CHAPTER 2

LITERATURE REVIEW

2.1 Brake Pads

Brake pads are steel-backed plates with friction material bonded to the surface that faces the disk brake rotor. Brake pads convert the kinetic energy of the vehicle to thermal energy through friction. Two brake pads are contained in the caliper, with their friction surfaces facing the rotor (Henderson and Haynes, 1994). Brake pads were originally made with organic ingredients, such as asbestos and carbon, held together by a strong resin.

In disc brake applications, there are usually two brake pads per disc rotor, held in place and actuated by a caliper affixed to a wheel hub or suspension upright. Although almost all road-going vehicles have only two brake pads per caliper, racing calipers utilize up to six pads, with varying frictional properties in a staggered pattern for optimum performance. Depending on the properties of the material, disc wear rates may vary. The brake pads must usually be replaced regularly (depending on pad material), and most are equipped with a method of alerting the driver when this needs to take place.

2.2 History of Brake Pad Materials

In order to achieve the properties required by brakes, most brake materials are not composed of single elements or compounds, but rather are composites of many materials. More than 2,000 different materials and their variants are now used in commercial brake components. According to Nicholson (1995), Herbert Frood is credited with inventing the first brake lining materials in 1897. It was a cotton-based material impregnated with bitumen solution and was used for wagon wheels as well as early automobiles. His invention led to the founding of the Ferodo Company, a firm that still supplies brake lining materials to this day. The first brake lining materials were woven, but in the 1920s, these were replaced with molded materials that contained crysotile asbestos fibers a plentiful mineral. Resin-bonded metallic linings were introduced in the 1950s, and by the 1960s so-called ‘semi-mets’ were developed that contained a higher amount of metal additives. Table 2.1 lists the common brake materials in the early days.

Table 2.1: Historical Compositions of Automotive Friction Brake Materials (Blau, 2001)

Material Description	**Application(s)**	**Approximate Year**
Cast iron on steel	railroad car brake blocks and tires	prior to 1870s
Hair or cotton belting (limited by charring at about 150^oC)	wagon wheels and early automobiles	1897
Woven asbestos with brass and other wires for increased strength and performance	automobiles and trucks	1908
Molded linings with shorter chrysotile fibers, brass particles, and low-ash bituminous coal	automobiles and trucks	1926
Dry-mix molded material to replace cast iron brake blocks that produced metallic dust that shorted electric train rails	London underground	1930
Flexible resin binders developed along with more complex formulations	brake drum linings	1930
Resin-bonded metallic brake linings	industrial and aircraft applications	1950
Glass fibers, mineral fibers, metal fibers, carbon, and synthetic fibers to provide semi-metallics with higher performance	automobiles and trucks	1960

than asbestos (beginning of safety issues with asbestos)		
Non-asbestos (fiberglass) materials	brake drums on original equipment cars	1980
Suggested use of carbon fibers	automotive brakes	1991

2.3 Fundamental of Brake Friction

Generally, friction phenomenon is exist everywhere in our normal life. It will occur as long as there is a relative motion between two components. During a braking process in the brake system, brake pads or brake shoes are pressed against the rotating rake disc or drum. During this process the friction materials and the brake disc are subjected to wear. The friction behaviour of automotive brakes is determined by the character of the active surfaces of the disc and pad and third bodies between these surfaces. This tribosystem is very complex and variable.

2.3.1 Tribological System of Disc Brakes

The first definition of tribology was stated by Jost (1966): “Tribology is the science and technology of interacting surfaces in relative motion and related subjects and practices.” According to DIN 50 323 tribology embraces the science and associated technology devoted to the interaction of surfaces in mutually opposed states of motion. It focuses on the entire range of friction, wear and lubrication, and also includes the effects at the contact surfaces of solids as well as those between solids and gases.

When two surfaces, round or flat, are in contact and one moving, we recognize that friction is preventing smooth and easy movement, that we may wish to squirt a bit of lubricant onto one surface to reduce the friction, and that one or both surfaces may show wear tracks after some time has passed. When engineers change the design of a shaft and bearing, the friction may be reduced and the bearing may show less wear. For existing machines, such as our cars, we make decisions about lubricants that will change friction and wear, hopefully in the direction of a long useful life.

In our everyday life, we need to be concerned with lubrication of equipment such as cars, outboard motors, sewing machines, snowmobiles, and smaller equipment and tools. Then there are the workplaces such as textile mills, mines, steel mills, power plants, and other industries, where lubrication is essential. Industries such as steel mills would grind to a screeching halt without proper attention to lubrication.

Friction creates heat, promotes wear, and wastes power, so the reduction of friction, by any means, is vital. It is estimated, that from 1/3 to 1/2 of the total energy produced in the world is consumed by friction. It is also estimated that the cost of wear in the United States is equivalent to 2/3 the cost of energy. If we add these two together, we see that the cost of friction and wear in the U.S. is equivalent to the cost of energy.

Take our own car for an example. The engine delivers useful work only after overcoming the friction of the moving parts such as bearings, valves, pistons, cams, etc. The useful work is then consumed in gear friction, the rolling friction of tires, brake friction, and wind friction. Wear is the cause for most maintenance and repair of brake, clutches and gearboxes, as well as replacement of the entire automobile. By the time that you are tired of your car because it is dripping oil onto the driveway and the brake pads and clutch plates need replacement, it has lost, in wear debris, less than 3/1000 of its original weight. Of even greater concern are the millions of dollars lost due to friction and wear in various industrial machines. Reduction of friction and wear leads to increases in service life, less downtime and lower operating costs, which can add up to tremendous savings.

Hertz was the first to solve the normal contact problem in 1881. According to Mao et al. (1994) Hertz' theory is for perfectly smooth surfaces of elastic homogeneous and non-conforming bodies and the surfaces are assumed to be frictionless, so that only a normal pressure is transmitted between them. Since then, various authors have expanded the understanding of contact mechanics, which is far beyond the scope of the present work. Summary and further references are presented by Willner (2003).

Real surfaces are generally rough. Therefore the real area of contact, where the asperities of the opposing rough surfaces are in contact, is only a fraction of the nominal macroscopic area of contact. According to Bowden and Tabor (1986), if two solids are placed in contact, the upper surface will be supported on the summits of the irregularities, and large areas of the surfaces will be separated by a distance, which is large compared with the molecular range of action. They expect that in most practical cases, for all types and shapes of surface irregularities, the real area of contact will be very nearly proportional to the load. They found a linear load dependent area of real contact for steel and silver surfaces by measuring load dependent electrical resistances.

For disc brakes, multiple authors have done research on the contact situation in recent years. Based on their experimental research Eriksson and Jacobson (2000) introduced the theoretical concept of the disc brake contact situation processes, schematically shown in Figure 2.2: The primary plateaus are first formed, due to better wear resistance of some ingredients (mostly fibers) with regards to the three-body abrasion generated by wear debris (Eriksson et al, 2001). Debris, in the form of small particles, piles up against the primary plateaus, as observed in-situ by monitoring the contact of pads running against a glass disc (Eriksson et al, 2001).

The normal pressure, shear forces and the frictional heat combine to compact the debris, forming secondary plateaus. The lateral size of the secondary plateaus varies with the brake pressure, as described by Eriksson et al (1999 and 2001) . The top layer of the secondary plateaus is less than 1 μm thick, more homogeneous (compared to the rest of the 5 - 10 μm thick secondary plateau) and has nanoindentation hardness values, which are in the same range as the fibers, according to Eriksson and Jacobson (2000).

Österle and Bettge (2001) investigated a brake friction material using topographic examination methods such as a confocal laser scanning microscope and an interference microscope as well as micro-analysis and surface layer characterizing methods like scanning electron microscopy, light microscopy and Focused Ion Beam. They contradicted Eriksson and Jacobson (2000) that the characterization of contacting surfaces as the plateaus protruding from the surface is generally valid. However, they did confirm a lower roughness on the contacting surfaces compared to the area surrounding them. Kemmer (1998) experimentally investigated the friction layer between pad and disc and modeled it as a granular medium. In his simulations he found the contact stiffness of the granular friction layer to be directly dependent on the particle diameter, the shear modulus of the particle’s material, the friction coefficient for the interactions among the particles, the normal force, and inversely dependent on the friction layer’s thickness. With his experiments, he showed that for one friction material, higher pressures lead to smaller wear debris particles.

2.3.2 Basic of friction

One of the most interesting and most important physical phenomenon related to brake systems is the lateral force between two rubbing surfaces, i.e. the friction force. If a block is dragged over a horizontal floor, the lateral force required to move the block is equal to the friction force between the two surfaces.

Historically, the study of friction began approximately 500 years ago with Leonardo da Vinci (1452-1519), whose notebooks show that he found that:

1. Friction is proportional to load.
2. Friction is independent of contact area.

Dowson, 1998, from his experiments and calculations was estimated that the frictional resistance of a body is about 1/4 of its weight. He furthermore discovered that the friction force between two rubbing surfaces is independent of the apparent, nominal contact area, as show in Figure 2.1.

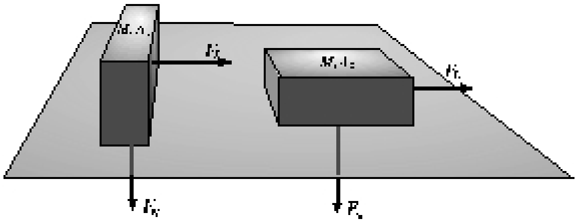


Figure 2.1: Illustration of a block dragged over a horizontal surface

Amontons, a 17th century physicist, was unaware of da Vinci's work and published his own work on friction in 1699. Attempting to explain friction, he theorized that friction is caused by surface roughness. The peaks of one surface lay in the valleys of the adjoining surface and Amontons believed that friction is the force required to pull the peaks up the other surface until they clear. Coulomb published a paper in 1785 on his investigations of both static and kinetic friction, with five conclusions:

- Verified Amontons' law, which showed that friction is to be proportional to load.
- Verified Amontons' finding that friction is independent of contact area.
- Kinetic friction is independent of velocity.
- Friction force depends on the nature of the materials in contact and their coatings for both static and kinetic (moving) conditions.
- Static friction depends on the length of contact time.

As to the cause of friction, Coulomb theorized that at least part of the frictional force might result from the cohesion of molecules of the two sliding surfaces.

In the 1490's, Leonardo da Vinci found that when the normal force on the block increases, the friction force also increases. These relations between the normal force, F_N, and the lateral force, F_L, can be mathematically formulated as:

$$\mu = \frac{F_L}{F_N} \qquad [2.1]$$

Where **μ** is the *coefficient of friction*. For many materials this relation is true, within limited load intervals.

In order to explain why the friction force is independent of the nominal contact area, one must study the two facing surfaces. All technical surfaces have a roughness, even if some appears very smooth. If two rough surfaces are pressed against each other, only small parts of them will actually contact each other. Consequently, the area of real contact will be very small. As a matter of a fact, the normal load and the hardness of the two materials will define the area of real contact (Jacobson and Hogmark, 1996). An increased hardness or a reduced load will lead to a reduced contact area, see Figure 2.2. Thus, for a given material combination, the real contact area depends on the normal load only and has no correlation to the nominal contact area. If the load is doubled, the area of real contact will also be doubled.

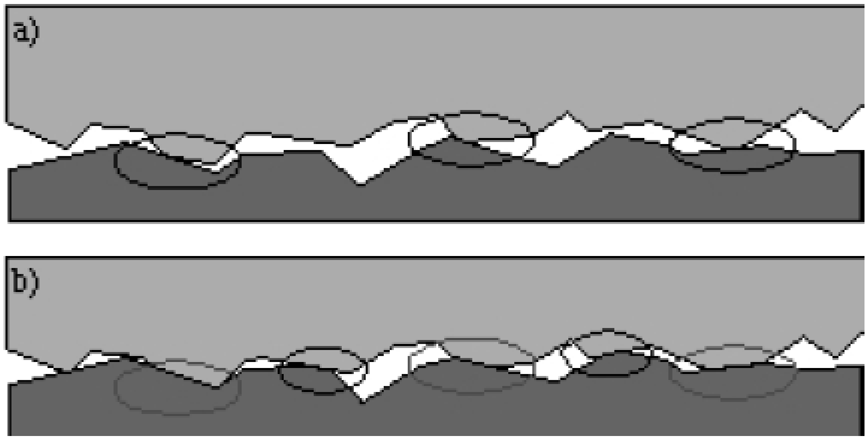


Figure 2.2: Contact situation between two rough surfaces.

a) Low load and/or high hardness. b) High load and/or low hardness

Figure 2.2 was shown only small parts of the surfaces are in real contact with each other, encircled. The area of real contact increases with increased load and with decreased hardness.

In general, the area of real contact is very small. If a 100x100x100 mm steel cube, with a hardness of 3 GPa, rests on a flat steel plate, the nominal contact area is, of course, 10 000 mm2. According to Jacobson and Hogmark (1996), the area of real contact, however, is only 0.03 mm2, a factor 300 000 times smaller. Now, if the friction force is identified as the force required shearing the real contact between the two surfaces, it can easily be understood that the nominal contact area does not affect the friction force. It can also be understood that a doubled normal load, resulting in a doubled area of real contact, will lead to a doubled friction force.

Friction is a continuous process, but wear is a more complicated process than friction because it involves plastic deformation plus localised fracture event (Rigney, 1997), microstructural changes (Talib et al., 2003), and chemical changes (Jacko, 1977). Wear mechanism in the operation during braking is a complex mechanism and no single mechanism was found to be fully operating (Rhee, 1973 & 1976; Bros & Sciesczka,1977; Jacko et al. 1984; Talib et al., 2007).

2.3.3 Wear

Hundreds of equations for wear may be found in the literature. These equations may depend a variety of factors, including the materials involved, the temperature, and the environment under consideration, i.e., the liquid or gas present, the formation of surface films, and so on (Ludema, 1996). Two of the relations that pertain to the following discussion are the specific wear rate and the wear rate. The first of these, the specific wear rate, or wear coefficient, is a dimensional constant K that appears in the relation

$$\delta \mathrm{A} = \upsilon = K\rho \mathrm{A} d = KFd \qquad [2.2]$$

From which υ may be written as

$$\upsilon = KFd \qquad [2.3]$$

In these relations, δ represents the thickness of the lining material removed, υ is the volume material removed, K is a dimensional constant that is termed the specific wear rate or the wear coefficient, and p is the pressure acting over the surface area A that is in contact with the lining material. Force F is given by the integral of the pressure acting on the specimen integrated over the area A over which it acts. Upon rewriting equation [2.3] to evaluate K we have that

$$K = \upsilon/Fd \qquad [2.4]$$

Hence the units of K are lt^2/m where $l,t,$ and m denote length, time, and mass, respectively. As a practical matter, if υ is millimeters cubed (mm^3), if force F is in newtons (N), and if the distance d is in meters (m), then the units of K become $\mathrm{mm}^3\ \mathrm{N}^{-1}\ \mathrm{m}^{-1}$, which explicitly shows the physical quantities involved. According to Bush et al. (1972), the average wear rate of a typical automotive brake pad material is 0.5 micrometers per brake application. This corresponds to approximately 3 mg of material loss per brake application. The major wear phenomena observed during the braking process were; (i) abrasive (ii) adhesive (iii) fatigue (iv) delamination an (v) thermal wear.

2.3.4 Role of filler in Wear Properties

Present day industries are experiencing an escalating trend in the application of particulate and fibre reinforced polymer matrix composites. Some of these applications related to mechanical engineering experience surface interactions with the surroundings as well as with the pairing element such in the braking system.

Functional fillers are added to the thermoset matrix for improving its physical, mechanical and tribological properties. The modification of the mechanical, and the tribological behavior of various polymers with the addition of filler materials has shown a great promise ad hence, it has been a subject of considerable interest. The filler materials include organic, inorganic and metallic particulates in both macro and nano levels (Naveed et al., 2013).

In recent times, there has been a remarkable growth in the large-scale production of fiber and/or filler reinforced epoxy matrix composites. Because of their high strength-to weight and stiffness-to-weight ratios, they are extensively used for a wide variety of structural applications as in aerospace, automotive and chemical industries. On account of their good combination of properties, fiber reinforced polymer composites (FRPCs) are used for producing a number of mechanical components such as gears, cams, wheels, brakes, clutches, bearings and seals. Most of these are subjected to tribological loading conditions. The FRPCs exhibit relatively low densities and they can also be tailored to our design requirements by altering the stacking sequences to provide high strength and stiffness in the direction of high loading (Suresha, 2006).

A number of material-processing strategies have been used to improve the wear performance of polymers composite. Glass fiber reinforced polymeric composites traditionally show poor wear resistance and high friction due to the brittle nature of the reinforcing fibers. This has prompted many researchers to cast the polymers with fibers/fillers. Considerable efforts are being made to extend the range of applications. Such use would provide economical and functional benefits to both manufacturers and consumers. Various researchers have studied the tribological behavior of FRPCs.

Studies have been conducted with various shapes, sizes, types and compositions of fibers in a number of matrices (Sung et al. 1979, Chang, 1983, Suresha et al. 2006, Tripaty and Furey 1993). In general, these materials exhibit lower wear and friction when compared to pure polymers. An understanding of the friction and wear mechanisms of FRPC's would aid in the development of a new class of materials so as to counter the challenges faced by researchers. Reviews of such works found in articles have shown that the friction and wear behavior of FRPCs exhibits anisotropic characteristics (El Sayed et al. 1995, Cirino et al. 1988, Lankaster 1972).

The use of inorganic fillers dispersed in polymeric composites is increasing. Fillers not only reduce the cost of the composites, but also meet performance requirements, which could not have been achieved by using reinforcement and resin ingredients alone. In order to obtain perfect friction and wear properties many researchers modified polymers using different fillers (Bahadur et al., 1985,1992,1994). Briscoe et al. (1974) reported that the wear rate of high density polyethylene (HDPE) was reduced with the addition of inorganic fillers, such as CuO and Pb_3O_4.

Wear rate was reduced with addition of PTFE into polymers such as polyphenylene sulfide (PPS) (Yamaguchi, 1990). Bolvari et al. (1997) also reported that the PTFE filled PPS reduced the wear rate of polymer remarkably. Tanaka (1986), concluded that the wear rate of polytetrofluroethylene (PTFE) was reduced when filled with ZrO_2 and TiO_2. Bahadur et al. (1985, 1992 and 1994) found that the compounds of copper such as CuO and CuS were very effective in reducing the wear rate of PEEK, PTFE, Nylon and HDPE. Kishore et al. (2000) studied the influence of sliding velocity and load on the friction and wear behavior of G-E composite, filled with either rubber or oxide particles, and reported that the wear loss increased with increase in load/speed. Solid lubricants such as graphite and MoS_2 when added to polymers proved to be effective in reducing the coefficient of friction and wear rate of composites (Wang et al. 2003).

Suresha et al. (2006) investigated the influence of inorganic fillers like silicon carbide and graphite an the wear of the glass fabric reinforced epoxy composites under dry sliding conditions. The higher wear volume loss has been recorded with an increase in sliding velocity and the coefficients of friction showed an increase in load and sliding velocity. Akram et al. (2013) reported the mechanical properties of glass reinforced epoxy with fillers, namely aluminum oxide, calcium carbonate, silicon dioxide, and lead oxide, incorporated into the epoxy matrix to improve the mechanical properties.

The use of graphite as a particulate filler has been reported to improve tribological behavior in metal matrix composites (MMCs)(Basavarajapa and Chandramohan, 2005). Most of the above findings are based on either randomly oriented or unidirectionally oriented fiber composites. Woven fabric reinforced composites are gaining popularity because of their balanced properties in the fabric plane as well as their ease of handling during fabrication (Vismanath et al., 1992). Mody et al. (1998) have shown that the simultaneous existence of parallel and anti-parallel oriented carbon fibers in a woven configuration leads to a synergistic effect on the enhancement of the wear resistance of the composite.

2.4 Automotive Brake Pad Formulations

Friction and wear characteristics of friction material play an important role in deciding which new formulations developed are suitable for the brake system. The friction and wear behaviours of automotive brake pads are very complex to predict which depend on the various parameters such as microchemical structure of the pad and the metallic counter face, rotating speed, pressure and contact surface temperature (Ingo et al., 2004). Composition and formulation of brake pads also play a big role on the friction behaviour, and since composition-property relationship is not known well enough, the formulation task is based on trail and error and thus is expensive and time consuming (Osterl& Urban, 2004).

Although friction materials have been developed for a century, the formulation used in the most commercial frictional brake pad materials varies and complicated. Generally the ingredients in brake pad comprise fibre reinforcement, binder, friction modifiers, solid lubricant, abrasive, and filler. Fibres are usually used because of their friction properties, heat resistance, and their thermal conductivity. Besides that fibre can impart toughness and strength to the binder. Filler materials are added to improve or optimize the properties. Phenolic resin as a binder, which is currently used in most commercial friction materials, is added to hold all ingredients together (Asri Selamat et al, 2006).

