in the surface functional groups produced during the different preparation stages.

2.4.2   Chemical Activation

Chemical activation is known as a single step method for preparation of activated carbon in the presence of chemical agents. Chemical activation is carried out at lower temperatures and shorter times for activation of the material. The carbon yields obtained by chemical activation are higher than by physical activation with better pores structure. However, the large amount of chemical agents need to be recovered

after the process which might restrict its application due to environmental issues (Grima-olmedo *et al.*, 2016).

The production of activated carbon by chemical activation usually produces carbon with the high surface area. This method consists of impregnation of the precursor with a dehydrating reagent, such as $ZnCl_2$, H_3PO_4, $FeCl_2$ or potassium hydroxide (KOH), followed by carbonization process. It was found that , KOH reagent was to be more effective in creating porosity in chars due to the difference in the activation mechanism. The activated carbons prepared from KOH treatment have their specific uses, such as the removal of SO_2 from flue gas and halogenated HCs and pesticides in drinking water purification (Teng *et al.*, 2011).

Hu et al. (2001) used coconut shells and palm seeds as a starting materials to obtain activated carbons with the high surface area by simultaneous treatment with zinc chloride and carbon dioxide as the chemical and physical agents respectively. They observed that both the surface area and the mesopore content could be controlled by controlling the experimental parameters such as the $ZnCl_2$- to-raw material ratio, duration of exposure to the carbon dioxide atmosphere and temperature of activation. They found that the $ZnCl_2$-to-shell ratios above 1 produce yield high surface areas, and ratios above 2 resulted in high mesopores content. They investigated the adsorption capacity and nature of the porosity by adsorption experiments using adsorbates with different molecular sizes. They noticed that the capacities of the mesoporous activated carbon were much higher than those of microporous carbon for larger adsorbates, confirming the presence of large amounts of mesopores in the former.

Özer et al. (2002) produced activated carbon from sugar beet pulp treated with phosphoric acid (30%) and carbonized at different temperatures (300-500 °C) and time

(90, 120, 180, 300 min). It was obtained that, the BET surface area value of activated carbon increases with an increase in temperature and time of carbonization. The highest BET value, (104.6m2 /g) was obtained when carbonization temperature was 500 °C and carbonization time was 300 min.

2.5 Fillers

Fillers are defined as materials used in a rubber formulation to reduce the cost of compounding and improve the properties of rubber such as processing and mechanical properties. In fact, fillers can change one or more properties such as improve surface characteristic, optical properties, and colour. The most commonly used filler in rubber compounding are carbon black and non-black such as silica, calcium carbonate and clay (Kamal et al., 2009).

The dispersion of the filler in the rubber matrix is one of the most important processes that needs to be achieved during the mixing process. Therefore, the dispersion of filler depend on filler-related parameters including filler size, filler shape, and structure of filler. Table 2.4 shows that as the particle size smaller, the surface area increases such that allows more effective reinforcement between rubber molecules and the filler particles (Thomas et al., 2013).

Table 2.2: Role of fillers according to particle size measurements (Thomas et al., 2013)

Particle size (µm)	Role of filler
>10	Degradants
1 to 10	Non-reinforcing
0.1 to 1	Semi-reinforcing
0.01 to 0.1	Reinforcing

Fillers are usually made up of primary particles at the smallest size scale which is strongly bonded to other primary particles to form aggregates structures. Aggregates can be defined as an assembly of particles which bonded strongly while agglomerates are known as when particles are joined loosely together, they can be simply broken by mechanical forces. The aggregates can interact with other aggregates through weaker secondary bonding to form agglomerates (Boverhof et al., 2015). High filler structure filler which has a high number of primary particles per aggregates is known as the strong aggregation, while the low structure filler has weak aggregation because of these aggregates may form loose agglomerates that linked by van der Waals interactions. Formation of aggregates and agglomerates reduces the effective reinforcement surface area and reduce the ability of the filler to provide reinforcement to the rubber matrix.

