UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF CARBON FIBER-REINFORCED CARBON COMPOSITE FORMULATIONS FOR BRAKE PAD

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DEVELOPMENT OF CARBON FIBER-REINFORCED CARBON COMPOSITE FORMULATIONS FOR BRAKE PAD

By

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DEDICATED TO

HUBBY, MY LOVING FAMILY, with love

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGHASILAN KOMPOSIT GENTIAN KARBON YANG DIPERKUATKAN DENGAN KARBON UNTUK PENGGUNAAN PAD BREK

Oleh

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Sebelum ini, asbestos dan logam telah digunakan dalam pembuatan pad brek. Namun pengunaan asbestos telah diharamkan kerana boleh menyebabkan kanser. Malah, penggunaan logam juga telah dihadkan kerana habuk dari pad brek semasa pembrekan boleh menyebabkan pencemaran air. Sejak itu, banyak kerja penyelidikan telah dilakukan untuk menghasilkan pad brek tanpa penggunaan asbestos. Dalam kajian ini, formula gentian karbon yang diperkuatkan dengan karbon untuk penggunaan pad brek telah dihasilkan dan kekuatan mekanikal komposit ini telah dikaji. Komposit ini dihasilkan kerana mempunyai kekuatan yang tinggi, ringan dan berkeupayaan untuk mengekalkan sifat mekanikalnya pada suhu lebih daripada 2000 ^{o}C dalam atmosfera yang tidak mempunyai oksida. Kaedah yang digunakan dalam penghasilan komposit karbon-karbon untuk penggunaan dalam brek automotif adalah dengan gentian karbon dan phenolic resin ditekan panas oleh alat penempaan tekanan panas. Kemudiannya, komposit berkenaan dikarbonkan pada suhu 1000^{o}C dan akhirnya dibakar pada suhu 1700^{o}C. Empat langkah rendaman dilakukan semasa proses pengkarbonan pada suhu

1000^{o}C. Dalam kajian ini, kesan penambahan gentian karbon dan pengeras dan kesan pengkarbonan dan penggrafitan pada sifat komposit karbon dan pad brek komersil telah dikaji dengan menggunakan ujian mekanikal, haba dan geseran. Komposit dengan pengunaan 40 peratus gentian karbon dan 15 peratus pengeras menunujukkan sifat mekanikal dan terma yang bagus selepas diawet. Kekuatan ketegangan dan lenturan bagi komposit yang telah diawet adalah masing-masing, 411.9 MPa dan 51.7 MPa sebelum diturunkan pada suhu 523^{o}C. Kekuatan lenturan dan ketegangan bagi komposit yang telah melalui proses pengrafitan pada suhu 1700^{o}C adalah masing-masing, 10.7 MPa dan 10.8 MPa. Ketumpatan komposit yang telah diawet adalah 1.21 g/cm^{3} dan meningkat kepada 1.45 g/cm^{3} setelah digrafitkan pada 1700^{o}C. Kekuatan lentur dan ketumpatan meningkat dengan proses rendaman semasa proses pengkarbonan. Analisis terma menunjukkan pad brek dalam pasaran diturunkan pada suhu 700^{o}C, iaitu jauh lebih rendah daripada komposit karbon. Komposit karbon yang telah melalui proses pengrafitan tidak diturunkan walaupun pada suhu 800^{o}C. Komposit karbon telah menunjukkan sifat mekanikal, haba dan geseran yang baik jika dibandingkan dengan pad brek komersil.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia or other institutions.

SARINA BINTI SULAIMAN

Date:

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LIST OF ABBREVIATIONS

T_g	Glass transition temperature
CF	Carbon fiber
Hr	Hardener
CC	Carbon Carbon Composites
HRR	Hardness unit
σ	Strength
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
DMA	Dynamic mechanical analysis
CVI	Chemical vapour infiltration
RDD	Rapid direction diffused
Vol	Volume
E	Modulus of elasticity, MPa
d	Depth of beam tested for flexural test, mm
m	Slope of the tangent to the initial straight line portion of the load-deflection curve for flexural test, N/mm of deflection
b	Width of beam tested for flexural test, mm
L	Support span for flexural test, mm
R	Rate of crosshead motion for flexural test, mm/min
Z	Rate of straining of the outer fiber for flexural test, mm/mm/min. Z shall be equal to 0.01