According to Anderson (1980), friction coefficients for brake material pairs span a range of 0.07 to 0.7, but practically, most vehicles operate within a narrower range. Typical values range from about 0.3 - 0.6 in friction coefficient (Blau, 2001). Anderson (1992) lists six classes of friction materials depending on operational capabilities. The higher the class number, the more severe the operating conditions. Materials must be formulated to withstand the energy dissipation requirements of use. Classes III and IV used in trucks, for example, must withstand 3 - 4 MPa of pressure and speeds of 35-50 m/s, respectively. The counter face temperatures can reach up to 600-800°C. This temperature range is at least 150°C above the estimated use temperature for aluminum metal matrix composites.

The history of brake materials shows that some of the simplest compositions (fiber plus resin) can be effective, but there have been all kinds of commercial additives introduced and promoted. According to the report by Nicholson (1995), the ratio of resin to carbon and metallic fibers in semi-metallic brake materials has changed very little during the 20th century (+/- about 1%). On the other hand, there are at least six types of resins alone. The reasons for so many additives are partly based on function, but also on ingredient cost, availability, and processing issues, the latter including mixture blending, dimensional stability, and pre-forming capability. Nicholson (1995) also reported that the same ingredients can be sent to several plants and the resulting brakes can have friction coefficients that vary by over a factor of 2. Therefore, the friction brake composition is only a part of the picture in ensuring satisfactory brake performance.

According to Blau (2001) the ingredients may be grouped based on their expected functions into abrasives, friction modifiers, fillers and reinforcements or binder materials.

A lot of different materials are used within each category as summarized by Blau (2001) or, within a more recent review of automotive brake friction materials, by Chan and Stachowiak (2003). Typical compositions of industrial friction materials are shown in table 2.1. While nearly all of the constituents are self-explanatory, ‘Friction dust’ commonly consists of processed cashew shell resin and may have a rubber base which includes some additives used to reduce spontaneous combustion or help particle dispersion.

A common classification of disc brake pads is based on its ferrous and non-ferrous metal content as shown in table 2.2. In some publications (e. g. by Chan and Stachowiak, 2003) the No-Steel Low-Metallic friction material type is also termed Non-Asbestos Organics friction material (NAO), which is a quite confusing term, because asbestos have been banned in friction materials nearly throughout the whole world since the 1990s. According to Wiaterek (2004) in Japanese friction material philosophy NAO refers to friction materials with organic binders and without steel wool.

The brake disc consists of the friction ring, where the contact between brake pads and disc takes place, and the hat section, where it is mounted on the hub bearing unit. For lighter vehicles the friction ring is solid, while for heavier or high performance cars and trucks vented discs, two friction rings are connected via vanes for better heat dissipation are used. Besides transforming kinetic energy into heat, there are various needs, which should be met by the friction couple, namely by the brake pads and disc, in a disc brake. These needs include low wear rates, good machine ability, stability of the coefficient of friction and low price among other things, as described by Blau (2001), Kemmer (2002) and Nguyen and Taylor (2000). Changes to improve the friction couple are mostly made within the brake pad.

Automotive and truck brake pads and shoes usually contain a binder, performance modifiers, abrasives, lubricants, and fillers. A representative sample of compositions follows. Some examples are listed constituents by composition, but other examples are included here to illustrate the kinds of formulations that are specified by using commercial additive products of proprietary composition. Note that in a number of cases, a range of compositions is reported rather than a single value. This was done, at least in part, to conceal the actual compositions of the materials. Therefore, the percentages of the constituents may not add to a total of 100%. Note also that some of the compositions are given in weight percent and others are given in volume percent. Nicholson (1995) asserts that volume percent is the correct unit of measure for friction material composition. The exact compositions of commercial friction materials are almost never published in the open literature.

Tsang et al.(1985) conducted friction tests of several asbestos-free materials that had the following compositions given in table 2.2, 2.3 and 2.4:

Table 2.2 Asbestos-Free Material “Formulation I” (Tsang et al., 1985)

Function	Material	Amount (wt%)	Comments
Binder	resin	13-18	thermoset
Fiber reinforcements	fiberglass	6-24	
Inorganic fiber		8-16	
“Friction dust”		0-20	
Elastomer	polymer	0-20	
Carbon / graphite	carbon	1-4	
Inorganics		12-32	
Metals / oxides		0-19	

Table 2.3 Asbestos-Free Material “ Formulation II” (Tsang et al., 1985)

Function	**Material**	**Amount (wt%)**	**Comments**
Binder	resin	8-14	thermoset
Fiber reinforcements	fiberglass	14-16	
Inorganic fiber		10-16	
“Friction dust”		0-7	
Elastomer	polymer	0-7	
Antioxidant	carbon/ graphite	18-34	
Filler	barium sulfite	30	
Inorganics		7-24	
Metals/ oxides		4-22	
Other		0-10	

Table 2.4 Asbestos-Free Material “Formulation III” (Tsang et al., 1985)

Function	**Material**	**Amount (wt%)**	**Comments**
Binder	resin	10-20	thermoset
Metal fiber	steel	0-70	
Metal powder	iron	20-70	
“Friction dust”	proprietary	0-18	
Elastomer	polymer	0-18	
Antioxidant	carbon/ graphite	10-30	
Filler	barium sulfite	0-15	
Inorganics	proprietary	0-10	

The other typical composition is a formulation used in car, for example Volvo 850

Table 2.5 Brake pad formulation for Volvo 850 (Eriksson et al., 2000)

Function	**Material**	**Amount (wt%)**	**Comments**
Matrix	binder material	8	
	Other	11	
Fillers	clay and iron oxide	8	
Fibers	steel, aramid, glass	30	
Friction modifiers	brass/bronze	15	
	graphite	15	
	metal sulphides	8	
Abrasives	quartz	5	

Various brake pad formulations also used by different researchers in their studies; for example Gudmand-Hover et al. (1999) investigated the effects of solid lubricants on disc brake behavior using a dynamometer by Volvo standard, unventilated rear brake discs with the formulation shows in Table 2.6. Conditions for test type 1: 600 stops from 50 km/h at 30 bars pressure and 70°C. Conditions for test type 2: 350 stops from 120 km/h at 40 bars pressure and 200°C. It was found that friction films were formed under test 2 conditions. Under test 1 condition, the solid lubricant additives had no significant effects.

Table 2.6 Formulation used in the research handles by Gudmand-Hover et al. (1999)

Function	**Material**	**Amount (wt%)**	**Comments**
Matrix	resin and rubber	23-26	
Fillers	barytes, friction dust and vermiculite	25.5 - 41	
	brass	0 or 5	
Fibers	aramid	0 or 9	
Friction modifiers	metal sulphides	8	Cu, Pb, or Sb sulphides
Abrasives	zirconia	0 or 5	
	alumina	0 or 5	

Howell and Ball (1995) compared the friction and wear of an aluminum/SiC composite with that of cast iron against three pad materials. A modified drilling stand was used with a contact pressure of 1.034 Mica and sliding speeds of 0.52 to 3.16 m/s. The following pad compositions shows in Table 2.7 were reported. Friction and wear results were mixed, depending on material combination and severity of test conditions.

Table 2.7 Brake pads compositions used by Howell and Ball in their study

Function	**Material**	**Organic pad (wt%)**	**Semi-met pad A (wt%)**	**Semi-met pad B(wt%)**
Binder	phenolic resin	43	25	16
Fibers	organic fiber	20		
Metal	Cu	0.6	15	15
	Fe		43	3
	Al		3	2
Lubricant	graphite	15	7	4
Abrasive	alumina			5
Filler	rubber	2	5	
	paper	15		52
Other	unspecified	4.4	2	3

Kato and Soutome (2001) used this following formulation in their research. A subscale pad-on-disc tester was used to generate friction and wear data on the effects of each component. The standard disc material was cast iron. There were ten potential components in the pad material. The ‘optimized’ composition for the combination of the highest friction coefficient ($\mu = 0.38$) and lowest wear rate was shown in Table 2.8 as follows:

Table 2.8: Potential component in brake pads by Kato and Soutome, (2001)

Function	**Material**	**Amount (wt%)**	**Comments**
Matrix	phenolic resin	25.0	
Fillers	barium sulphate	0.02	
	cashew dust	19.4	
	calcium carbonate	0.0	not in the optimal composition
Fibers	aramid	3.0	
	ceramic	15.0	
Metal	Cu powder	20.0	
Abrasive	alumina	10.0	
Lubricant	graphite	7.3	
	molybdenum disulphide	0.0	not in the optimal composition

2.4.1 Composition of Brake Pads

The compositions of commercial and experimental pad materials varied widely, although some constituents were common to nearly all of them. Table 2.9 shows typical ranges of the most common constituents in brake pads.

Table 2.9 Typical Ranges of the Constituents in Brake Pads (Blau, 2001)

Constituent	**Range (vol.%)**	**Typical Value (vol. %)**
Thermoset resin	10 - 45	20 - 25
Filler	0 - 40	20 - 25
Fiber	3 - 30	15 - 20
Lubricant	0 - 15	5 - 10
Abrasive	0 - 10	3 - 5

Some materials added in the brake pad ingredient are serving multiple functions. The mechanical strength of brake pads is mainly achieved by a metal backplate. In a complex process 10 - 20 different ingredients in powder form are pressed on the back plate. This part of the brake pad is normally referred to as friction material or lining by Kemmer (2002), while the mix of ingredients is called formulation within the brake industry. To improve adhesive strength and damping of the friction material, an under layer with a different composition is inserted between the back plate and the friction material before pressing. On the reverse side of the back plate often a shim (also called insulator) is attached to the back plate to decrease emitted noise.

2.5 Brake Materials and Additive Functionality

Brake pad and shoe additives serve a variety of functions. Even a difference of a percent or two of additive concentration can affect performance; as such, composition control is important. This review lists additive materials by function. Information is referenced using the first author’s name and year. If the information is from a handbook or commercial source, the reference will be listed by the publisher or company name.

According to Nicholson (1995), one can group brake materials and additives based on their expected functions as follows:

Binder Materials

Friction Modifiers

Abrasives

Lubricant

Fillers and Reinforcements

This categorization results in a little uncertainty. Some of the additives can be placed into more than one category since they fulfill several functions. Consequently, some inevitable overlaps occur in the tabular listings. In addition to the basic brake materials, some porosity (5-10% or more) is normally present (Blau, 2001).

When analyzing the role of additives in friction and wear control, it is insufficient to simply know their composition, since their forms, distribution, and particle size can affect the friction and wear behavior. For example, rounded beads of a hard, abrasive material can have a different effect than angular grits on the formation and stability of the friction-induced surface films that control stopping behavior.

2.5.1 Binder (Matrix) Materials

Binder materials refer to material that can hold other materials in a composite system. The purpose of a binder in brake pad composition is to maintain the structural integrity under mechanical and thermal stresses. It has to hold the components of a brake pad together and prevent its constituents from crumbling apart. The choice of binders for brake pads is an important issue because, if it does not remain structurally intact at all times during the braking operation, other constituents such as the reinforcing fibers or lubricants will disintegrate. Therefore, the binder materials have to have a high heat resistance. For this reason, epoxy, phenolic, and silicone modified resins would generally be ideal as the binder for most braking applications. The other binders would have to be applied-specific such that their disadvantages would not compromise their functionality (Lu, 2002; Chan and Stachowiak , 2003).

The needs or desired properties of the matrix that are important for a composite structure are reduced moisture absorption, low shrinkage, low coefficient of thermal expansion, good flow characteristics to penetrate the fiber bundles completely, elimination of voiding during the compacting/curing process, reasonable strength, modulus, and elongation (elongation should be greater than the fiber). The binder must also have some elastic properties to transfer the load to fibers, have a moderate strength at an elevated temperature (depending on the application), have low temperature capability (depending on the application), demonstrate excellent chemical resistance (depending on the application), be easy to process into the final composite shape, and be stable in dimension in order to maintain its shape (Pandey et al., 2001).

Phenolic resins are typical binder materials for automotive and truck brake pads. Three common types of aircraft friction brake materials are (1) sintered metal (most widely used), (2) carbon-carbon, and (3) organic materials. Fe-based metallics tend to have a lower friction response than Cu-based matrix materials (Tatarzicki and Webb, 1992). According to Tatarzicki & Webb, 1992, and Blau, 2001 there are a few other materials that have been used as binder in brake pads such as metallic alloys of Cu, Fe, and Ni for brake pads widely use by aircraft and a variety of modified resins such as cresol, epoxy, PVB, rubber, linseed oil and boron mostly produced by Borden Packing and Industrial Products. Inc. since 1994.

i. Phenolic Resin

Phenolic resin is a type of polymer formed by a condensation reaction between phenol and formaldehyde, and is able to act as a matrix for binding together different substrates (Critchley, Knight and Wright, 1983). This condensation reaction may be initiated by acidic or alkali catalysts, resulting in different classes of phenolic resins. For example, phenolic resins produced using an acid catalyst and reacted with insufficient formaldehyde are called novolac resins. When these phenolic resins are cured, they change from a thermoplastic state to a denser, cross-linked thermoset matrix with relatively high heat resistance.

Phenolic resins (phenol-formaldehyde condensation products) in unmodified or modified form are almost exclusively used these days in the manufacture of friction material. The proportion of phenolic resin in brake material formulations varies from 5 to

35% by weight. Apart from certain exceptions, temperatures of more than 150ºC are required to cure these resins (Soib Selamat,2007).

Phenolic resin has desirable characteristics, such as superior mechanical strength, heat resistance, and dimensional stability as well as high resistance to various solvents, acids, and water. Its ability to maintain good mechanical strength at high temperatures is its best characteristic. Compared to other resins, it is also flame resistant and emits smaller quantities of smoke, with relatively low toxicity upon incineration. Although many other materials are superior to phenolic resin in some properties, phenolic resin provides a well-balanced overall performance at a relatively low cost (Akihiro Matsumoto et al, 1993).

Experts have been aware of phenolic composites for nearly a century, but their use in large-scale structural applications is relatively new. The traditional uses of phenolic are in heat-resistant, dimensionally stable applications. Although this remains true today, it represents a narrow viewpoint. The usefulness of phenolic composites stems from a fortunate combination of strength with good resistance to flame, chemical agents, and energy across a broad range of the electromagnetic spectrum. If these materials catch on fire, there is ample evidence that they will neither produce large amounts of toxic fumes or smoke nor easily loses stiffness from the heat. These are the synergy of properties inherent in phenolic composites. An interesting aspect of phenolic resins is their ability to adapt to stress, which has been observed with exposure to moderate to high doses of ionizing radiation, heat, and certain chemicals (Waitkus, 2005).

Phenolic resins are not the best performing bonding material for high temperature applications. The temperature range before curing is 150ºC to 185ºC. Normally friction products operate below this temperature. In normal service, passenger car brakes go to 150ºC, and truck brakes go to almost 200ºC. However, during emergency stops or repeated hard stops, friction materials can get much hotter. Emergency stops routinely exceed the decomposition temperature of phenolic resin (automotive brakes can get as hot as 750ºC), so that the resin does in fact decompose or char (Soib Selamat,2007).

Modified and unmodified phenolic resins are invariably used as binders in friction materials due to low cost along with a good combination of mechanical properties such as high hardness, compressive strength, moderate thermal resistance, creep resistance, and very good wetting capability with most of the ingredients. However, these resins are sensitive to heat and humidity and in situ polymerization starts slowly, even at ambient temperature; leading to its poor shelf life (Waitkus, 2005).

The criteria for the selection of phenolic resins are based on the following:

- The process used to manufacture friction materials (process parameter)
- The final properties of the friction material (material properties, friction parameter)
- Environmental and workplace aspects.

Table 2.10 highlights some advantages of phenolic resin as well as the rationale that make it suitable to choose as a material in manufacturing a brake pad.

Table 2.10: Advantages of Phenolic Resin (Swift, 2003)

Advantage	Rationale
Inexpensive, widely available	Other resins are higher performance, none are cheaper
Reasonably strong	Stronger resin might lead to longer-lasting friction products
Good char strength	Although phenolic resin does char, it still maintains reasonable structural strength
Easy to handle	Well-known material, used for many years

ii. COPNA resin

COPNA resin refers to “condensed poly-nuclear aromatic” resin. As its molecular structure is the same as graphite (a lubricant used in brake friction material), the bonding strength between the latter and COPNA resin will be very high (Komori, Miyake and Senoo, 1990). As such, the structural integrity of graphite-containing brake friction materials will be better with the use of COPNA resin, giving rise to higher shear strengths than if phenolic resin were used. Its heat resistance is not significantly better than phenolic resin as it decomposes at approximately the same temperature (400 - 500°C), although the volume of decomposed gas is less than phenolic resin (Kakegawa, Yasuda and Wang, 1999).

iii. Silicone-modified resin

Base materials are also referred to as phenolic siloxane resins. Silicone-modified resins are typically produced by reacting silicone oil or silicone rubber with phenolic resins. They are modified with tougheners to reduce their brittleness. However, in this process, the original characteristics of thermal and chemical resistance of phenolic resins are compromised. Kane and Mowrer (1998) succeeded in combining phenolic resins with silicone to form phenolic siloxane resins with enhanced impact resistance.

iv. Cyanate ester resin

Cyanate ester resins, formed from polyfunctional cyanate monomers, are stable at elevated temperatures, are chemically inert, and have damping properties. However, they are brittle like phenolic-based resins (McCormick et al, 2000). According to Ohya and Kimbarya (1990), brake pads that use cyanate ester resins as binders maintain their friction coefficient at elevated temperatures above 350^{o}C and are also able to maintain good adhesion with the backing plate during service life while addressing the serious pollution problem stemming from the use of asbestos in conventional brake pads.

v. Epoxy-modified resin

A pure epoxy resin is not able to withstand high temperatures. At temperatures above 260^{o}C, typical epoxy resin binders degrade (Tsang et al, 1985). To increase the operating temperatures of epoxy resins, special curing agents have to be used. For example, Shell Chemical Company has a grade of epoxy resin cured with an anhydride agent that is operable at 400^{o}C, despite showing linear increases in wear above 290^{o}C. Therefore, epoxy is usually used to modify phenolic resins, resulting in the synergistic effect of having a higher heat resistance than phenolic resin or epoxy resin alone and has a high frictional stability (Lam and Chen, 1999). Epoxy-modified phenolic resin has been claimed to be a resin that can stand high temperatures and have good strength even under extreme conditions (http://www.bendix.com.au/content/technologies).

vi. Thermoplastic polyimide resin

Thermoplastic polyamide resin is the product of fluoro resin and calcium carbonate. It is abrasion resistant and does not exhibit thermal fade commonly experienced with phenolic-based resins or induce excessive brake disc wear (Nagahiro and Umemto, 1993). Such a resin is easily produced using injecting molding or other melt-processing methods. However, its thermal conductivity is approximately three times lower than that of phenolic resins (Avallone and Baumeister III, 1997), so it is less able to dissipate heat away from the friction surface.

2.5.2 Friction Producers/Modifiers

Frictional additives are components added to the brake material in order to modify the friction coefficients as well as the wear rates. These materials lubricate, raise the friction, or react with oxygen to help control interfacial films. They are divided into two main categories: lubricants, which decrease the friction coefficients and wear rates, and abrasives, which increase friction coefficients and wear rates. It is also important to note here that certain frictional additives may be loosely regarded as fillers by certain manufacturers if they are present in large quantities (Blau, 2001; Chan and Stachowiak, 2003; Pandey et al., 2001).

By using brake pads with varying quantities of antimony sulphide (a lubricant) and zirconium silicate (an abrasive), Jang and Kim (2000) drew the following conclusions:

a. Brake pads with increased lubricant content show increased stability of the friction coefficient.
b. Brake pads with increased abrasive content show increased friction coefficient variation (instability).

Therefore, it is important to achieve a compromise between the amount of lubricants and abrasives in brake friction material.

Nicholson (1995) was reported that antimony trisulfide has been used as solid lubricant for the function of friction modifier in order to enhance frictional stability, but was not famous because of potentially toxic. Metallic based friction modifiers were more popular such as brass and copper, especially to control heat transport. Carbon (graphite) and ‘friction dust’ commonly consists of process cashew resin are also widely used because of low cost and available in many forms and sources.

PQ Corperation in the year 1993 was introduced ceramic ‘microspheres’ a special product consisting of of alumina-silica with minor iron or titanium oxides. This low-density filler said to reduce rotor wear and control the friction. According to Gudmand Hoyer et al. (1999) various metal sulfide, such as Cu_2S, Sb_2S_3, PbS also used; studies show the effect of additives on disc brake pads with and without metal fibers. Those metal sulfide used can modify and stabilize the friction coefficient. Highest µ can be obtained with Sb (0.47-0.49) and PbS (0.40-O-47). Metal sulfide also said to reduce pad and rotor wear and reduce noise. MoS_2 and ZnS are low-cost solid lubricant adheres more readily to metal surfaces than graphite and recommended for high loads and temperatures. Beside that metal sulfide mixture was also used.