Fillers can be divided into two categories:
1. Reinforcing Filler
2. Non-reinforcing filler

2.5.1 Reinforcing Filler

In general, the characteristic of reinforcing filler are small particle size with larger surface area. The relationship between particle size and properties of rubber reinforcement shown in Table 2.3 below :

Table 2.3: The general relationship between particle size and properties of rubber (Ismail, 2000)

Particle Size	Reinforcement level
Particle > 5000 nm	Rubber weaken
Particle between 1000 nm – 5000 nm	The larger quantity is required for small filler reinforcement
Particle < 1000 nm	Rubber become stronger
Particle < 100 nm	The actual reinforcing agent

The reinforcing fillers are commonly used with rubber matrix during mixing process that can improve the mechanical properties of rubber, such as tensile strength, modulus, elongation at break and hardness. The higher performance can be achieved by the high level of chemical links with the polymer network. Filled rubber polymer has significantly higher stiffness than unfilled rubber polymer at the same degree of deformation. Furthermore, filled rubber polymer has as well as considerably higher strength and deformation to break than unfilled rubber polymer. Examples of reinforcing fillers that are widely used for rubber matrix are carbon black, and silica which lead to increases in viscosity of the rubber compound as well as to increase the mechanical properties and the abrasion resistance by increasing the amounts of filler loading (Thomas et al., 2013)

The term of reinforcement refers to an improvement of rubber performance in addition of filler (Kapgate et al., 2015). The influence with filler reinforcement in the rubber matrix can be summarized as follow:

- Smaller particle size with larger external surface area results in higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity and higher Mooney viscosity, higher reinforcing power..

- The higher the filler loading in rubber matrix , it will effect in higher reinforcement of rubber itself .

- Porosity of filler

- Physical and chemical nature of the filler

Furthermore, the stress values and the hardness are increased. The reinforcement effect of fillers can change the viscosity of a rubber compound and also the vulcanizate properties with increasing amount of filler loading. The specific activity of the filler is determined by the physical and chemical nature of the filler surface in relation to that of the rubber. Therefore, general chemical compatibility is the potential for specific interaction between the rubber and active sites on the filler surfaces (Rothon, 2003).

2.5.2 Non-reinforcing Filler

Non-reinforcing fillers are known as inert fillers. Most commonly used non-reinforcing fillers in rubber compounding are talcum, calcium carbonate ($CaCO_3$), and clay. Non-reinforcing fillers usually used for reducing the cost of the compound and do not exhibit any reinforcing effect but increase the viscosity of the compound, hardness, and modulus (Grossman, 2012).

2.6 Carbon Black

Carbon black is a form of carbon element consisting of 90% to 99% of carbon. The main non-carbon elements in carbon black are oxygen, hydrogen, and sulfur. Carbon black is classified according to their particle size, surface activity, porosity, and structure. These parameters affect the properties of a rubber compound. For example, the smaller the particle size, the greater the increase in modulus and tensile property, higher abrasion resistance, higher viscosity and high electrical conductivity. It reinforces the rubber compound besides lowering the compound cost. Reinforcement of rubber by carbon black improves the rubber properties due to a combination of physical and chemical interactions between carbon black and rubber. Modulus is a primarily a function of carbon black structure and loading. A compound containing higher structured blacks have the highest modulus.

2.7 Bound and Occluded Rubber

Bound rubber is essentially the gel formed in a filler-rubber mix and its estimation is considered to be a practical means of assessing rubber-filler interaction in the uncured state. The gel formed due to polymer-polymer crosslinking is not considered as bound rubber. Bound rubber is generally determined by swelling measurements. Physical as well as chemical interactions are believed to involve in bound rubber formation. In the case of carbon black, free radical interaction between the filler surface groups and the polymer is proposed a; a mechanism for bound rubber formation. Bound rubber is also related to filler surface area and surface activity. High structure black generally exhibits larger rubber- filler interaction. Freshly formed filler surfaces have great adsorption capacity. In the polymer matrix, above a critical concentration (C_{crit}) filler transforms from a disperse to coherent gel and C_{crit} decreases with increasing surface area. The filler-filler aggregates, which get broken down during

mixing with the elastomers may get reformed during the post-mixing period. The trapped rubber in such aggregates can also cause bound rubber. Comparatively higher bound rubber exhibited by black filled NR and SBR can be attributed to the high dispersive component of the surface energy of carbon black. High bound rubber exhibited by these rubbers is attributed to physical phenomena la. Graphitised carbon black (surface groups are lost) exhibits lower bound rubber. Chemical interaction of a filler particle with elastomer can affect the properties of both the uncured mix and the vulcanizate. Covalent bonds between rubber and carbon black contribute to reinforcement, while it is not a necessary condition for bound rubber formation. The bound rubber retained at higher temperature (>100°C) is likely to be due to rubber-filler covalent bonds. Polarity of the polymer also contributes to enhanced bound rubber. Polarization of the unsaturated polymers in the presence of polar fillers also contribute to polymer-filler interaction. Bound rubber can be formed even when effective reinforcement is not there as in the case of silica in hydrocarbon rubbers. Important reinforcement properties are considered to be resultant of rubber- filler interaction.