P	Load for flexural test, N
HS	High strength
IM	Intermediate modulus
HM	High modulus
UHM	ultra high modulus
PAN	Polyacrylonitrile
CFRP	Carbon fiber reinforced thermoplastic

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Carbon fiber was introduced as a filament material for the lamp in 1890 by Thomas Alva Edison. It was stated that this carbon fiber had poor mechanical strength. Therefore, around 1950s, The National Carbon Company in USA introduced a carbon cloth made by carbonizing rayon cloth. In 1964, Thornel 25 was introduced in the market with ultimate tensile strength (UTS) of 1.25 GPa and Young Modulus's of 170 GPa at a price of more than £1000 per kg (Morgan, 2005).

The unique features of carbon fiber are low density, high strengths, lightweight, high modulus and high stiffness leading to the development of new industrial applications. Commonly, carbon fiber is used in the following three sectors: (1) High technology areas including aerospace and nuclear engineering; (2) General engineering and transportation sector, including engineering components such as bearing, gears, cams, fan blades and automobile bodies; (3) Sporting goods, such as golf clubs and bicycles (Donnet *et al.*, 1998).

The cost to purchase commercial-grade carbon fibers is between $8 and $10 per pound, and at the moment, the manufacturers are trying to reduce the price to between $3 and $5 per pound. At that price, annually automakers can use approximately 300 pounds of composites per vehicle in the manufacturing of cars. According to some studies, replacing half of the ferrous metals in current automobiles could reduce a vehicle's weight by 60 percent and fuel consumption by 30 percent (www.azom.com).

Table 1.1 shows the long fiber reinforced thermoplastics market. Volume of fiber utilized globally is 108 million kg. In North America, Western Europe and Asia, the usages are 44, 34 and 31 million kg respectively. It is estimated in 2009, the volume will increase up to 245 million kg (Markarian, 2005). This indicates that in future long fibers will be used widely and will play an important role than short fibers.

Table 1.1: The long fiber reinforced thermoplastics market (Markarian, 2005)

	Volume (2004), million kg (million lbs)	Volume (2009), million kg (million lbs)
Global	108 (239)	245 (541)
North America	44 (96)	77 (169)
Western Europe	34 (74)	73 (162)
Asia	31 (69)	95 (210)

Carbon fiber reinforced carbon (CC) composites consist of carbon fibers embedded in carbonaceous material. The real development of CC composites started in 1958 with US Air Force sponsored work and later developed for the space shuttle (Torsten and Blount, 1997). Usually, CCs are produced with thermosetting resin, pitch and chemical vapor infiltration (CVI) methods. CC are among the strongest materials yet devised (Buckley and Edie, 1988). CC composites are considered as one of the most attractive materials in the space shuttle applications and used as components that can withstand high temperature (Manocha, 2003).

CC composites are introduced as automotive brake pad to substitute asbestos based brake pad. Since asbestos are banned because of its carcinogenic, a lot of researches are done to produce asbestos free brake pads. Thus, brake pads have experienced major changes in their formulations during the last two decades due to health issues related to asbestos fibers. There has been a significant effort to develop high performance non-asbestos linings (Cho *et al.*, 2001).

Brake pad can be categorized into four major types: metallic, semi-metallic, non-asbestos organic and CC composites. In the late 1970s, teams Brabham (Formula 1 team) were interested in CC brake pad and entered into agreement with HITCO Carbon Composites to develop CC brake pad for F1 racing circuit (Morgan, 2005 and Ho *et al.*, 2005). Semi-metallic friction material was introduced in the late 1960s and has gained widespread usage in the mid-1970s. It has been exploited for parts such as clutches and brake pads used in automotive transmission in both dry and wet circumstances.