2.5.3 Lubricants

The main purpose of a lubricant is to stabilize the developed friction coefficient during braking, particularly at high temperatures. Commonly used lubricants include graphite and various metal sulphides. Graphite is widely used as it is able to form a lubricanting layer on the opposing counter friction material rapidly (Taylor,1998). This self-sustaining layer ensures a stable friction coefficient. The graphite used in brake friction materials can be of natural or synthetic origin and can exist in flake or powder form. Graphite in the flake form has improved lubrication properties (Takahasi,1999), while graphite in the powder form is able to dissipate heat generated during braking more effectively (Booher , 1992).

Graphite has unique physical and chemical properties, which facilitate its use in the high-tech industrial sector. It can easily and cheaply be thermally or chemically purified to over 99.99% purity on a large commercial scale with consistent results. In the processing other elements can be added to enhance performance, according to the manufacturer's specifications. This assures the end user of a high-performance product specifically formulated for their use at a competitive cost.

Graphite is a natural form of carbon characterized by its hexagonal crystalline structure. It occurs naturally in metamorphic rocks such as marble, schist and gneiss. The same element crystallizing in an octahedral system becomes a diamond. It is a lustrous black carbon mineral, unctuous, and relatively soft with a hardness of 1-2 on the Moh's scale. It occurs naturally in the earth's crust and is the most abundant form of pure carbon.

It is an excellent conductor of heat and electricity which has a high melting temperature of 3,500 degrees Celsius. It is extremely resistant to acid, chemically inert and highly refractory. Because of these underlying physical and chemical properties, there is a global market for graphite. This commercial market is composed of three distinct grades of graphite:

1. Amorphous Graphite
2. Crystalline Lump Graphite
3. Flake Graphite

2.5.4 Abrasives

Abrasives help maintain the cleanliness of mating surfaces and control the build-up of friction films. They also increase friction, particularly when initiating a stop; in simple terms, they increase “bite and grip”. The abrasives in a friction material increase the friction coefficient while also increasing the rate of wear of the counter face material. They remove iron oxides from the counter friction material as well as other undesirable surface films formed during braking. However, friction materials with a higher abrasive content exhibit a greater variation of friction coefficient, resulting in instability in braking torque. Examples of abrasives are hard particles of metal oxides and silicates. The abrasives have to be hard enough to at least abrade the counter friction material, which is typically cast iron. The abrasives generally have Mohs hardness values of around 7 to 8; a few examples of commonly used abrasives include zirconium oxide, zirconium silicate, aluminum oxide, and chromium oxide (Kobayashi, 2002).

Alumina is the most cost effective and widely used material in the family of engineering ceramics. The raw materials from which this high performance technical grade ceramic is made are readily available and reasonably priced, resulting in good value for the cost in fabricating alumina shapes. With an excellent combination of properties and an attractive price, it is no surprise that fine grain technical grade alumina has a very wide range of applications. Alumina almost used as an abrasive in brake pads.

High purity alumina is usable in both oxidizing and reducing atmospheres to 1925°C. Alumina will show a weight loss in vacuum ranges from 10^{-7} to 10^{-6} g/cm^2.sec over a temperature range of 1700° to 2000°C. It resists attack by all gases except wet fluorine and is resistant to all common reagents except hydrofluoric acid and phosphoric acid. The elevated temperature attack occurs in the presence of alkali metal vapors particularly at lower purity levels.

2.5.5 Fillers

Fillers are used to maintain the overall composition of the friction material; some have other functions as well. Fillers are included in a brake pad in order to improve its manufacturability as well as reduce the overall cost of the brake pad (Eriksson, Bergman and Jacobson, 2002). Filler is a loose term that can also refer to anything used in large proportion in a brake friction material. For example, certain manufacturers use a large proportion of metal silicates (hard, abrasive particles) in their brake friction material and refer to them as ‘fillers’ instead of ‘abrasives’. Although not as critical as other components such as reinforcing fibers, fillers play an important role in modifying certain characteristics of brake friction material. However, the amount of filler is among the highest in a brake pad’s composition. Thus, to some extent, fillers affect the final properties of brake performance. The presence of fillers can affect properties such as resistance to heat, abrasion, and strength.

The actual choice of fillers depends on the particular components in the friction material as well as the type of friction material. For example, a metallic pad that generates a lot of braking noise would require more filler, such as cashew and mica (noise suppressors), than barium sulphate (heat stability). Meanwhile, semi-metallic brake pads with a mixture of metallic and organic compounds and varying thermal expansion coefficients would require a large amount of molybdenum trioxide to prevent cracks in the lining. Brake pads with large quantities of graphite or antimony sulphide as lubricants do not require alkali metal titanates as a filler (Chan and Stachowiak, 2003). Therefore, the specific filler to be used depends on the constituents of the friction material. They can be metals, alloys, ceramics, or organic materials.

i. Organic fillers

Common examples of organic fillers used in brake pads are rubber and cashew dust, both of which have that same properties in that they are usually incorporated into brake pads for the purpose of reducing brake noises due to their superior viscoelastic characteristics (Kamioka, Tokumara and Yoshino, 1995). However, these particles, especially cashew; fall off the friction surface easily, leaving behind large pores that eventually crack (Kinouchi, Hara and Yamaguchi, 2002). To prevent this from happening, the cashew or rubber particles are sometimes coated with an adhesive. Also, certain brake friction material manufacturers use cashew or rubber particles as under-layer material because their low thermal conductivity prevents heat from transmitting to the backing plate of the brake friction material (Nakagawa, 2001).

ii. Inorganic fillers

Typical inorganic fillers include barium sulphate, mica, vermiculite, and calcium carbonate. The common property of these fillers is that they possess a relatively high melting point. For example, barium sulphate has a melting point of 1350°C (Lide and

Kehianian, 1994) whereas Western Australian Mining and Petroleum Research Institute,(1989) reported that vermiculite rapidly exfoliates into fades at an approximately 800°C. Vermiculite is the cheaper of the two, but it is not as stable at higher temperatures as barium sulphate. Mica is also commonly used as filler. It is able to suppress low-frequency brake noise (Yamashita et al, 1993) due to its plane netlike structure (Kimura et al, 1998). However, its stratified structure results in a low interlayer strength. As such, mica causes interlayer splitting of the friction lining, especially at high braking loads.

To prevent the interlayer splitting of mica, aluminum phosphate can be used as a coating on mica powder (Seki, 1993). Like mica, vermiculite can also suppress noises generated during braking (Nagakawa, 1993). Molybdenum trioxide is a recent addition to the family of inorganic fillers. According to Nakajima and Kudo (2000), molybdenum trioxide can prevent thermal fade and the cracking of friction lining under high-temperature conditions. It has a relatively high melting point of approximately 800°C (Lide and Kehianian, 1994). Other researchers, such as Kesavan and Burmester (1999), have proposed the use of alkali metal titanates (such as sodium titanate) for use as fillers, claiming that they promote the stability of the friction coefficient. In addition, the addition of titanium compounds to abrasive particles (such as silicon carbide) has been found to lower its wear rates.

2.5.6 Reinforcing Fibers

The purpose of reinforcing fibers is to provide mechanical strength to the friction material. Recent research has shown that the braking load is actually carried by tiny plateaus that rise above the surrounding lowlands on the friction material (Eriksson, Bergman and Jacobson (2002). These plateaus are formed by the reinforcing fibers surrounded by the softer compacted components. Therefore, the importance of the reinforcing fibers in friction material cannot be underestimated. Friction materials typically use a mixture of different types of reinforcing fibers with complementing properties.

i. Glass

Glass fibers have been used as reinforcing fibers since the mid 1970s. Being physically strong when bonded together with resinous binders, glass fibers are suitable for use as reinforcing fibers as they also exhibit thermal resilience (Marzocchi, Jannarelli and Garrett, 1976). Typical glass has a melting point of 1430°C (Avallone and Baumeister III, 1997), which is significantly higher than the 800-850°C melting point of asbestos as reported in Priority Existing Chemical Report 9, National Industrial Chemicals Notification and Assessment Scheme, Commonwealth of Australia (1999). However, typical glass fibers only have a conductivity of 0.04 W/m K, which is even lower than that of asbestos at 0.15 W/m K and significantly less than metallic fibers such as copper. The brittleness of glass means that it cannot be the sole reinforcement in brake friction materials. The literature has discussed the advantages and disadvantages of organic fibers over metallic fibers (Hell, 2002; Jang, Lee and Fash, 2001; Samuels, 1996).

ii. Metallic

Metallic chips or granules are commonly used as reinforcing fibers; hence, they are referred to as metallic ‘fibers’ although they may not strictly be thread-like. Examples of metallic fibers include steel, brass, and copper. Semi metallic pads can contain up to 50% steel fiber, which does nothing for performance except create sparks and scratch rotors. Steel fiber gives a high grip, but it does not combat fade and it causes rotors and pads to wear out at almost the same speeds in a world where the brake pad is supposed to be the disposable item.

The drawback of using steel fibers is that they will rust, especially if the vehicle has an extended rest period or if the vehicle has been operating near a coastal environment. Steel fibers attacked by rust will be less resilient, thereby compromising their functionality as reinforcing fibers. Therefore, certain brake pads include metals such as zinc distributed over the cross-section of the friction lining, thereby forming a sacrificial anode for rusting to occur (Hell, 2002). Another drawback of using steel fibers is that they might cause excessive wear of the brake disc if they are present in large proportions. Steel fibers have also been shown to increase friction coefficient fluctuations (Jang, Lee and Fash, 2001), the likely reason being due to the fact that such fibers abrade the transfer film between braking surfaces, which is responsible for friction coefficient stabilization.

On the other hand, a significant advantage of using metal fibers is that they have very high conductivities and are able to remove heat from the frictional surfaces very quickly. Some brake pads contain oxidized or phosphatized fibers, resulting in improved fracture toughness and strength (Samuels, 1996).

iii. Aramid

Aramid fibers are extremely light and exhibit excellent thermal stability, with a very good stiffness weight ratio. Aramid fibers (a generic expression denoting fibers made from the condensation product of isophthalic terephthalic acids and m- or p-phenylenediamine (Okubo, Albertson and Nibert 1984) such as Kevlar ™ fibers are also widely used as reinforcing fibers, but they are a different class of fibers in that they are relatively soft fibers. According to Smith and Boyd (1999) of R.K. Carbon Fibers company, aramid fibers has a superior anti-fade property compared to asbestos. The advantage and disadvantage of aramid over metallic fiber has previously been discussed in the literature (Anderson, 1987; Buckley, 1981; Rabinowicz, 1995; Anderson, 1995; Katsuhiro et al, 1993). Aramid fibers in pulp form have also been utilized in maintaining the uniformity of the brake pad material mixture during the processing of a molded brake pad (Carlson and Headley, 1999). Another property they have is that of superior wear resistance (Brinzey, 1991). However, due to their relative softness, it is unlikely that they would be the only fibers supporting the braking load; there would most probably be other harder fibers, such as metallic fibers in the friction lining.

iv. Potassium titanate

Potassium titanate fibers are another type of reinforcing fiber used in brake friction materials. These fibers are prepared from highly refined materials with a high melting point (1250-1310°C) (Kim et al, 2001). However, they have the potential to cause mesothelioma (Adachi, Kawamura and Takemoto, 2001), a type of cancer that is predominantly caused by asbestos. For this reason, they are not commonly used and should not be thought of as a suitable replacement for asbestos. In an effort to eradicate the danger of potassium titanate fiber inhalation, Hikichi (2002) of Akebono Brake Industry has devised a process for producing potassium titanate in the form of powders, with the same frictional performance and strength as fibrous potassium titanate. The powder form is apparently more difficult to inhale than if it were in the fibrous form.

v. Ceramics

With a high thermal resistance (melting points ranging from 1850 to 3000°C), their lightweight nature, and high strength, ceramics are very suitable as reinforcing fibers (Warren, 1992; Tenth Report on Carcinogens, US Department of Health and Human Services, 2002). Ceramic fibers are a relatively new addition in brake pads compared to metallic fibers such as steel. They are typically made of various metal oxides such as alumina (aluminum oxide) as well as carbides such as silicon carbide. Their high strength-weight ratio means that they are preferred over metallic fibers, which are much heavier. Not only are they used in brake pads, but they are also used to reinforce brake discs as well. In one instance, aluminum brake discs were reinforced by ceramic fibers because the wear rates encountered when using aluminum brake discs against conventional friction materials were unacceptable (Tsugawa, Suzuki and Kubono, 1998).

vi. Asbestos

Besides being used as a filler in brake pad, according to the Automotive Disc Brake Manual by Haynes Publishing (1998) asbestos in fibrous form has been used as reinforcing material in brake pads since 1908, when English inventor Herbert Frood came up with a combination of asbestos, brass wire, and resins for use as a friction lining. Asbestos is cheap and provided friction linings with excellent durability and thermal resilience (Priority Existing Chemical Report 9, National Industrial Chemicals Notification and Assessment Scheme, Commonwealth of Australia, 1999). This is a key attribute as braking temperatures can reach hundreds of degrees Celsius. In the late 1980s, it became public knowledge that asbestos is a carcinogen, and brake pad manufacturers started looking for suitable alternatives.

Asbestos is hydrated magnesium silicate $Mg_3Si_2O_5(OH)_4$. When it is used, the content of asbestos in vehicle brakes varies between 30 and 70%. According to Nicholson (1995), the positive characteristics of asbestos are that (1) it is thermally stable to 500°C, above which it produces silicates; (2) it helps regenerate the friction surface during use; (3) silicates produced by asbestos are harder and more abrasive than asbestos; (4) asbestos insulates thermally; (5) it processes well; (6) it wears well; (7) it is strong yet flexible; and (8) it is available at a reasonable cost. The fibrous character remains intact until about 1400°C.

According to Spurr (1972), asbestos becomes dehydroxylated at high temperatures. It tends to transform into forsterite and silica above 810°C. The wear debris contains forsterite or amorphous material. The kinetic friction coefficient (μ_κ) of asbestos against clean iron is -0.80. The type of asbestos used is important because of differences in costs, properties, and processing. Chrysotile is normally used, but other asbestos minerals, such as amosite and crocodolite, may be used. Three other types (anthophyllite, tremolite, and actinolite) are rarer and found primarily as minor contaminants along with other minerals.

a) Wear of Asbestos Materials

The wear rate of asbestos brakes was studied and reviewed by Rhee of Bendix Corporation (1974). The wear rate of an asbestos-reinforced lining, in drum-type tests, was investigated, and the following general relationship shown as equation 2.5 was used to model the process:

$$\mathbf{AW} = \alpha P^{a} V^{b} t^{c} \qquad [2.5]$$

where **AW** = wear loss (grams), ***P*** = normal pressure (psi), ***V*** = sliding speed (r-pm), and ***t*** = sliding time (min.). The proportionality factor ***α*** depends on testing geometry. Values of exponents ***a, b,*** and ***c*** are material pair-related. The wear rate of asbestos-containing friction materials is reported to be constant up to about 232°C, after which it increases exponentially.

b) Regulations and the Current Use of Asbestos in Brakes

Medical research has shown that asbestos fibers can lodge in the lungs and induce adverse respiratory conditions. In 1986, the Environmental Protection Agency (EPA) announced a proposed ban on asbestos, which would have required all new vehicles to have non-asbestos brakes by September 1993 while the aftermarket would have had until 1996 to convert to non-asbestos. The EPA's proposed ban was overturned in federal court, but it resulted in a major shift away from asbestos by most friction material suppliers and vehicle manufacturers. Ford was still using asbestos linings as recently as 1993 on its Crown Victoria model, but it has since discontinued using them. A few high-end imports such as Land Rover are the only original equipment applications that still use asbestos (Pascoe, 1973).

Asbestos brake products are still used in the aftermarket despite the fact that many people think asbestos was replaced by non-asbestos organics years ago. In 1996, Market Scope research (Market Scope is a division of Babcox Publications, Inc.) reported that asbestos linings were still being installed on 9.5% of the vehicles serviced by its readers. That is a significant percentage of the total brake market, considering that many people believe that asbestos is no longer even available. Asbestos is still used because it is an economical fiber for low-temperature brake applications, but it is gradually being phased out for the aforementioned reasons. (http://www.babcox.com/cm/cm99628.htm)

Mandatory Occupational Safety and Health Administration, OSHA requirements concerning asbestos in brakes can be found in OSHA Standard 1910.1001, Appendix F: “Work practices and engineering controls for automotive brake and clutch inspection, disassembly, repair and assembly”; Subpart Number: Z “Toxic and Hazardous Substances. This mandatory appendix specifies engineering controls and work practices that must be implemented by the employer during automotive brake and clutch inspection, disassembly, repair, and assembly operations.

c) Possible Replacements for Asbestos in Brakes

Nicholson (1995) identified several replacement materials for asbestos: wollastonite (calcium silicate), vermiculite (hydrated calcium aluminum silicate), mica (aluminum silicate), basalt fiber, rockwool (blast furnace slag or basalt), Fiberfrax@ ceramic fiber, polyacrylonitrile (PAN), polyester, chopped glass fiber, and aramid fibers. None is exactly like asbestos, but they offer some similar performance characteristics.

2.6 Fillers Used in this Study

There are more and more technical applications in which friction and wear are critical issues. Polymer composites containing different fillers and/or reinforcements are frequently used for these purposes. In particular, they are now being used as sliding elements, which were formerly composed of metallic materials only. Nevertheless, new developments are still under way to explore other fields of application for these materials and to tailor their properties for more extreme loading and environmental temperature conditions.

The purpose of using fillers in brake materials can therefore be divided into basic categories; to improve the mechanical, thermal or tribological properties, and second, to reduce the cost of the component. There have been various reports on the use of materials such as minerals and inorganic oxides (alumina and silica), mixed into widely used thermoplastic polymers (Mareri et al., 1998; Jarvela et al., 1996; Rusu et al., 2001 and Barta et al., 1997). But very few attempts have indeed been made to utilize cheap materials like industrial wastes such as palm slag in preparing filled friction composites.

Additional fillers that enhance the thermal conductivity are often of great advantage, especially if effects of temperature enhancement in the contact area must be avoided in order to prevent an increase in the specific wear rate. It should also be noted, that not all the fillers are of benefit to the wear performance of composites. The wear resistance is increased when fillers decompose and generate reaction products which enhance the bonding between the transfer film and the counter face (Briscoe, 1993), whereas other fillers decrease the wear resistance because they generate more discontinuities in the material. It is thus important to understand the properties and morphology, which are strongly related to the wear mechanisms.

Due to the awareness of health hazardous of asbestos, the non asbestos organic friction composites are tremendously increased its application as automotive brake parts such as linings, pads, shoes and etc. These are essentially multi ingredient systems in order to achieve the desired amalgam of performance properties and more than several hundred ingredients have been reported in the literature for being used to tailor the friction composites (Jacko et.al., 1984; Orthwein, 1986; Nicholson, 1995; Bijwe,1997; Blau, 2000; Chan and Stachowiak, 2004). These are categorized as a binder, reinforced fiber, friction modifier and filler, based on the major function they perform as mentioned earlier in this chapter. Filler play a significant role because of their large in percentage and their specific functions.

Several researches have been conducted in the area of development of asbestos free brake pads. A lot of materials were introduced to the brake pad composites. The used of coconut shell, palm ash, palm kernel shell and etc. has been investigated (Dagwa, 2005;2006). All over the world, researchers are focusing on ways of utilizing either industrial or agricultural waste as a source of raw materials in the industry. Inorganic particle is always associated with the enhancement of mechanical properties of polymer composites, which have been widely investigated in the past decades.

The development of innovative friction materials for use in brake pads by using sustainable approaches, including the use of industrial waste byproducts from coal combustion and coal gasification, such as fly ash, would help control the health hazards associated with fly ash and reduce the rate of depletion of important natural resources such as forests and minerals. The most attractive factors associated with the utilization of waste materials in friction composites are their abundance and the fact that they have very low, or even zero, cost. Thus, their attractive performance-to-cost ratio has stimulated the idea of exploring their possible incorporation into friction composite formulations. In addition, the successful utilization of waste material, such as fly ash, also would indirectly contribute to the reduction in the rate of depletion of valuable natural resources (Kumar and Patil, 2006).

A few other researchers like Satapathy (2002), Malhotra et al. (2002), Hee and Filip (2005), Mohanty and Chugh (2007) were also concentrating on the studies of combustion waste particle as fillers. Those particles, such as fly ash, when used in friction braking application exhibit high temperature resistance and provide good integrity or compatibility with the resin, thereby enhancing the friction and wear performance of the composite materials.