2.8 Introduction to Natural Rubber

Rubber is an elastomeric material which can be characterized by their ability to reversible elastically deformation and return rapidly to approximately its initial dimension after substantial elastic deformation on a release of stress (Mark et al., 2013). Rubber is build up from long chains and flexible molecules which chemically crosslinked during the vulcanizing process. The vulcanizing process is a formation of crosslink between rubber molecules chains to form three-dimensional network. There are many types of rubber on the market that divided into many groups following different criteria such as saturated and unsaturated, natural and synthetic, polar and non-polar, crystallizing and non-crystallizing (Gent, 2012). Rubber also effective in

adhering to fibers and metals such as rayon, polyamide, polyester, glass or steel cord (Morton, 2013).

2.8.1 Natural Rubber

Natural rubber (NR) is obtained from the latex milk extracted from the tree called Hevea Brasiliensis belonging to Euphorbiaceae family. Their historical origin is found out the tree named Hevea Brasiliensis are growing formerly in the jungles of Brazil. Natural rubber practically contained pure cis-1,4-polyisoprene (which contains more than 99.9 % of cis-1,4-polyisoprene), and the molecular structure is shown in Figure 2.1 (Arreguín, 1958).

Fresh latex can be concentrated by centrifuging or creaming. Latex can be coagulated with hydrogen carboxylic acid or acetic acid, to it form sheets or granulates and subsequently dried to produce a solid rubber. Natural rubber also contains few percents of non-rubber constituents such as resins, proteins, sugars and fatty acids, and weak to oxygen and ozone attack. This weakness is due to ozone and oxygen can react efficiently with natural rubber functional groups (double bonds) and degrade the rubber. However, the ozone and weather resistance can be improved by the addition of antiozonants and protective waxes in the compound (Kamal et al., 2009).
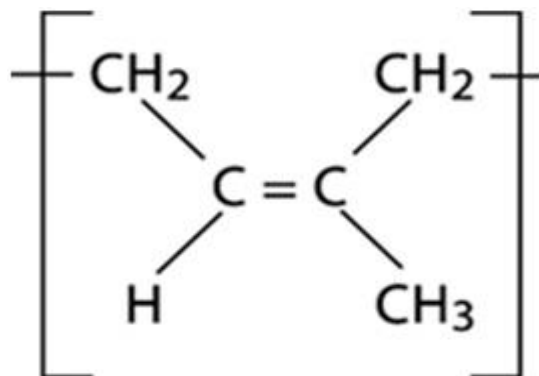

Figure 2.1: Polymer structure of cis-1,4 polyisoprene for natural rubber

(Arreguín, 1958).

Vulcanized NR rubber products have high mechanical properties and also excellent elasticity. Natural rubber also has excellent abrasion resistance with its low cost, and it also has good dynamic mechanical properties which often used in a lot of application such as tires, rubber spring, and vibration mounts. Other products include hoses, conveyor belts, gaskets, seals, rolls, rubberized fabrics, elastic bands and pharmaceutical goods compound (Kamal, M.M., J. Clarke, and M.A. Ahmad, 2009). Further advantages include low compression set and stress relaxation, good electrical insulation and excellent resistance to abrasion, tear, and fatigue.

NR vulcanizates have high tensile strength over a wide hardness range. The high strength is due to crystallization of the polymer chain at high strains enabling NR to be used in unfilled compounds. Furthermore, NR vulcanizates have the highest resilience of all elastomers (except BR), which is responsible for very low heat buildup. Further advantages include low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear, and fatigue. NR can be compounded for continuous use at 900 °C and for intermittent periods up to 1000 °C. The vulcanizates remain flexible at temperature down to -550 °C without adding plasticizers. However, they tend to crystallize readily when stored for long periods at low temperatures. Like other unsaturated elastomers, NR vulcanizates are susceptible to attack by atmospheric ozone. However, the ozone and weather resistance can be improved by blending with a saturated rubber such as ethylene-propylene rubber (EPDM) or by incorporating antiozonants and protective waxes in the compound. NR vulcanizates are not resistant to petroleum-based oils and fuels but they can be used with a wide range of organic and inorganic chemicals, such as nonpetroleum-based automotive brake fluids, silicone oils and greases; glycols; alcohols; water; and nonoxidizing aqueous solutions of acids, alkalis, and salts.