Phenolic resins are the oldest synthetic polymers used commercially, around the beginning of the 20th century. These thermoset resins have typically been cured at high temperatures (140-180^{o}C) and usually high pressures. Commonly, phenolic resins are used in a broad range of applications such as paints, adhesives and composites. There are two types of phenolic resins, the resole type and the novolac type, depending on the method of synthesis and the catalysts used. Phenolic resin provides intermolecular hydrogen bonding as a dominant driving force to interact with hydroxyl, carbonyl, amide, ester, and other hydrogen-bonding functional groups (Chen Chi *et al*., 2001).

Phenolic resins exhibits low-molecular-weight; fusible and soluble resin that may be easily handled and polymerized to a high-molecular-weight, strong, heat resistant cross-linked structures. That is the basis for the varied and important uses to which phenolic resins are put throughout the world **(Encyclopedia of Polymer Science and Technology, 1964**). Phenolic resin became brittle once cured and has low impact resistance. However this liquid is used widely as a binder for brake pad. It also been mentioned that phenolic resin carbonized at approximately 450^{o}C and will decrease the density of brake friction at the wear surface and increases the porosity. This process will change the structural and frictional characterization of the friction material (Chan and Stachowiak, 2004).

In this study, the main components of brake pad are carbon fibers and phenolic resin. Even though the raw material, carbon fibers are expensive but at the moment, the costs of replacement parts and service are expensive. Alternatively, high-performance materials i.e., CC composites are available at a slightly higher initial cost. In addition to replacement costs, consumer complaints of excessive noise and pad residue accumulating on the wheels have left manufacturers dissatisfied with the current semi metallic brake pads (Chapman *et al*., 1999).

1.2 Objectives and Scopes of Work

The objectives of this project are:

1. to develop and investigate the optimum formulation for carbon-carbon composites for brake pad application.
2. to analyze the properties of cure, carbonized and graphitized composites.

In order to achieve the project's objective, the following studies are carried out *i.e.*, the effects of volume fraction of carbon fiber, effects of percentages of hardener, effects of carbonization cycles and effects of graphitization on mechanical, thermal and tribological properties. Formulated composites are tested after each process: post curing, carbonization and graphitization. The mechanical testing that are used to analyze the formulated CC are tensile, flexural, dynamic mechanical analysis, hardness and density test. The thermal properties, DMA and TGA, and tribological property, friction are investigated. Finally, the properties of graphitized composites are compared with the commercialized brake pad.

1.3 Thesis Outline

This thesis consists of five chapters. Chapter one contains introduction and background of the thesis, objectives and finally the scopes of work. Chapter two consists of literature review of carbon fiber, composites, polymers, CC composites and brake pad, and previous works done that are related to the thesis. Chapter three presents research methodology and describes the equipment used in this project. Chapter four consists of results obtained from the experiment and comparison between the commercialized brake pad and graphitized composites. The chapter also includes the discussion of the results of each step: post curing, carbonization and graphitization. Finally, Chapter five summarizes and concludes the work that has been carried out. Lastly the future work is suggested at the end of chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Fibers

Carbon fibers are gradually becoming the most advanced product after the introduction of composite-bodied Corvette. In 1953, the unique features of carbon fibers were lightweight, low density, high strength, high modulus and high stiffness which led to the development of new industrial applications. Carbon fibers processes include controlled oxidation, carbonization and graphitization of carbon-rich organic precursors. Carbon fibers are usually grouped according to the modulus band: high strength (HS), intermediate modulus (IM), high modulus (HM) and ultra high modulus (UHM) (Buckley and Edie, 1988). On the whole, in 1993 United States consumption of carbon fibers was 2.8 million kg (Donnet *et al.*, 1998).

Structurally, carbon fibers contain a blend of amorphous carbon and graphitic carbon. Carbon fibers are commercially available in three forms: long and continuous tow, chopped and milled. Graphitic form of carbon fibers in which carbon atoms are arranged in crystallographically parallel planes of regular hexagon, results in high modulus carbon fibers. The advantages of carbon fibers are high tensile strength, high modulus, low coefficient of thermal expansion, lightweight and high fatigue strength (Mallick, 1993).

The mechanical properties of composites are related to the length of the reinforcing fibers. In composites, carbon fibers are usually used in the form of short, long and long and continuous. Usually an average fiber length of approximately 5-20 mm is considered a long fiber and less than 1 mm is considered short fiber (Frank *et al.*, 2005).