It also has been found that the size of the particles plays an important role to improve, in particular, stiffness and toughness simultaneously (Friedrich, 2005). Particle size of filler and other material that involved in brake pad composites are also expected to be able to strongly influence the wear properties and performance.

In brake pad, for an improvement of the wear resistance, various kinds of micron size particles were incorporated into a different polymer binder. The improvement of the wear properties is due to either mechanical or chemical reasons. Bahadur and his co-researchers were found that the incorporation of micron size inorganic particle led to two opposite trends in the wear resistance. They concluded that a transfer film develops due to the adhesion and interlocking of the polymer fragments into metal asperities during sliding. Some inorganic particle helps to enhance the wear properties and others in a contrary effect due to generation of more discontinuities in the materials.

Beside those studies involving various filler materials, the processing parameters, especially during the production of brake pad also play a significant role. Kawabe et al. (2011) was investigated the effect of molding pressure on the structure of the friction materials. As the friction materials of the commercial brake pad, consist of various materials, it is very important to examine the mechanical and as well as morphological changes in the brake pad as a function of material composition and processing load. However, the compression effect on microstructure and morphology of friction materials in the brake pad has been reported very few.

Naturally, the mechanical and wear properties of the phenolic resin based friction composites like brake pads are greatly dependent on the interactions and synergetic effects among the multiphase ingredients (Yi and Yan, 2006). In this sense, it is crucial to correctly and properly select and combine the different components so as to satisfy a number of requirements for the properties such as good wear resistance, small wear to the counterparts, stable coefficient of friction and reliable strength at a wide range of stressing conditions of the friction materials (Blau, 2001, Osterle and Griepentrog, 2001)

The availability of industrial waste and government regulations have promoted researchers to try for industrial waste reinforced composites. With low cost, ease of manufacturing and high mechanical and other properties, industrial waste represents a good alternative to the most common composites. According to Vijay Kumar et al., (2014) the slag is reinforced with polypropylene due to its low density, high corrosion resistance, ease of fabrication and low cost. The major advantages offered by polymer slag composite are their increased specific strength, stiffness, high hardness and wear resistance. Beside that, the low coefficient of thermal expansion, superior dimensional stability, good forming characteristic, easy availability of cheaper reinforcement along with the availability of comparatively low cost, and high volume production methods are the additional advantages.

In this study, three different particle materials were employed as fillers in a typical brake pad formulation together with phenolic resin as binder, alumina as abrasive component, graphite as lubricant and metal fiber as reinforcing material. Those three materials are palm slag, calcium carbonate and dolomite.

a. Palm Slag

Palm slag that is used in this study was found as waste from the processing of extraction palm fruit for oil. Palm oil mill produces a lot of solid waste byproduct. After the combustion in the steam boiler, about 5% of ash was produced. After oil extraction, large amounts of solid wastes i.e. empty fruit bunches (EFBs), shell and palm fiber are left behind. The EFBs are usually spread over the estate ground as mulch whereas the shell and fiber can be used as a boiler fuel supplement. A huge amount of ash and slag is also produced out of burning process involved in the oil extraction process. This ash and slag do not have nutrient to be used as fertilizer. In order to prevent environmental degradation and pollution, this study has come out with the used of palm slag as alternative filler in brake pad material to replace the existing filler especially asbestos.

The most attractive factors associated with the utilization of waste materials like palm slag in friction composites are their abundance and the fact that they have very low, or even zero, cost. Thus, their attractive performance-to-cost ratio has stimulated the idea of exploring their possible incorporation into friction composite formulations.

b. Calcium carbonate

Calcium carbonate or known as calcite, which gets its name from "*chalix*" the Greek word for lime, is a most amazing and yet, most common mineral. It is one of the most common minerals on the face of the Earth, comprising about 4% by weight of the Earth's crust and is formed in many different geological environments. Calcite can form rocks of considerable mass and constitutes a significant part of all three major rock classification types. It forms oolitic, fossiliferous and massive limestones in sedimentary environments and even serves as the cements for many sandstones and shales. Limestone becomes marble from the heat and pressure of metamorphic events.

c. Dolomite

Dolomite, which is named for the French mineralogist Deodat de Dolomieu, is a common sedimentary rock-forming mineral that can be found in massive beds several hundred feet thick. They are found all over the world and are quite common in sedimentary rock sequences. Dolomite differs from calcite, $CaCO_3$, in the addition of magnesium ions to make the formula, $CaMg(CO_3)_2$. The magnesium ions are not the same size as calcium and the two ions seem incompatible in the same layer. In calcite the structure is composed of alternating layers of carbonate ions, CO_3, and calcium ions. In dolomite, the magnesiums occupy one layer by themselves followed by a carbonate layer which is followed by an exclusively calcite layer and so forth.

Rocks containing only10-50% of the mineral dolomite are called dolomitic. Most, if not all, dolomite is a replacement of pre-existing limestone and this replacement process are known as dolomitisation. The process is often incomplete and rocks termed ‘dolomite’ are usually a combination of dolomite, dolomitic limestone and limestones. This fact, together with the presence of variable amounts of impurities, such as silica, sulphur, iron oxide and alumina, has an important bearing on the suitability of dolomite for specific applications.

Industrial dolomite is a commercial term for dolomite used for non-construction purpose where its chemical properties (or degree of whiteness) are important. The MgO content of dolomite is commonly expressed after calcinations (heat treatment involving the removal of carbon dioxide).Pure dolomite has an MgO content of about 40%. However, glass manufacturers normally use pre-calcined MgO content for control purposes and there is a theoretical maximum of about 21.8% MgO. Dolomite for industrial purpose accounts for a relatively small and decreasing proportion of the total dolomite output.

The principal uses of industrial dolomite, firstly as a refractory and later as a flux, have been linked with iron and steelmaking since the later part of the 19th century. For this reason industrial dolomite has been regarded as of vital importance to the iron industry. The other major markets for dolomite are in glass making and for agriculture use. Dolomite is also used for a range of filler applications in plastics, paints, rubbers, adhesives.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 Introduction

This research was focused on the study of the development of brake pads using palm slag as the filler material. In this study palm slag was used to replace the filler used in brake pad such as asbestos or other organic or inorganic filler, resulting in a non-asbestos brake pad composite. Different palm slag particle sizes and different pressures during processing of brake pad were investigated. Comparisons with other fillers, i.e., dolomite and calcium carbonate ($CaCO_3$) were also conducted.

3.2 Experimental Design

The methodology of this study, which covers the overall process discussed in the chapter, is summarized in Figure 3.1. The process can be classified into three (3) sections, i.e., characterization of the raw materials, preparation of the samples, and characterization of the products.

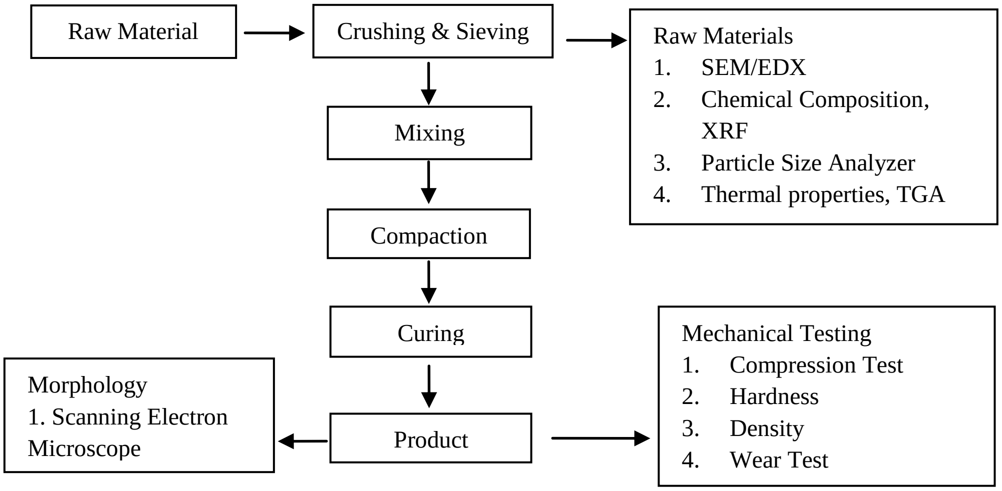


Figure 3.1: Flow chart of the development of the palm slag brake pad

3.3 Raw Materials

3.3.1 Binder

Phenolic resin was selected as the binder in this brake pad composite. Phenolic resin is the most commonly used binder in existing commercial brake pads all over the world. Phenolic is a type of thermoset polymer form by a condensation reaction between phenol and formaldehyde and is able to act as a matrix for binding together different substances (Salamone, 1999). It was obtained from one of the largest manufacturers of commercial brake pad i.e., AFI Sdn. Bhd., operated in Terengganu, Malaysia.

3.3.2 Fillers

Three (3) different fillers were selected in this study as alternative filler and for comparison purposes, i.e.; palm slag, calcium carbonate ($CaCO_3$) and dolomite.

a. Palm Slag

The palm slag used in this study was the waste material from the palm oil industry. Palm slag is a byproduct of the palm fruit processing after burning, during palm oil extraction. It was supplied by a local palm oil producer in Seberang Perai, Penang, Malaysia. Figure 3.2 shows the raw palm slag obtained from the palm oil industry.

Figure 3.2: Chunky raw palm slag from local palm oil industry

b. Calcium carbonate

Calcium carbonate is a chemical compound with the formula of, $CaCO_3$, used in this study was supplied in powder forms by a local supplier in Penang, Malaysia. The particle size of the $CaCO_3$ was in the range of 10 to 100 μm. $CaCO_3$ was used for comparative purposes since already is being used extensively as a replacement for asbestos. Figure 3.3 shows the SEM micrograph of raw calcium carbonate powder.

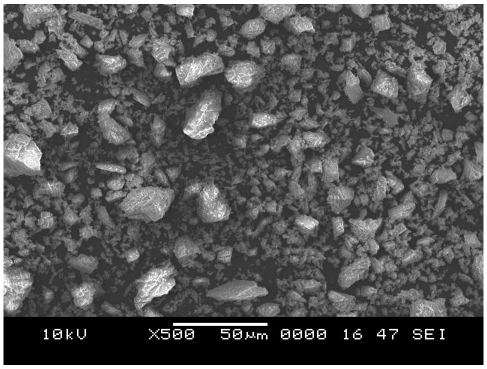


Figure 3.3: SEM micrograph of calcium carbonate powder.

c. Dolomite

Dolomite, which is known as ‘Batu Reput’ by the local people of Perlis is a mineral that is abundantly available, which can be found in massive beds several hundred feet thick in the northern part of Perlis, Malaysia. The dolomite used in this study was obtained locally from the Bayan Mas Quary in Perlis. Figure 3.4 shows the SEM micrograph of dolomite powder. Dolomite was chosen in order to compare with the palm slag and $CaCO_3$ because dolomite is a mineral substance which is very close to $CaCO_3$ which is easily and abundantly available in this country.

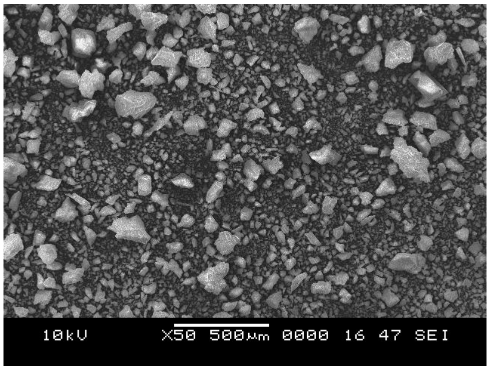


Figure 3.4: SEM micrograph of dolomite powder.

3.3.3 Reinforcement

Steel fibre is used as a reinforcement in this study. It was selected because steel fibre are often used in the commercial semi-metallic brake pads since it provides good wear resistance and maintain friction at elevated temperature (Jang et al., 2004 and Sung et al., 2009). Steel fibre provides excellent grip, but it does not combat fade and causes the disc plate and pads to wear out at about the same time, which is a problem since the brake pad, not the disc plate is supposed to be a disposable item. Steel fibres also were obtained from AFI Sdn. Bhd., Terengganu, Malaysia.

3.3.4 Abrasive

Alumina is the most cost-effective and extensively used material in the family of engineering ceramics. The raw materials from this high performance, technical-grade ceramic is readily available and reasonably priced, resulting in better value for fabricating alumina shapes. With an excellent combination of properties and an attractive price, it is no surprise that fine grain technical grade alumina has a very wide range of applications. Alumina almost used as an abrasive in brake pads. The alumina used in this study also was obtained from AFI Sdn. Bhd., Terengganu, Malaysia.

3.3.5 Lubricant

Graphite is a polymorphic of carbon, has unique physical and chemical properties that facilitate its use in the high-technology industrial sector. It can be thermally or chemically purified easily and cheaply to over 99.99% purity on a large commercial scale with consistent results. It is an excellent conductor of heat and electricity, and it has a high melting temperature of 3,500 ^{o}C. It is extremely resistant to acid, chemically inert and highly refractory.

3.3.6 Formulation of the Friction Composite

The formulation used in the friction composites for this study is shown in Table 3.1. The amounts (as percentages) of each material in the composite material are shown in Table 3.1. This combination of composite materials for the composite was chosen because the presence of relatively dominant filler can have a significant effect on the end properties of the brake pads. This formulation was chosen based on the typical formulation suggested by Blau (2001) as also typically used in most of the simple formulation of commercial brake pad.

Table 3.1: Percentage of each type of materials used in the composite samples

Material	Percentage (%)
Binder (Phenolic resin)	20
Filler (Palm slag/ $CaCO_3$/ Dolomite)	40
Fibre Reinforcement (Steel fibre)	20
Abrasive (Alumina)	10
Lubricant (Graphite)	10

3.4 Experimental Procedures

3.4.1 Preparation of Different Palm Slag Fillers

Palm slag an industrial waste, collected from the palm oil industry was delivered in solid chunks. This raw material needs to be crushed and sieved into smaller size before ready to use and served the purpose as a filler in the friction composite.

a. Crushing

Crushing process was obtained by a jaw crusher in order to crush the solid chunks to become smaller size. After that the high speed grinding were used to obtain the smaller sizes filler required. Then, the different sizes of the ground palm slag were segregated by the sieving process into a series of uniform sizes.

b. Sieving

A simplistic definition of sieving is the separation of fine material from coarse material by means of a meshed or perforated vessel. In this study, a UTS Sieve shaker was used to sieve the crushed and ground palm slag. Sieving is a method or procedure used to separate specific sizes of crushed and ground palm slag from a mix of different sizes. A stacking type sieve was used in this research to obtain a series of particle sizes. In this process, the palm slag is sieved through a series of sieves stacked in order, with the sieve that has the smallest openings at the bottom. For the purposes of this research, the palm slag was divided into three sizes, i.e., less than 300 μm, 300 - 600 μm and greater than 600μm up to 2 mm as shown in Table 3.2.

Table 3.2: Palm slag fillers of three different sizes

Type	Size
Palm slag 1	<300 μm
Palm slag 2	300 – 600 μm
Palm slag 3	>600 μm – 2 mm

The sieved particles were approximately spherical and irregular in shape and they would pass through the square openings on the sieve screens when the diameter of the particles was less than the size of the square opening. For elongated and flat particles a sieve size will not yield reliable mass-based results, because it still can pass through or might pass through the screen end-on, even though they could not pass through side-on as reported by Jain (2003).

3.4.2 Raw Materials Characterization

The characterization of the raw materials was very important because there was a need to know the details of each material used in the research. It was designed to thoroughly characterize the raw materials and identify risks that could affect the performance of the products and try to develop strategies to minimize those risks. Understanding the properties of each raw material is a key factor in the development of multi-component composites, such as brake pad composite materials. Detailed descriptions of the raw materials are essential for structured and target-oriented product development. The goal/deliverable of the detailed characterization of the raw materials was to develop a comprehensive base of knowledge concerning the raw materials used in the formulations and their impacts on the performance of the products. However, chemical and physical characterizations always describe the raw material itself, which may not reflect the interactions of the raw materials in a tribological system.

The five raw materials used in this study were phenolic resin, palm slag, graphite, alumina and steel fibre as shown in Table 3.1. First, the raw materials must be tested in order to study and understand their individual properties. The characterization methods used included composition or elemental analysis of the powders by X-Ray Fluorescence (XRF), thermal analysis by Thermogravimetric Analyses (TGA), and morphological observation of raw materials using Scanning Electron Microscopy (SEM). Microstructure and elemental data on each raw material were compiled for reference during the analysis outcome of the formulation of the brake pad materials.

c. Chemical Compositions of Raw Material by XRF

An X-ray fluorescence (XRF) spectrometer is an X-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron probe microanalyzer (EPMA).

The chemical composition of the palm slag was determined by using a MiniPAL 4 standardless mode ED-XRF spectrometer.

d. Thermal Characterization by TGA

Thermogravimetric Analyses, TGA, is a thermal analysis technique that is used to determine changes in the weight of the respective samples as a function of temperature. The analysis can be performed under nitrogen, air or other reactive atmospheres. TGA operates on a null-balance principle. A pair of photodiodes is used to register the displacement of the balance beam. A low thermal resistance furnace performs the heating of the sample. The temperature of the sample is monitored by a thermocouple located close to the sample pan, and recorded as the X-axis. A plot of mass or mass percent versus time or temperature is called a thermogram or thermal decomposition curve.

For this study, samples of palm slag, dolomite, calcium carbonate, and phenolic resin particles were subjected to thermogravimetric analyses (TGA). The TGA test procedures were performed on a single sample during the course of a single experiment. They also were performed on separate combinations of palm slag, dolomite, or calcium carbonate (each as the filler) with the phenolic resin (as the binder) for representing a brake pad with the same experimental setup. The weights 10 mg of the samples were monitored as a function of temperature. All of the samples were tested over the temperature range of 30 - 1000 °C. Nitrogen was used as the inert gas during the experiments.

e. Morphology by SEM

In the field of material science, morphology studies include the shape, size, texture and phase distribution of physical objects. The morphologies of the raw materials used in this research were determined using a JEOL JSM-6460LA scanning electron microscope (SEM). All the test specimens were handled very carefully to avoid any damage or contamination that would affect the results.

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter by, analysing the X-rays emitted by the matter in response to being impacted with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure, and the X-rays that are characteristic of an element's atomic structure are unique and can be used to identify that element on various spots.

3.4.3 Preparation of the Composite Samples

a. Mixing

In the first step of sample preparation, the raw materials were mixed to get a homogeneous condition. The starting material was a mixture of various sizes of powder of different compositions and the, binder. The mixing operation was conducted under dry conditions, and dust emissions were reduced to the extent possible to lessen explosion hazards. Large lots of powder were homogenized with respect to both chemistry and distribution of the components' sizes and shapes.

The raw materials were mixed by using a ball mill machine. The raw materials were placed in a closed bottle and the bottle was placed between two rollers. The rotational milling speed for a cylindrical mixer was determined according to the equation:

$$N=32/\sqrt{d} \qquad [3.1]$$

where N is the speed in RPM, and d is the diameter of the drum in meters.

According to equation 3.1 a cylinder with a 1 m diameter will have an optimal speed of 32 RPM. Smaller diameter requires faster speeds to achieve equivalent optimization. The rate of mixing varies with the inhomogeneity of the raw materials (Randall, 1997).

The objective of milling is to reduce the particle size. In the case of a product with multiple materials, proper mixing is imperative to form a uniform homogenous composite media. The two-roll ball mill use in this research had a pair of rollers with vertical 'nips' between them. The raw materials are subjected to high shear in the nip as the rolls rotate in opposite directions. Mixing on two-roll ball mill is time consuming, i.e., it depends on the skill of the operator, and a 100-g mix takes about three (3) hours. Either palm slag, $CaCO_3$, or dolomite was mixed with the other filler ingredient, i.e., phenolic resin, alumina powder, graphite powder and steel fibres, and the mixtures - were milled using a two-roll ball mill for three (3) hours at 273 rpm with 50 balls in the mill jar to ensure that the final mixtures were homogeneous. The speed of 273 rpm has been used is due to the calculation obtained from the equation 3.1 by using jar mill with 13 cm diameter.

b. Compaction

Cold compaction is a process in which powder materials are compressed at room temperature so that the deformation mechanics associated with high temperatures, such as dislocation and diffusion creep, can be neglected. In this process, the powder is compacted by axially loaded punches in rigid dies that usually are made of steel.

Cold compaction equipment was used to compact the homogeneous materials after the milling process. The loose powder was compressed at room temperature, and it was moulded into a shape that is known as a green compact or green body. High density and the uniformity of that density throughout the compacted materials generally are desirable characteristics. During compaction, the powder particles move primarily in the direction of applied force, and the approach that was used is referred to as a powder metallurgy method.

Compaction is the most important criterion in the powder metallurgy method. It starts from bulk powders that contain very small amounts of lubricants or binder material, and sometimes there is none of either. In this research, powder compaction via the cold press technique was used with the appropriate tools and dies (moulds). Normally, a die cavity that is closed on one end (vertical die, bottom end closed by a punch tool) is filled with powder.

After all of the ingredients of the brake pad had been milled to form a homogeneous mixture, this mixture was ready to be placed in the mould and compacted.

However, before placing it in the mould, a lubricant, such as WD-40 was sprayed on the mould to lubricate it and prevent the powder from sticking to the surface of the mould. After the lubricant had been applied to the mould, the homogeneous mixture of ingredients produced by the ball mill were placed in the mould and compacted with a pressure of 15 – 17 MPa using a uni-axial, hydraulic hand press machine. The compaction process produced brake pad ingredients that were compacted into the shape of the mould at room temperature and these compacted materials were ejected from the die cavity (mould). All of the specimens were compacted into cylindrical shape with diameters of 10 mm, as shown in Figure 3.5. Their size and shape were established according to the design of the mould. The compacted samples are known as green bodies of the brake pad composite materials. These green bodies were compacted further and cured.

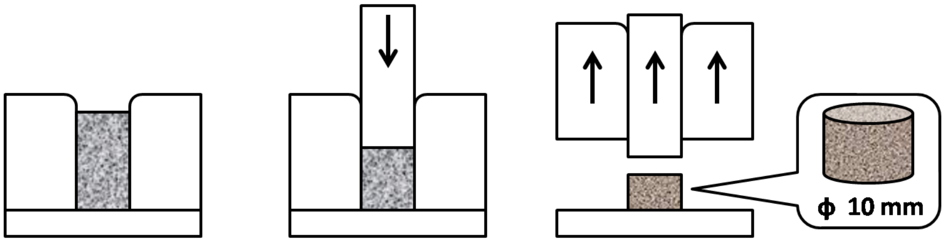


Figure 3.5: Schematic of the cold press technique for the preparation of the 'green body' samples

c. Hot Press Curing

The green body was cured until the pad binder system was fully cured and formed a rigid block. The green body was cured in a hot press at specified pressures. Five different moulding pressures were used, i.e., 1, 10, 20, 40 and 60 tons. The temperature of the hot press was 160 ºC. The curing process took five (5) minutes, after which the samples were allowed to cool at room temperature. Then the samples were post cured in an oven with air circulating at temperature of 160 °C for four (4) hours. The importance of post cure step is to ensure that all parts of the brake pad have been fully cured.

The samples were weighed on a balance and diameters of the samples were measured using a vernier caliper before and after curing process. The measurements were used to calculate the percentage of change in the dimensions of the samples. In this case, changes in the physical properties were due to chemical reactions between the raw materials that occurred at the curing temperature of phenolic resin.

3.4.4 Characterization of the Composite Samples

a. Hardness of the samples.

Hardness value is an expression that usually is applied to describe the durability of the friction material. It is generally perceived that a hard brake pad is more suitable for race conditions. Brake pad hardness has been used as a general term because there is no standard way for brake pad manufacturers to describe their different products. However some brake pads clearly are harder than others, and there is a vast range of hardness among the brake pads that are produced throughout the world.

Performance-type and race-type brakes, which generally are referred to as ‘hard’ usually contain a large proportion of steel fibres and these fibres can be abrasive and very damaging to the disc brake. This is what disc and rotor manufacturer mean when they use the term brake pad hardness when grouping brake pads. Rotor and disc manufacturers are indicating that hard (very abrasive) pads may damage their disc and that such pads normally are not recommended for street driving, as mentioned in the article published in the website.

(http//www.ebcbrakes.com/ebc_brakes_technical_articles/car_brake_technical_articles/brake_pad_hardness.shtml)

In this research the Rockwell type E hardness values of the samples were obtained using a digital Rockwell hardness tester. Different samples with diameters of 10 mm were used to conduct the tests. The tests were conducted using a 1/8 in diameter steel ball indenter with a load of 100 kgf.

b. Density

Density is a physical property of matter, and each element and compound has a unique density. Density is defined qualitatively as the measure of the relative "heaviness" of objects with a constant volume. Density may also refer to how closely "packed" or "crowded" the material appears to be (Charles, 2003). The densities of the samples of the brake pad composite materials were determined by weighing the samples on a digital weighing machine, measuring their dimensions using a vernier caliper, using those dimensions to calculate the volumes of the samples, and obtaining the ratio of mass to volume. Subsequently their specific gravities were determined. Density of composite samples was obtained using Archimedes principle in accordance with Malaysian Standard MS 474: 2003 test procedures.

c. Morphology

The morphology of the surfaces of the brake pads also was observed by using a scanning electron microscope (SEM) JEOL JSM-6460LA as shown in Figure 3.6. The

SEM is a microscope that images surfaces of the samples by scanning them with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the topography of the surface of the sample, its composition, and other properties such as electrical conductivity. Imagings of the surfaces of the sample of brake pads with different fillers were obtained before and after the wear test.

Figure 3.6: Scanning electron microscope (SEM)

d. Compressive strength test

Tests of the compressive strength of the brake pads were conducted by using an Instron Universal Testing Machine (UTM) to measure the compressive strength of the brake pad based on ASTM D695 standard (Figure 3.7). Each sample had an initial cross sectional area of 86.6 mm^2, were placed centrally between the lower cross member and lower cross head. The samples were placed in such a manner that the load was applied to the opposite sides of the brake pad at a crosshead speed of 5mm/minute. The machine used the load at which failure occurred to calculate compressive strength. Five compression tests were conducted for each type of sample.

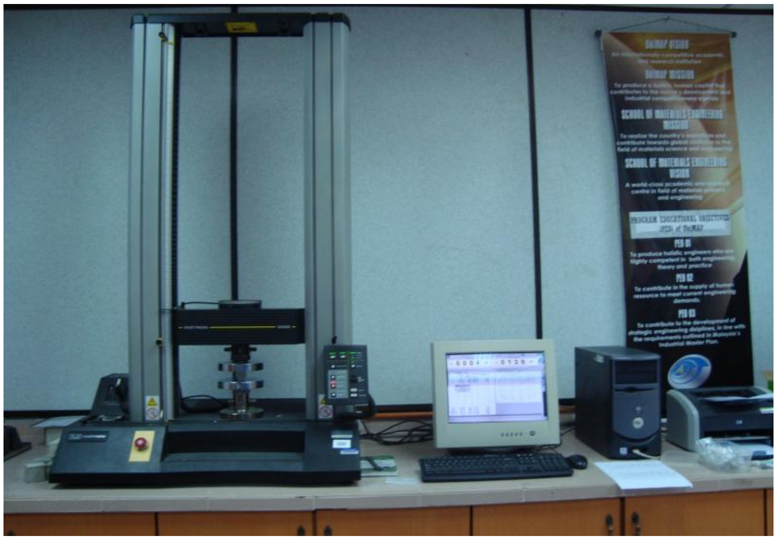


Figure 3.7: Universal Testing Machine

e. Wear properties of the brake pad composite

The wear properties of the brake pad composites were determined using a polisher machine with a constant load as shown in Figure 3.8. The setup was similar to the concept of the pin-on-disc test which compliance the ASTM G 99 standard procedures. The tested samples were in the form of cylindrical pins that were 10 mm in diameter and 15 mm in height. The pins were placed on a stainless steel wheel with a load of 10 N and a wheel speed of 100 rpm. The test was run for a constant distance of 1 km. The samples were weighed before and after testing to determine weight loss within an accuracy of 0.0001 mg. Wear volume and wear rate for the brake pad composites were determined using the following equations:

$$\text{Wear volume} = \frac{Wg_{\text{before}} - Wg_{\text{after}}}{\text{Density}, \rho} \qquad [3.2]$$

$$\text{Wear rate} = \frac{\text{Wear volume } (m^3)}{\text{Sliding distance } (m)} \qquad [3.3]$$

Figure 3.8: Wear testing setup

Wear damage that leads to substantial loss of material is perhaps the most straightforward situation to describe quantitatively. Wear loss can be determined by measuring mass change, dimensional change or weight loss. It is necessary to weigh an original part of a specimen, and that the weight of the object after wear exposure be determined and subtracted from the original to determined the difference in weight (i.e., mass change).

Other problems with this approach include the need to clean the specimen carefully to avoid having extraneous matter on the surface that could contribute to any weight difference. Of course, any fluids or solids used in cleaning must be thoroughly dried or removed. Another consideration is, the material that was plastically displaced by the wear process but not actually removed from the part, will not be included in the weight difference.

The amount of wear can be described by the absolute amount of mass loss (in grams), by the rate of mass loss per unit of usage (grams per day), or by a fractional change in the mass of the part involved (i.e., a 1% change per 100 hours of operation). In many areas of engineering, the reporting unit of choice frequently is a conventional unit. In most of the ASTM wear standards, the unit used to report wear is cubic millimeters of volume, rather than mass, so that materials with different densities can be compared.

Chapter 4

Results and Discussions

4.1 Introduction

The results and discussions for these studies were divided into four main parts in order to achieve the objectives mentioned in Chapter 1. The first part will discuss the characterization of the raw materials, such as chemical composition by XRF and thermal behaviour by TGA, for all main materials involved in these studies. The second part of this chapter will discuss further the effect of different fillers on the morphology and properties of the brake pads. Density, hardness, compressive strength, wear properties, and SEM morphology studies of the brake pads are covered.

The third part of this chapter concentrates on the studies of palm slag brake pads. It covers the effects of the moulding pressure used during the production of palm slag brake pads on the density, hardness, compressive strength, and wear properties. Also the correlations between these properties are assessed. The last part of this chapter presents a discussion of the effect of different palm slag filler sizes on the properties and morphology of the palm slag brake pads.

4.2 Characterization of the Raw Materials

4.2.1 Chemical Composition

Chemical compositions and the concentration of elements in palm slag, $CaCO_3$, and dolomite are presented in Table 4.1. The data obtained from the XRF analyses of these three materials also were compared with the properties of asbestos that were obtained from the literature. All three of the fillers were found to contain silica, potassium, calcium, and iron. The same elements also were found in the analysis data for asbestos obtained by Dellisanti et al. (2002). The percentages of these elements in those four filler materials were varied from each other's.

Asbestos contains a large amount of Si, approximately 44%, which was the greatest among the four fillers. Palm slag was second with 22.0% of Si, followed by $CaCO_3$ with about 14%, and dolomite contained only about 0.4% of Si. Palm slag also had a significant amount of potassium, calcium and iron. These quantities will indirectly influence the end properties of the final product, i.e., the brake pads. Overall, it contains semi-metals and non-metal elements that are similar to the elements being used in many of current commercial brake linings/ pads (Aigbodion, et al.,2010).

Table 4.1: Concentration of compounds in different fillers (determined by an XRF spectrometer)

Compounds	Concentration (%)			
	Palm slag	$CaCO_3$	Dolomite	Asbestos (Dellisanti *et al.*, 2002)
SiO_2	22.0	14.11	0.42	43.74
K_2O	23.8	0.71	0.044	0.43
CaO	20.4	41.32	30.00	16.97
MgO	-	2.19	21.0	6.13
Fe_2O_3	29.3	1.63	0.46	14.87
Al_2O_3	-	-	0.28	2.16
TiO_2	2.11	0.16	-	0.23
NiO	0.13	-	trace	-
CuO	0.38	-	-	-
Rb_2O	0.39	-	-	-
SrO	0.33	0.12	0.011	-
Cr_2O_3	0.39	-	-	-
MnO_2	0.58	0.038	trace	1.31

P_2O_5	-	0.15	trace	0.03
Na_2O	-	0.39	-	trace
SO_3	-	0.66	0.036	-

4.2.2 Thermal Characterization

Figure 4.1 shows the TGA- DTA curve for the thermal behaviour of palm slag as the filler. The figure shows that palm slag is a very stable material. Over the range of test temperatures, i.e., 50 to 1000 °C, there was essentially no change in the weight percent of the palm slag. The slight increase in mass that occurred at temperature between 500 and 1000 °C could be attributable to phase changes. Palm slag was very stable at high temperature because of it processing thermal history, which most of the slag comes from the furnace processes in molten state with temperature exceeding 1480 ^{o}C.

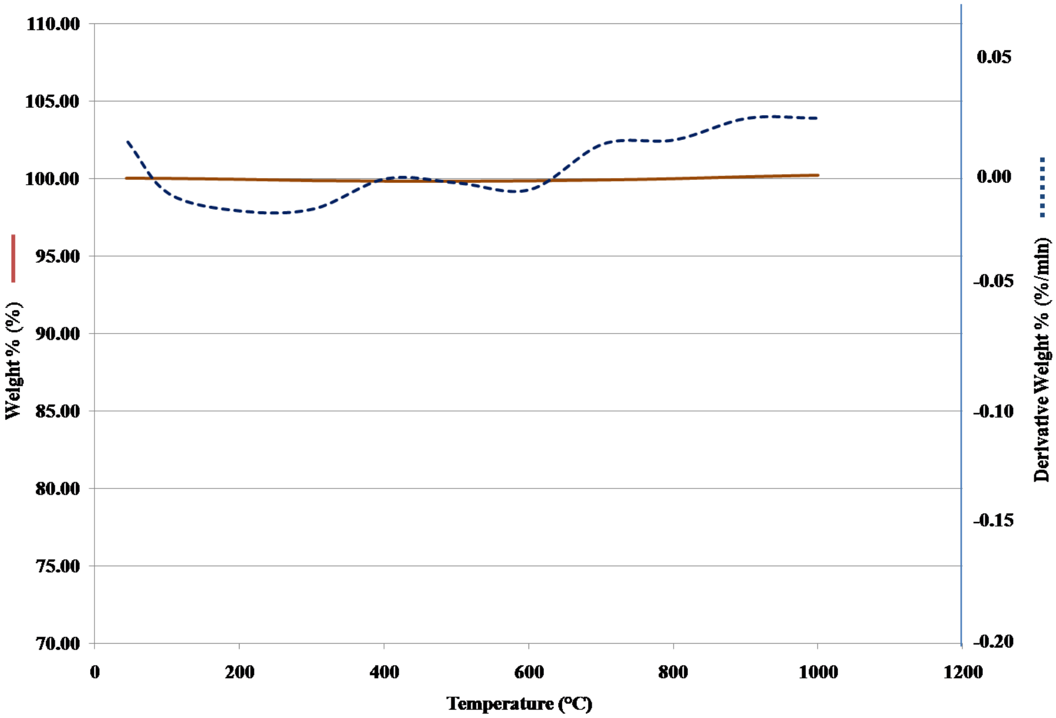


Figure 4.1: TGA-DTA curve of the raw palm slag sample

The thermal characterizations of $CaCO_3$ and dolomite are shown Figures 4.2 and 4.3, respectively. These two mineral fillers were used to compare to the palm slag filler. Figure 4.2 shows that the mass of calcium carbonate decreased dramatically at temperatures above 620 °C, and almost a mass decrease of almost 40% at 850 °C. The mass of dolomite, however, decreased in two distinct stages (Figure 4.3). The first stage was initiated at temperature of 420 °C, and the second stage began at 620 °C. An overall decrease in mass of 50% was observed between 420 °C and 850 °C, which might be due to the combustion of carbon. Ramousse *et al.* (2001), in their study of the thermal characterization of brake pads also suggested that the lost of mass between 600 and 850 °C was due to the combustion of carbon.

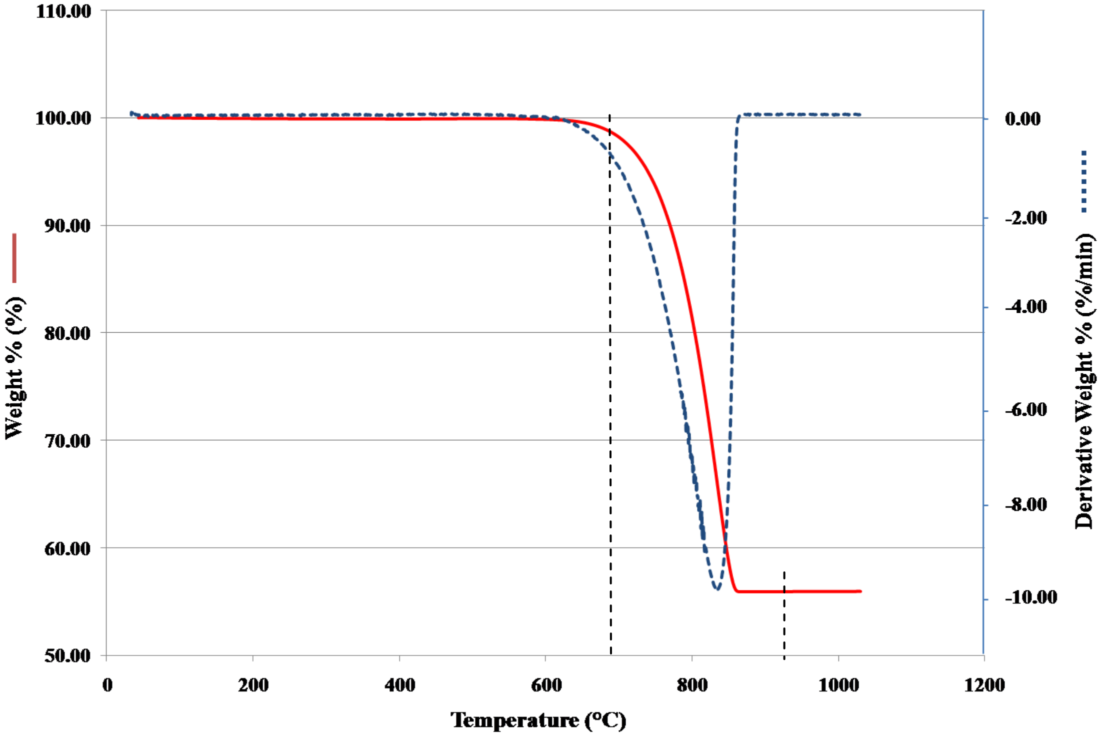


Figure 4.2: TGA-DTA Curve of $CaCO_3$ sample

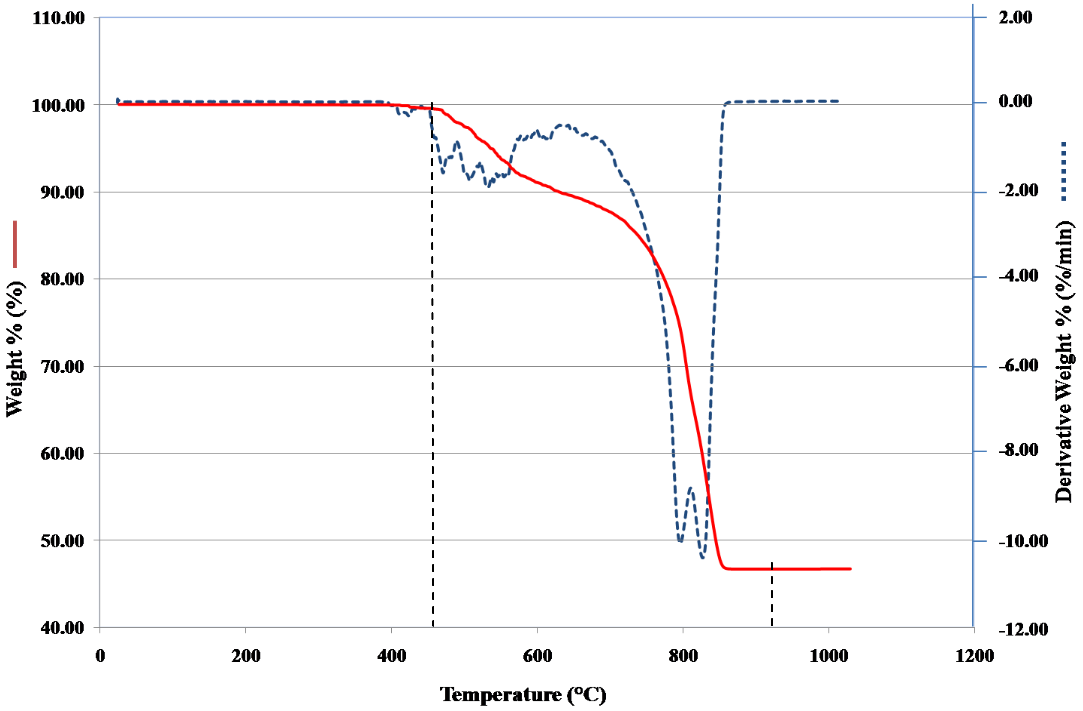


Figure 4.3: TGA-DTA curve of dolomite sample

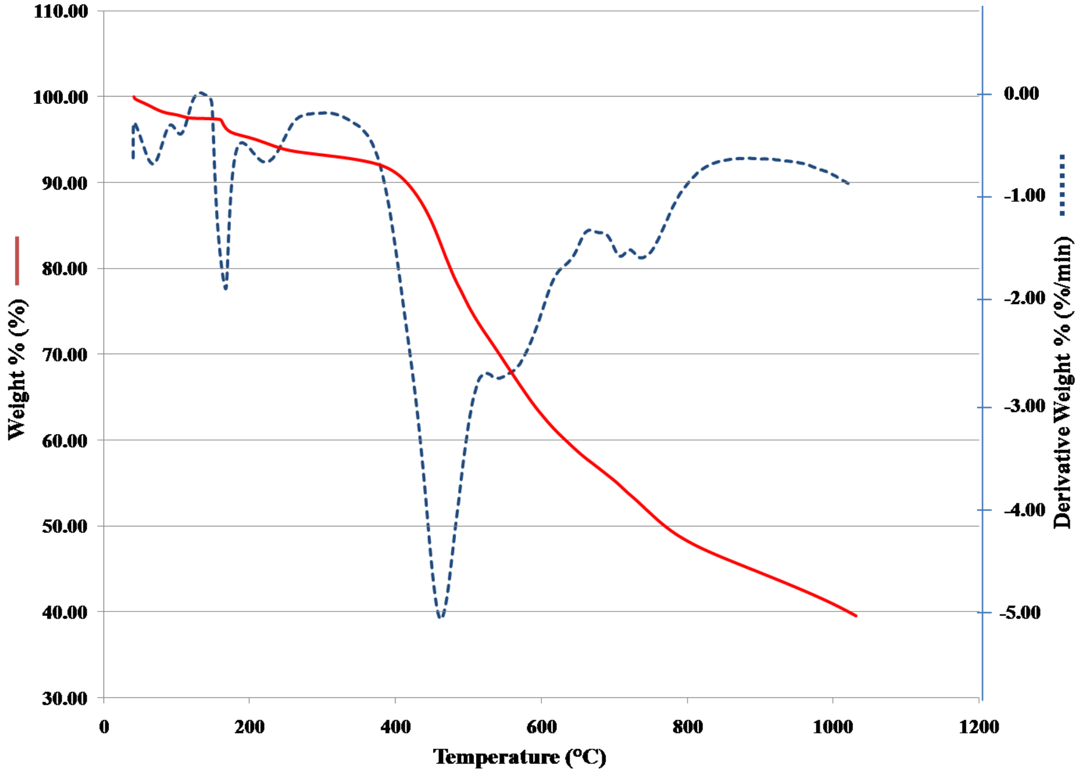


Figure 4.4: TGA curve of phenolic resin sample, a binder material

Figure 4.4 shows the TGA-DTA curve of the phenolic resin binder. The small weight loss at 160 °C resulted from the curing behaviour of the phenolic resin. The binder started to decompose at a temperature of 250 °C, and at 850 °C, almost 55% of the mass was lost.