Common methods of processing carbon fibers are by using polyacrylonitrile (PAN) and pitch. PAN is a synthetic fiber that is pre-manufactured and wound into spools, while pitch is a coal-tar petroleum product that is melted, stretched and made into fibers. In the carbon fibers manufacturing process, these fibers are first stretched and heated (up to 400°C) in the thermoset polymer treatment. This first step results in the oxidation of the organic material. The material is then carbonized by being heated to approximately 800°C in vacuum and the non-carbon impurities are removed. After the material is carbonized, it is graphitized by stretching the fibers between 50-100% and heating them up to temperatures between 1100°C and 3000°C. Processes to produce carbon fiber can be seen in Figure 2.1 (Sung *et al.*, 2001).

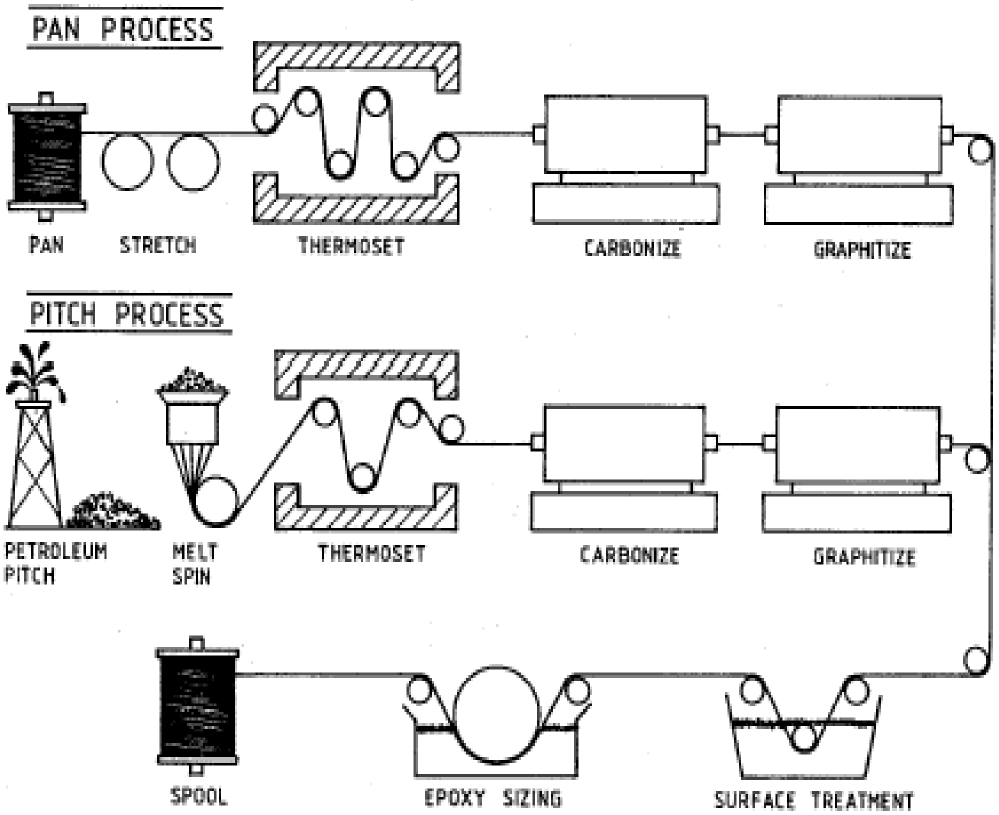

Figure 2.1: Schematic drawing of PAN and Pitch processes (Sung *et al.*, 2001)

2.2 Carbon Fiber Reinforced Composites

In order to formulate carbon fibers into the required high performance products, they are usually reinforced in certain matrix materials to form composites such as CC composites, polymer matrix composites and carbon-metal composites. Fiber reinforced composite material consists of fibers of high strength and modulus embedded to a matrix. Fibers are the reinforcement and the main source of strength while the matrix bonds all the fibers together in shape and transfers stresses between the reinforcing fibers. Sometimes,