The combination of filler and binder was particularly interesting because it provided an overall picture and gave a better understanding of the thermal characteristic of the different fillers used in brake pads. Figures 4.5, 4.6 and 4.7 show the TGA-DTA curve of the mixture of filler and binder, palm slag-phenolic resin, calcium carbonate-phenolic resin and dolomite-phenolic resin, respectively.

Small weight losses at 160 °C were observed in Figures 4.5, 4.6, and 4.7. This observation might be due to the curing behaviour of the phenolic resin that was used as a polymeric binder in the brake pads. After that, two regions in which mass decreased can be observed, i.e., between 200 and 400 °C and between 420 and 850 °C. The decomposition of the binder resulted in a mass loss. The decrease in mass in the region between 200 and 400 °C might be due to the degradation of the organic material in the binder. The second region, between 400 and 850 °C had larger mass losses, which were thought to be the result of the combustion of carbon. All of the above mentioned results that we obtained were in good agreement with the result of previous research conducted by Ramousse *et al.* (2001) and Blau (2001).

In these two temperature regions mentioned earlier, two possible compounds are released, i.e., water and carbon dioxide. Water is released between 230 and 450 °C, and this release corresponds to the decomposition of the binder. The release of carbon dioxide is due to the combustion of carbon, which seems to occur between 250 and 850 °C. The previous work of Chang and Tackett (1991) and Ramousse *et al.* (2001), in which they conducted experiments using thermogravimetry and mass spectroscopy (TG-MS) to study the phenolic resin, also supported the results we acquired. They also found that carbon dioxide were released in the temperature range of 420 – 580 °C.

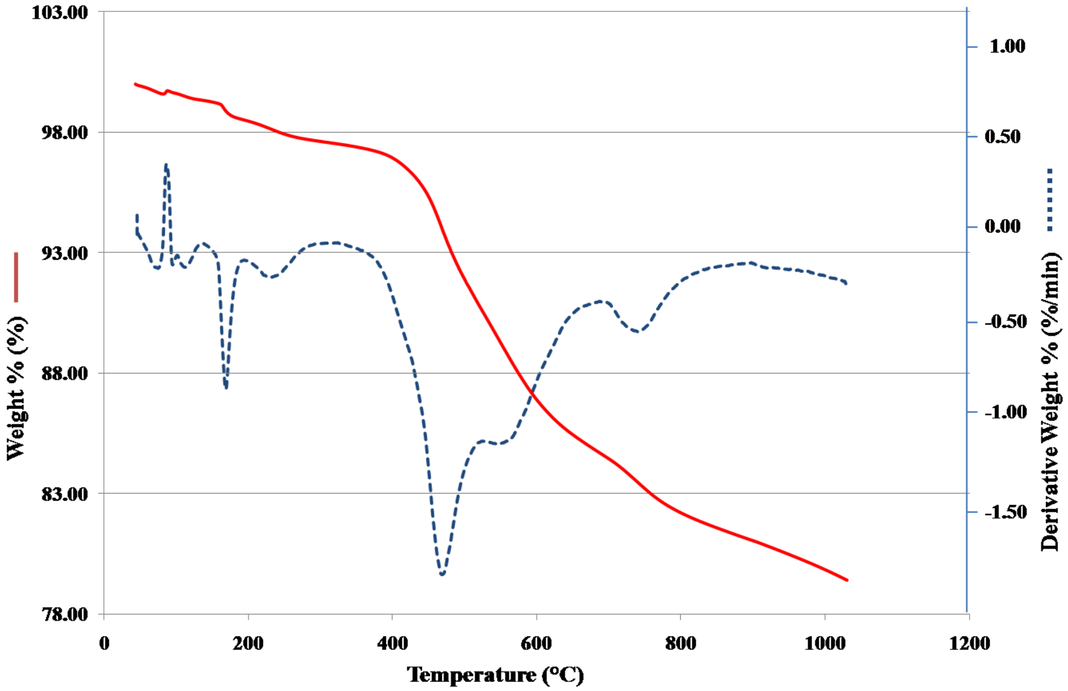


Figure 4.5: TGA-DTA curve of a mixture of palm slag and phenolic resin

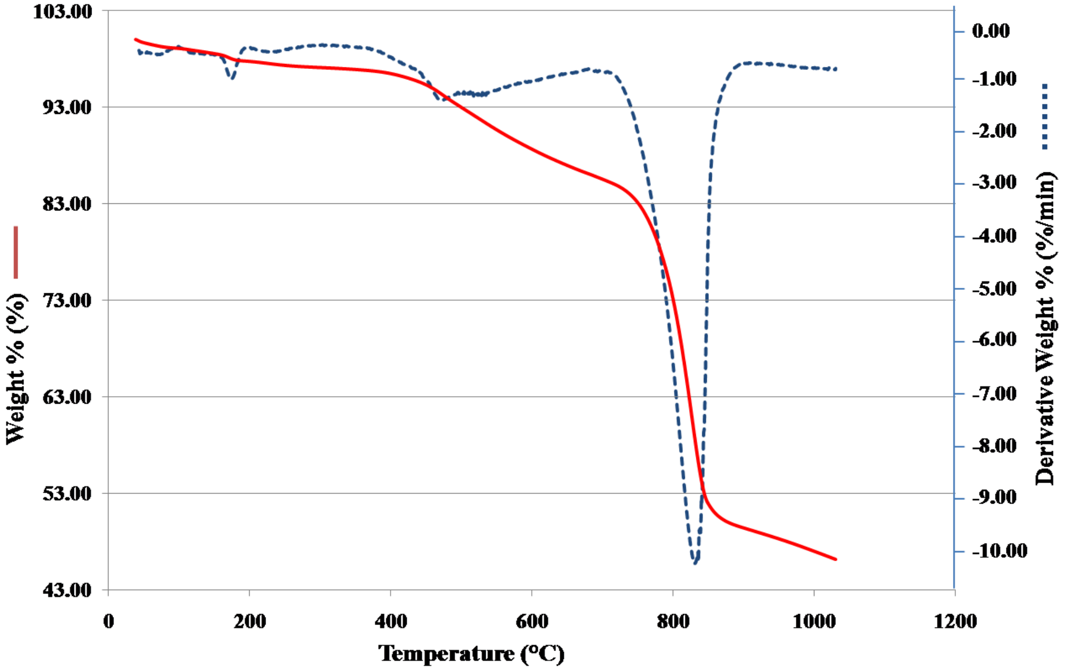


Figure 4.6: TGA-DTA curve of a mixture of $CaCO_3$ and phenolic resin

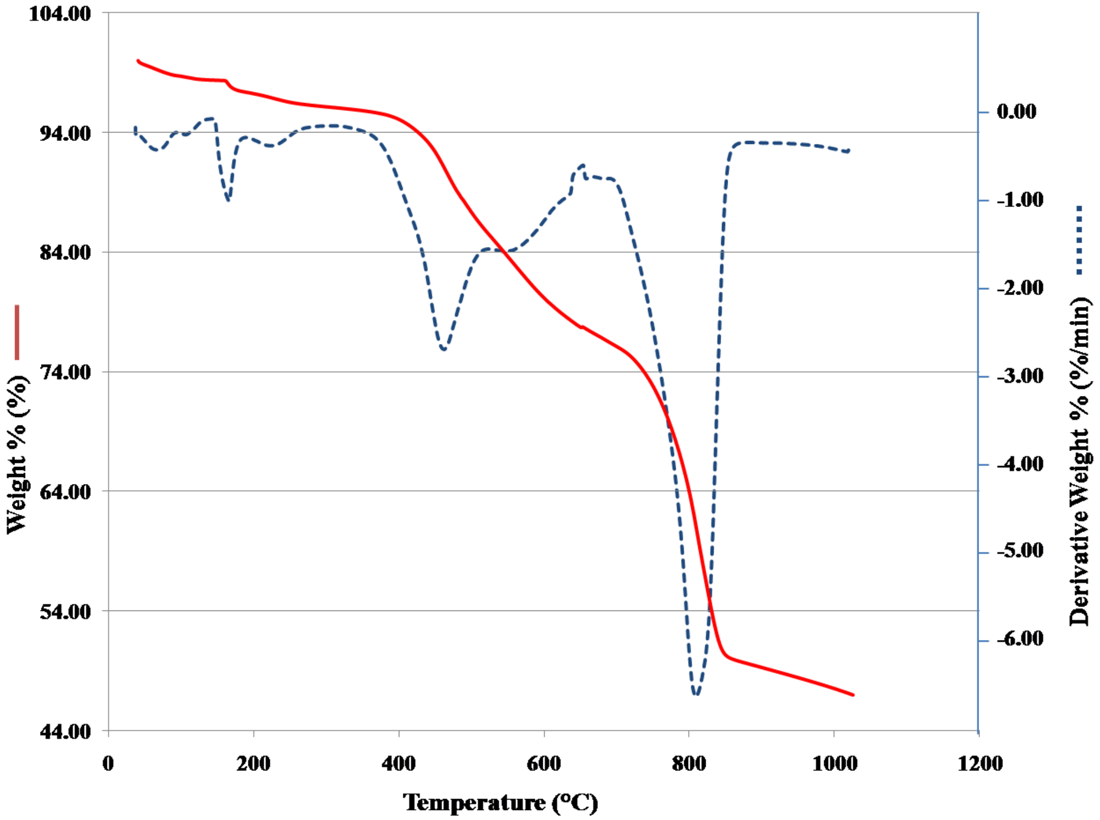


Figure 4.7: TGA-DTA curve of a mixture of dolomite and phenolic resin

Due to the mass reduction in Figures 4.5, 4.6, and 4.7 it clearly can be seen that the palm slag filler was very stable, with only 18 - 20% mass loss occurring up to 850 °C. The calcium carbonate and dolomite both had mass losses of about 30 - 50% for the same temperatures.

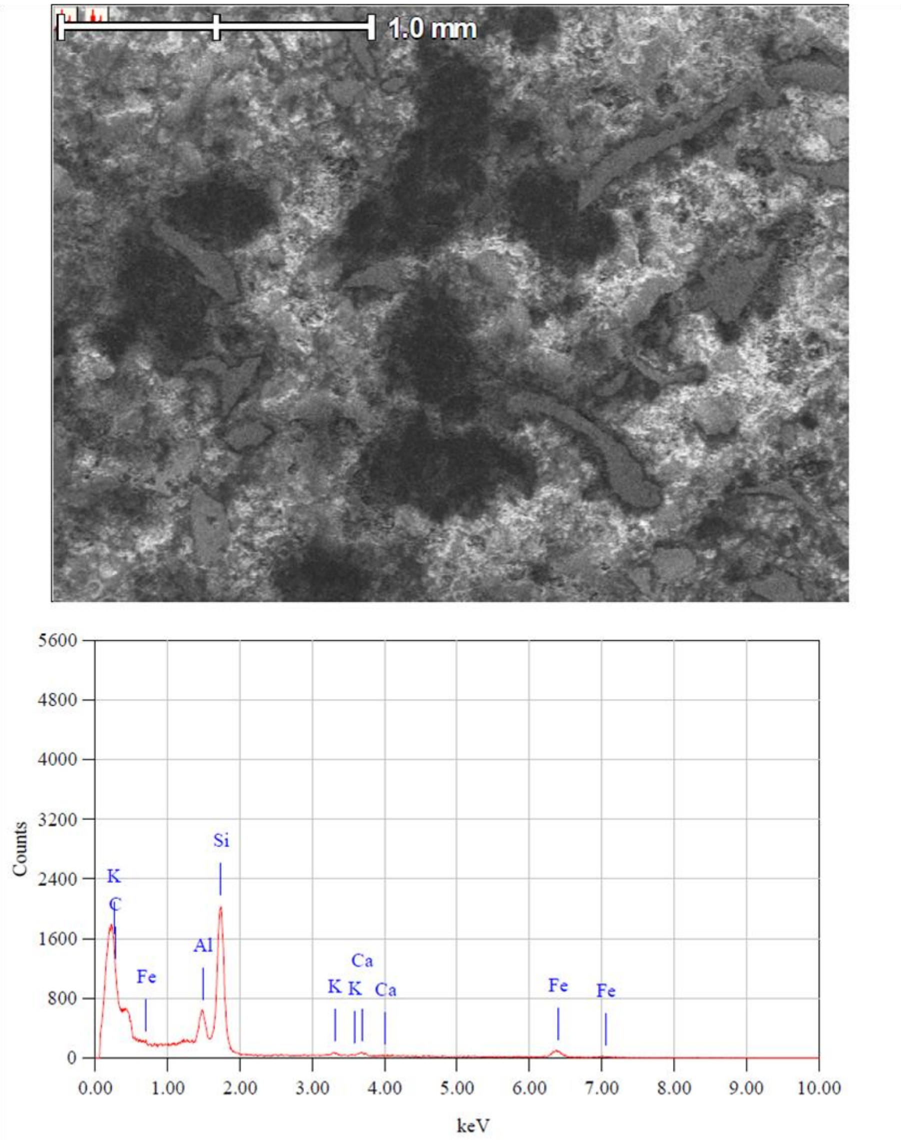
4.3 Effect of Different Fillers on the Properties and Morphology of Composite Samples

4.3.1 Morphology of the samples with different fillers

In this study, the morphology of the brake pads with different fillers was examined using SEM and EDS. In general all of the materials used in the brake pad were well distributed. The SEM micrograph, EDS analysis and topography of the palm slag, $CaCO_3$, and dolomite are shown in Figures 4.8(a), 4.8(b), 4.9(a), 4.9 (b), 4.10(a) and 4.10(b) respectively. Figures 4.8(a) and 4.8(b) shows the SEM and mapping of the palm slag-filled brake pad, respectively. It was observed the particles of the filler materials, i.e., palm slag, alumina powders, graphite particles, and steel fibres were spread evenly and distributed with the phenolic resin. Figures 4.9(a) and 4.9(b) shows the SEM and mapping of the $CaCO_3$-filled brake pad respectively. Calcium carbonate powders, alumina powders, graphite particles and steel fibres also were well distributed with the phenolic resin. More fine filler particles of $CaCO_3$ were observed when this compound was used as a filler than were observed when palm slag was used as the filler.

Figures 4.10(a) and 4.10(b) shows the SEM and mapping of the dolomite-filled brake pad respectively. A similar observation was made, i.e., dolomite filler particles, alumina powders, graphite particles, and steel fibres were spread and distributed uniformly with the phenolic resin.

Based on our observations, it was apparent that all materials were well dispersed and distributed uniformly in the brake pad composite, as was expected due to the effective mixing by the roll mill method we used. Similar distributions also were observed by other researchers, e.g., Darius and Mohamad (2007), Aigbodion et al. (2010), and others.



```
ZAF Method Standardless Quantitative Analysis(Oxide)
Fitting Coefficient : 0.5181
Total Oxide : 24.0
Element        (keV)    mass%  Error%      At%  Compound   mass%      Cation        K
C  K*          0.277     3.91    0.14    18.41  C           3.91        0.00   5.9745
O                       39.47
Al K*          1.486     4.97    0.48     5.21  Al2O3       9.39        1.79  22.4390
Si K*          1.739    23.65    0.62    47.68  SiO2       50.59        8.19 115.7716
K  K*          3.312     1.24    0.76     0.90  K2O         1.49        0.31   6.6248
Ca K*          3.690     1.66    1.12     2.34  CaO         2.32        0.40   9.3112
Fe K*          6.398    25.11    5.95    25.46  FeO        32.30        4.37 113.8992
Total                  100.00           100.00            100.00       15.07
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Figure 4.8 (a): SEM micrograph and quantitative analysis of palm slag sample by EDS

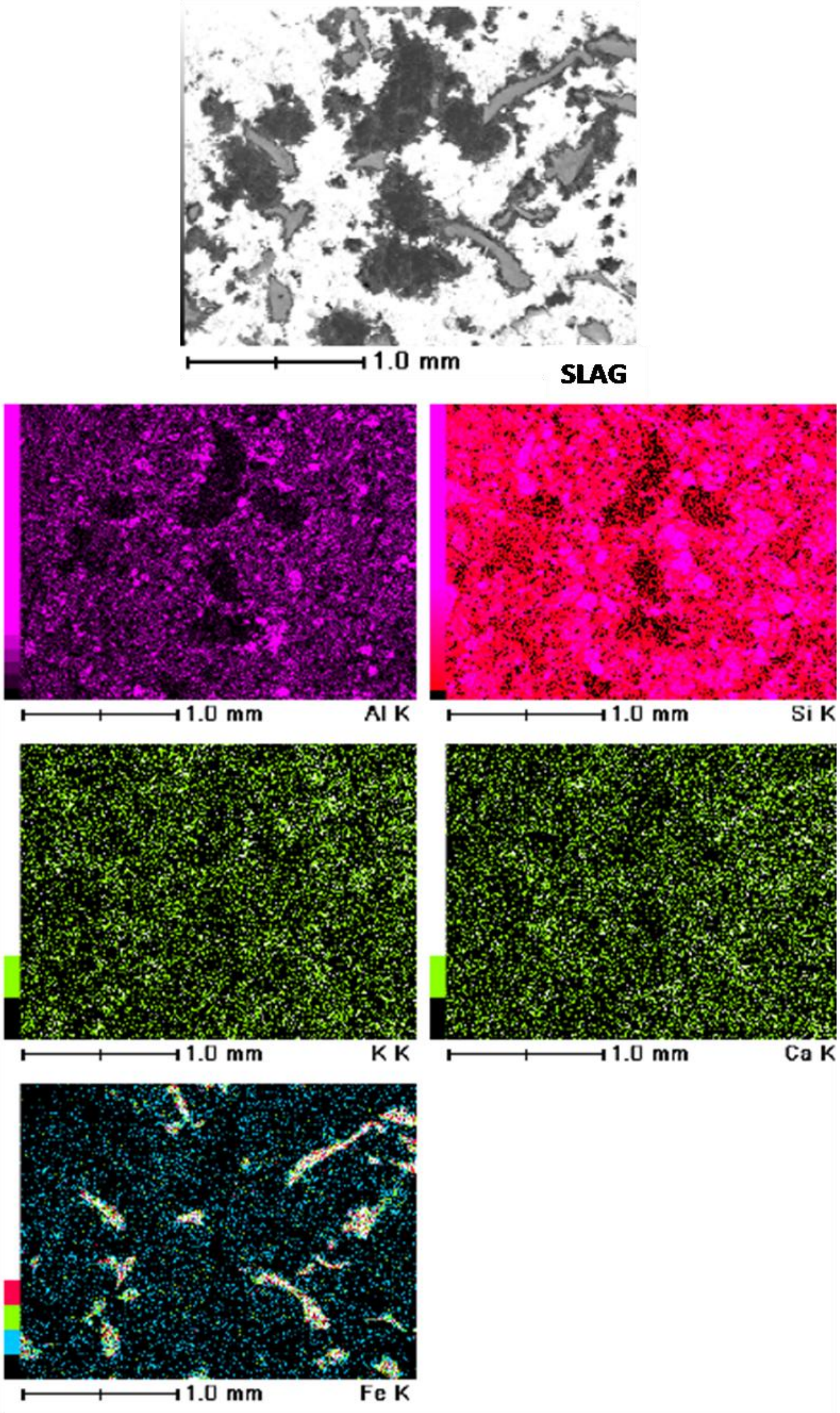
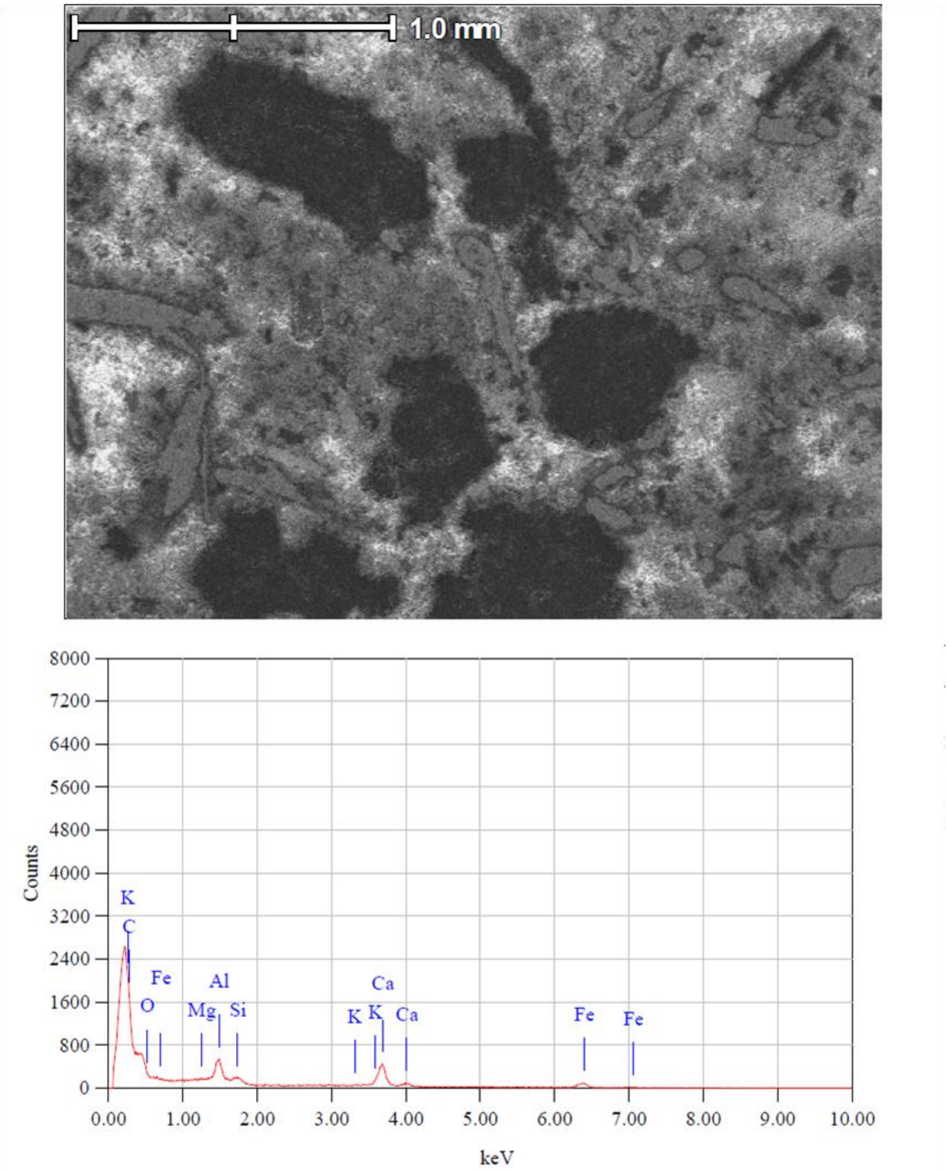


Figure 4.8 (b): SEM and topography of palm slag sample



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Fitting Coefficient : 0.7507
Total Oxide : 24.0
Element       (keV)    mass%  Error%     At%  Compound   mass%     Cation        K
C  K          0.277     8.16    0.19   33.37  C           8.16       0.00  17.0262
O                      26.44
Mg K*         1.253     0.26    0.88    0.53  MgO         0.44       0.16   0.8978
Al K          1.486     6.86    1.06    6.25  Al2O3      12.96       3.69  26.0426
Si K          1.739     1.19    1.35    2.08  SiO2        2.54       0.61   4.9420
K  K          3.312     0.66    1.52    0.41  K2O         0.80       0.25   3.2841
Ca K          3.690    22.31    2.31   27.35  CaO        31.22       8.08 113.7751
Fe K          6.398    34.12   12.42   30.01  FeO        43.89       8.87 138.5869
Total                 100.00          100.00            100.00      21.66
```

Figure 4.9 (a): SEM micrograph and quantitative analysis of $CaCO_3$ sample by EDS

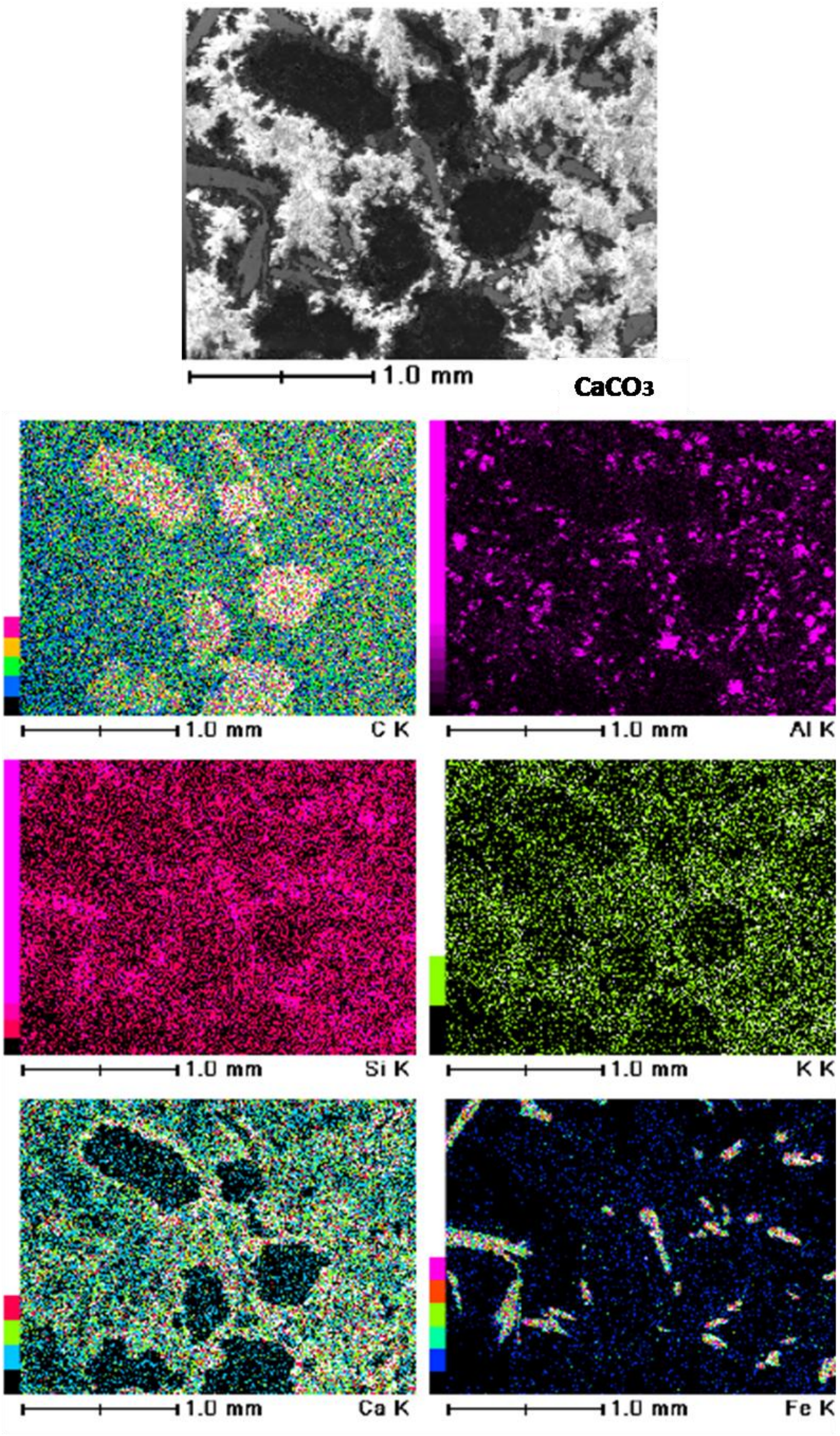
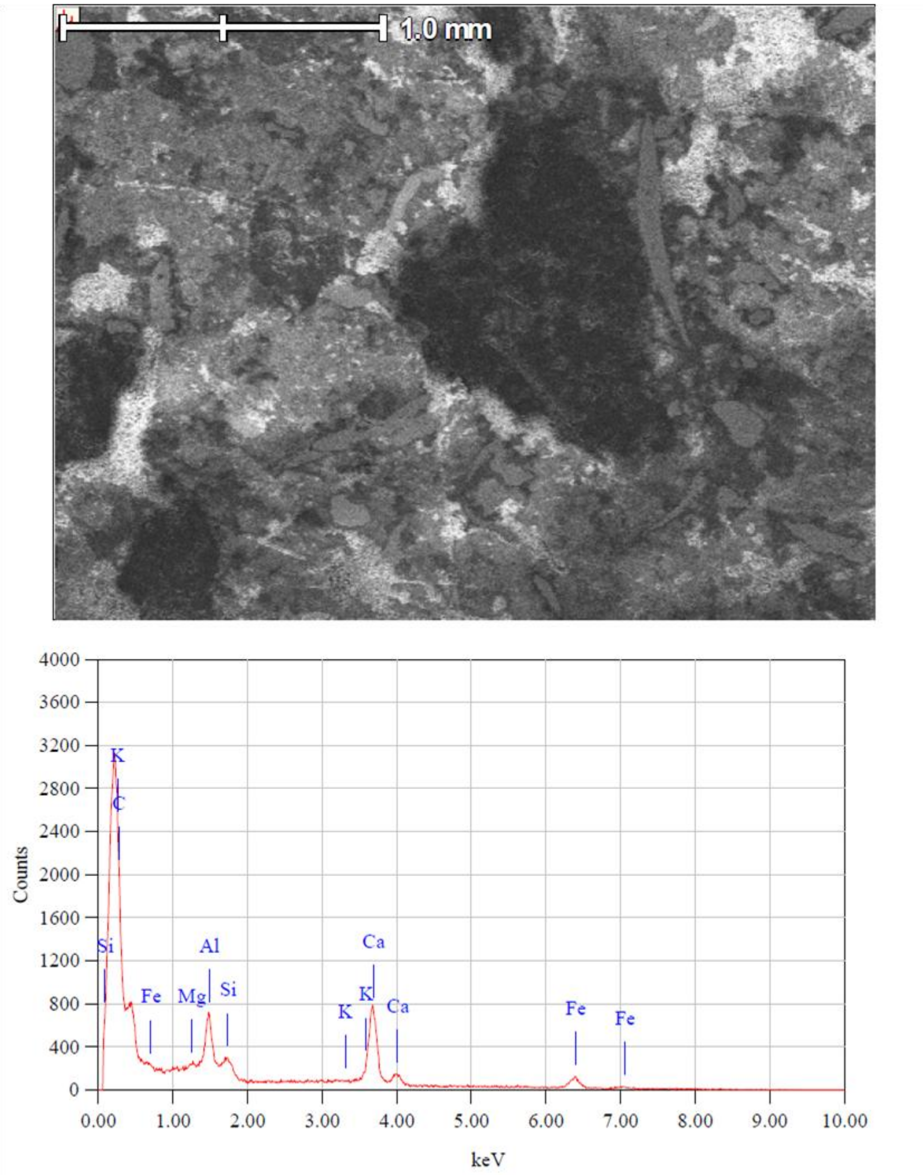


Figure 4.9 (b): SEM and topography of $CaCO_3$ sample



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ZAF Method Standardless Quantitative Analysis(Oxide)
Fitting Coefficient : 0.6950
Total Oxide : 24.0
Element        (keV)   mass%  Error%     At%  Compound    mass%      Cation         K
C  K*          0.277    6.20    0.16   26.47  C            6.20        0.00   12.7411
O                      27.18
Mg K*          1.253    0.68    0.75    1.43  MgO          1.12        0.39    2.2091
Al K           1.486    6.09    0.92    5.79  Al2O3       11.51        3.19   22.1753
Si K           1.739    1.12    1.17    2.05  SiO2         2.40        0.57    4.4989
K  K           3.312    0.24    1.30    0.16  K2O          0.29        0.09    1.1486
Ca K           3.690   28.70    2.00   36.74  CaO         40.16       10.12  139.6637
Fe K           6.398   29.79   10.81   27.37  FeO         38.32        7.53  115.1706
Total                 100.00          100.00             100.00       21.88
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Figure 4.10(a): SEM micrograph and quantitative analysis of dolomite sample by EDS

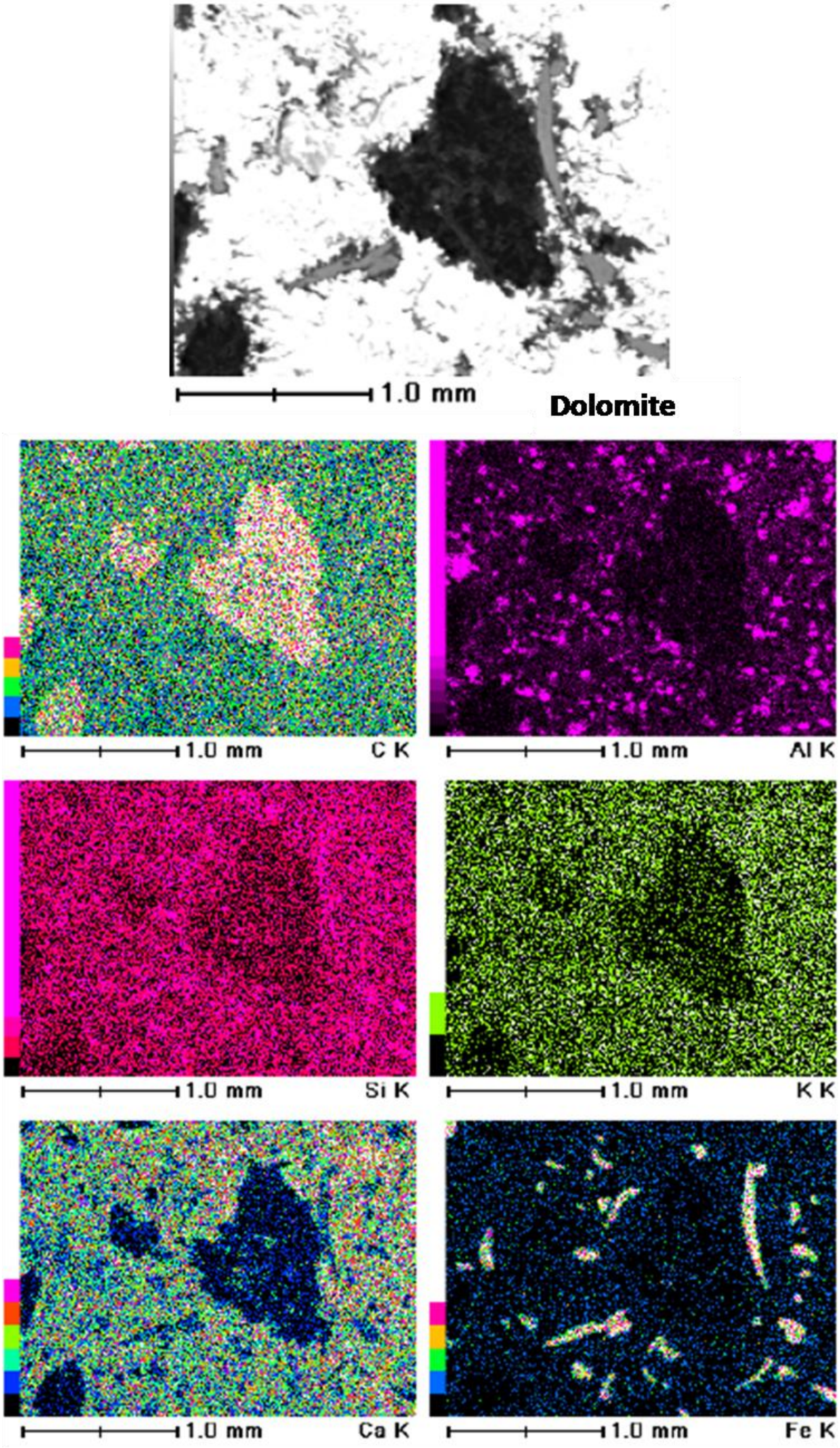


Figure 4.10: SEM and topography of dolomite sample

Figures 4.8(a) and 4.8(b) shows the SEM micrograph, EDS quantitative elemental analysis and topography elemental mapping of palm slag brake pad. The amounts of C, Si, Al, Fe and Ca were significantly greater than other elements. Those are the main elements that were contributed by palm slag, alumina, steel fibre and graphite used in the brake pad formulation. The previous data, obtained by XRF spectrometery as reported earlier in Table 4.1 also confirmed that Si and Fe are the major elements in palm slag.

Figures 4.9(a) and 4.9(b) also show the elemental distribution and mapping studies, respectively, for $CaCO_3$ as filler in the brake pads. In this brake pad Al, Fe, and Ca were among the most plentiful elements as determined by EDX, and they were contributed by the use of $CaCO_3$ as the filler. This observation also was supported by the XRF data shown in Table 4.1 which confirmed that the significant percentage of Ca was due to the element in $CaCO_3$.

A similar trend was observed in the dolomite filled brake pad, as shown in Figures 4.10(a) and 4.10(b). Ca and Mg made up the greatest amount of the elements in those brake pads, which obviously was due to the fact that dolomite contains significant amount of these two elements.

4.3.2 Density of different fillers

Figure 4.11 shows the density of the different brake pad composite fillers at 60 tons of processing pressure. It can be seen that the dolomite brake pad composite had the greatest density, which mean that it was the heaviest brake pad among the types being tested. This was due to the density characteristics of the individual fillers that were used. Dolomite had the highest bulk density among the three fillers that were tested, followed by $CaCO_3$ and palm slag, as shown in Table 4.2. Consequently, among those three different fillers, palm slag filler would be much more suitable as filler material than the other two or even asbestos, due to the reduced overall weight of the sample.

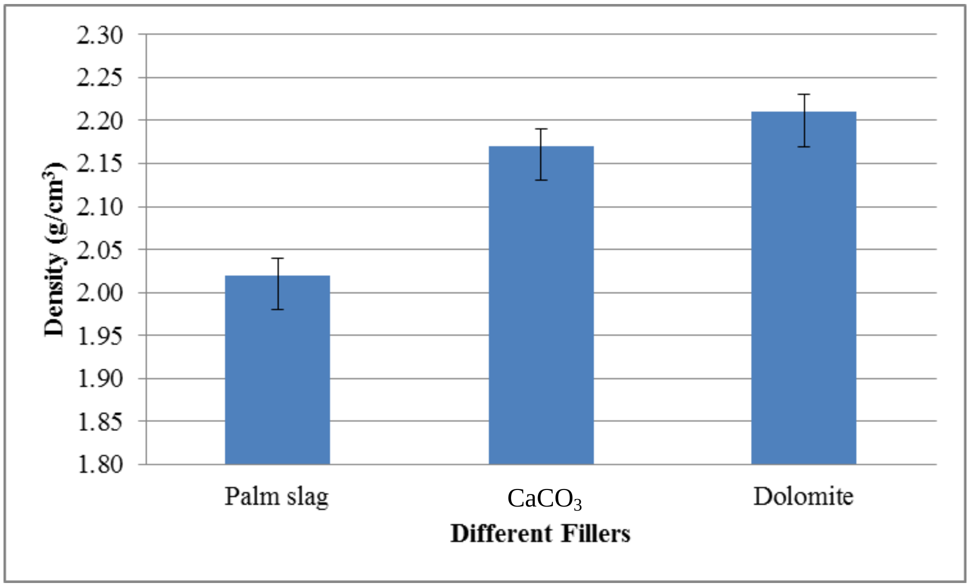


Figure 4.11: Density of the different fillers used in the sample

Table 4.2: Bulk density of the raw fillers used in this research.

Filler	Bulk density (g/cm^3)
Dolomite	1.61
$CaCO_3$	1.44
Palm Slag	1.12

4.3.3 Hardness of the different fillers used in the samples

The hardness values of the brake pad composites with different fillers are shown in Figure 4.12. The result shows that the hardness of the palm slag brake pad composite had the highest value of 59.1, whereas the hardness values for $CaCO_3$ and dolomite were 53.6 and 57.3, respectively. This might be due to the low hardness of the raw $CaCO_3$ and dolomite mineral compared to the palm slag. $CaCO_3$ and dolomite are classified under the soft to medium scale of rock hardness, which is equivalent to 3 and 4 Mohs whereas the palm slag was fall classified as medium to hard, which equivalent to 6 Mohs of hardness.

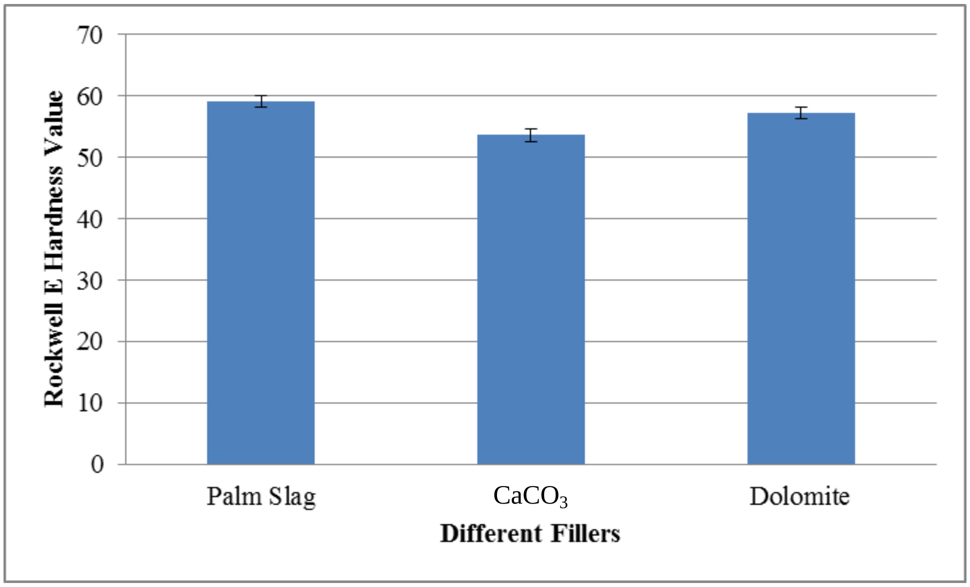


Figure 4.12: Rockwell hardness value of different fillers brake pads.

4.3.4 Compressive Strength of the Different Composite Fillers

Figure 4.13 shows the compressive strength of the different brake pad composites fillers at 60 tons of processing pressure. It can be seen that the compressive strength of the brake pad composite with dolomite filler was the highest compared to the compressive strength of composites made with either calcium carbonate or palm slag as the filler. This result was observed due to the compactness of the composite. From Figure 4.11 and Table 4.2, it is apparent that the dolomite brake pad composite was denser than the other two.

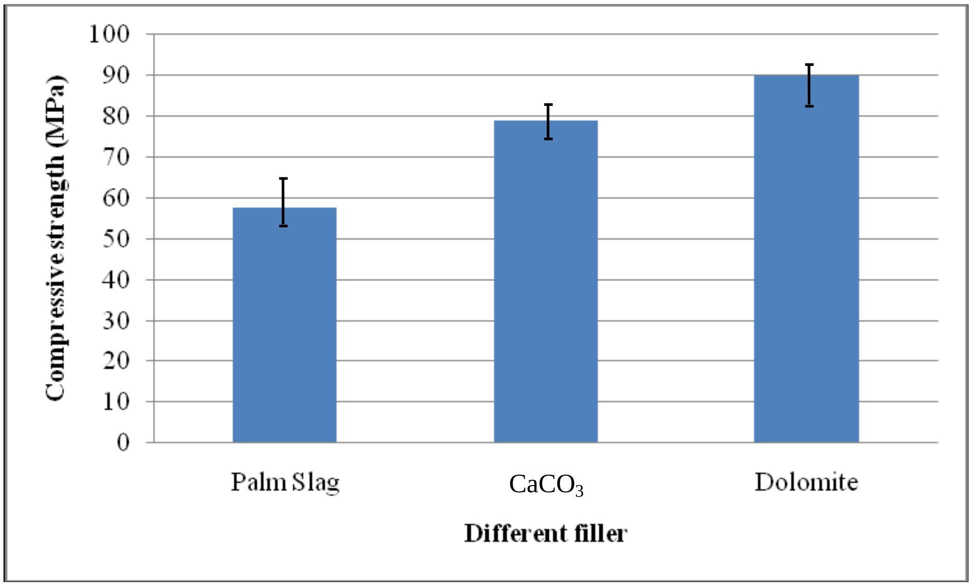


Figure 4.13: Compressive strength of brake pad composites with different fillers

4.3.5 Wear properties of different composite fillers

The wear properties of the different brake pad composite fillers under 10 N for 1-km sliding distance are shown in Table 4.3. Weight loss was measured after 1-km of sliding on the stainless steel plate; then wear volume and wear rate of the palm slag brake pad composite were calculated and compared with the asbestos brake pad described in the literature (Chand *et al.*, 2004).

From the data shown in Table 4.3, it is apparent that the calcium carbonate and palm slag brake pad composites possess mechanical and wear properties that are similar to those of a conventional, asbestos-based brake pad. Even though the dolomite brake pad composite had the highest compressive strength, as shown in Figure 4.13, it had poorer wear properties than either calcium carbonate or palm slag. Even though the palm slag composite material had the lowest density its wear properties were enhanced significantly by its high hardness value. This was supported by our findings, which showed a direct, inverse linear correlation between surface hardness and wear properties. According to Mandiskos (2001), wear decrease as the surface hardness of a material increases. Suresha et al.(2007 & 2009) and Veena et al. (2011) was also proved the incorporation of hard particles such as TiO_2, SiO_2, SiC and Al_2O_3 to polymer matrix has led to better enhancement in wear resistance.

Table 4.3: Wear properties of composites samples using different fillers under sliding wear condition.

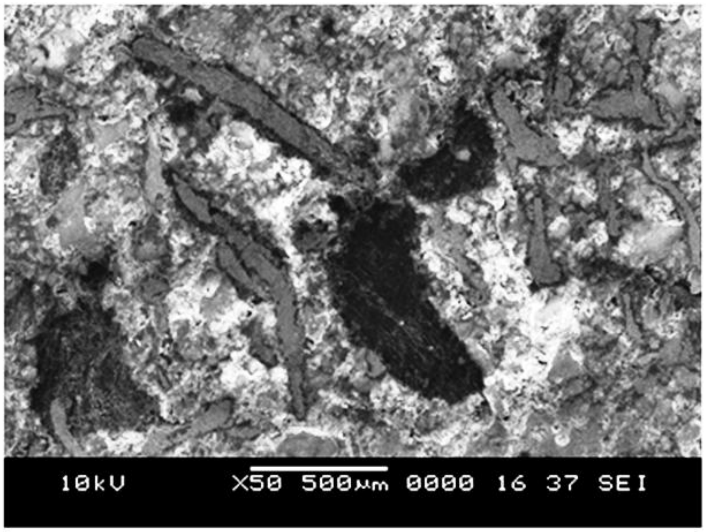
Sample	Density g/cm^3	Wear volume, cm^3 x 10 $^{-3}$	Wear rate, m^3/m x 10^{-13}
Palm slag	2.02	0.89	8.9
$CaCO_3$	2.17	0.60	6.0
Dolomite	2.21	1.22	12.2
Asbestos (Chand *et al.*, 2004)	2.22	0.72	7.2

The properties obtained shows that palm slag could have great potential for becoming an alternative filler material to replace asbestos. One of the strong points supporting that potential is that the palm slag has a low density but its wear rate is almost comparable to that of asbestos.

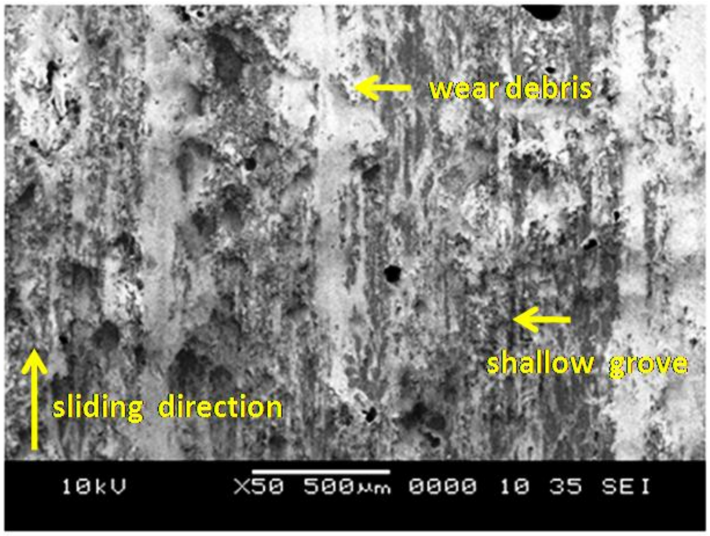
4.3.6 Morphology of the wear surfaces of composites with different fillers

The SEM micrographs in Figures 4.14, 4.15 and 4.16 show the microstructure before and after the wear tests of the brake pad composites with different filler. The surfaces of the brake pad composites showed a typical abrasive wear mode in which debris, deep grooves and wide scratches were formed along the wear direction. It was observed clearly that the worn surface of the dolomite composite had more groove defects than the palm slag and $CaCO_3$ brake pad composite. Debris was observed in the palm slag and $CaCO_3$ composites, which is one of the main factors that reduces the severity of wear.

Again the hardness of the brake pads is the reason this kind of worn surface was observed. The palm slag brake pad had the highest hardness amongst the three different fillers tested, and, as a result, it also had the least severe wear among the three. Luyckx and Love (2004), in their abrasive wear resistance study of metal alloys, found that the higher the hardness of the composite or alloy, the greater the resistance to wear becomes. The results of this study were in agreement with their findings.



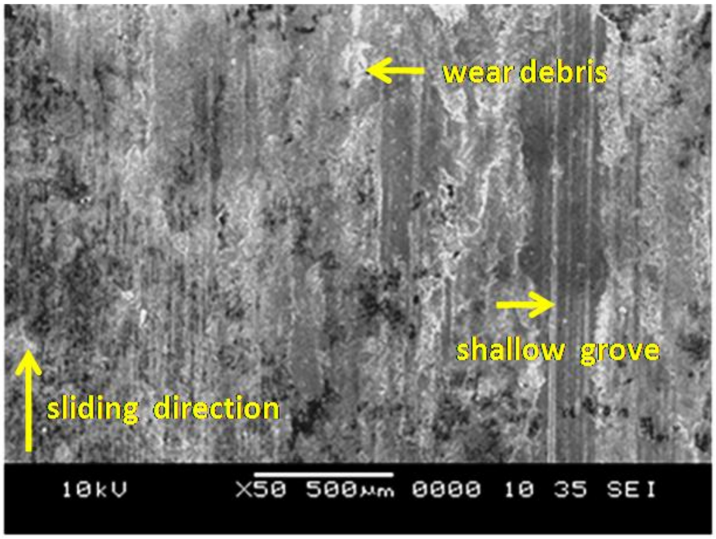
Before wear



After wear

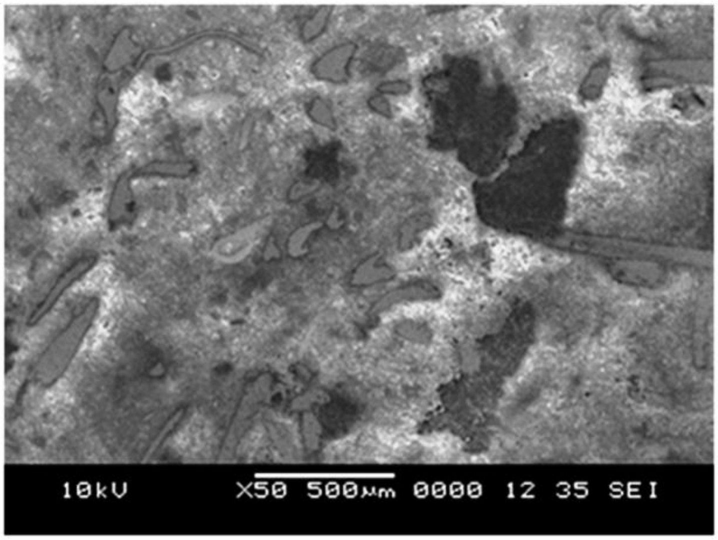
Figure 4.14: Microstructure of palm slag brake pad composites before and after 1-km sliding distance of wear under a consistent 10 N braking load

Before wear

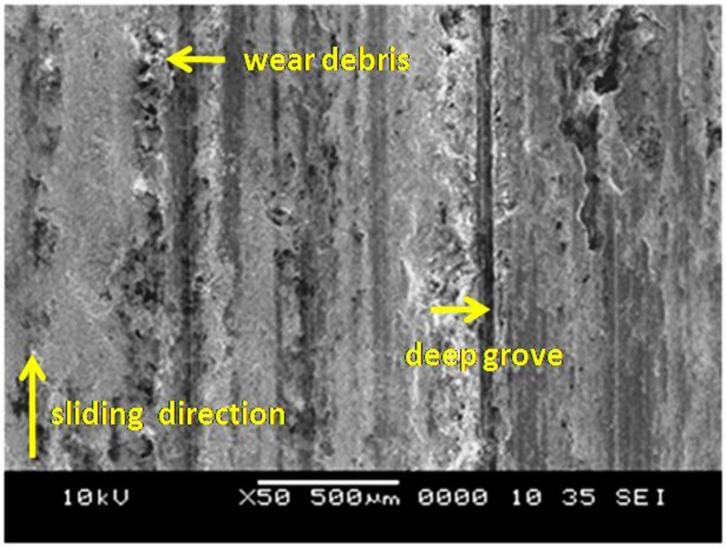


After wear

Figure 4.15: Microstructure of $CaCO_3$ brake pad composites before and after 1-km sliding distance of wear under a consistent 10 N braking load



Before wear

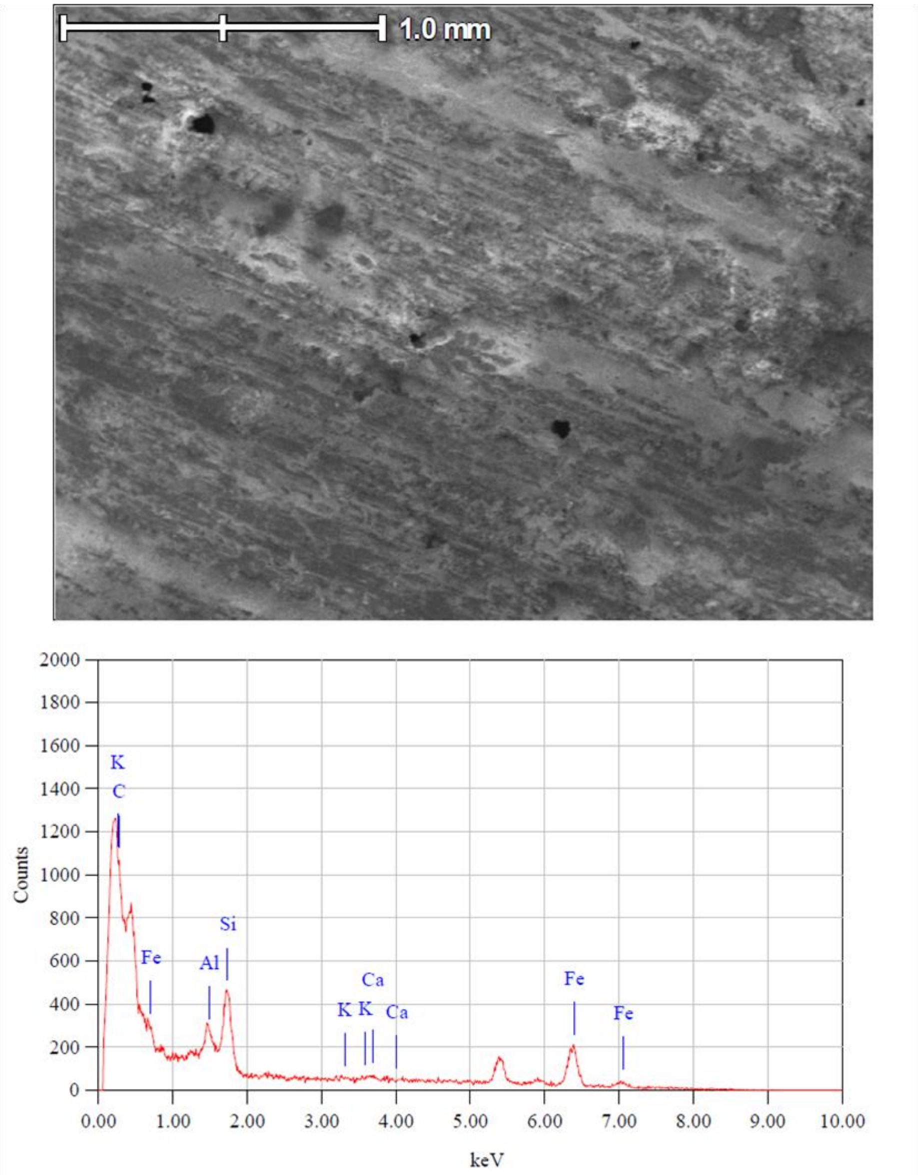


After wear

Figure 4.16: Microstructure of dolomite brake pad composites before and after 1-km sliding distance of wear under consistent 10 N braking load

Further observations were made on the changes in the morphology and topography of the worn surface of the brake pads after a 1-km distance of wear. In general, the brake pads' surfaces were rough on the microscopic scale and had peaks and grooves. The real contact point is known as the junction, while the total area of individual contact is known as the real area of contact. According to Collins (1981), the ratio of real contact area to apparent contact area is very small, only about 10^{-2} to 10^{-5}.

Figures 4.17, 4.18 and 4.19 show the details of the worn surfaces of palm slag, $CaCO_3$, and dolomite brake pads, respectively. While going through wear for a distance of 1-km under a consistent 10 N braking load, the wear debris that is generated will be either released into the environment or trapped between the contact areas. Occasionally, some of the wear debris also may be trapped in the porous or void areas. This phenomenon resulted in the contact areas increasing in size to form a friction layer and patches due to the compaction of wear debris trapped between the sliding surface as shown in Figures 4.17(a), 4.17(b), 4.18(a), 4.18(b), 4.19(a) and 4.19(b). Similar observations also have been reported by other researchers, including Filip et al. (2002), Chugh et al. (2004), Bressan et al. (2008), and Prasat et al. (2011).



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ZAF Method Standardless Quantitative Analysis(Oxide)
Fitting Coefficient : 0.7582
Total Oxide : 24.0
Element        (keV)    mass%  Error%      At%  Compound   mass%      Cation         K
C  K
O                       26.34
Al K           1.486     1.86    0.44     2.45  Al2O3       3.51        1.00    9.4372
Si K           1.739     4.78    0.54    12.09  SiO2       10.22        2.48   27.8937
K  K           3.312     0.38    0.60     0.34  K2O         0.45        0.14    2.6356
Ca K           3.690     0.63    0.88     1.12  CaO         0.89        0.23    4.7164
Fe K           6.398    66.02    4.67    84.00  FeO        84.93       17.23  397.2377
Total                  100.00           100.00            100.00       21.09
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Figure 4.17(a): SEM micrograph and quantitative analysis by EDS of worn surface palm slag sample

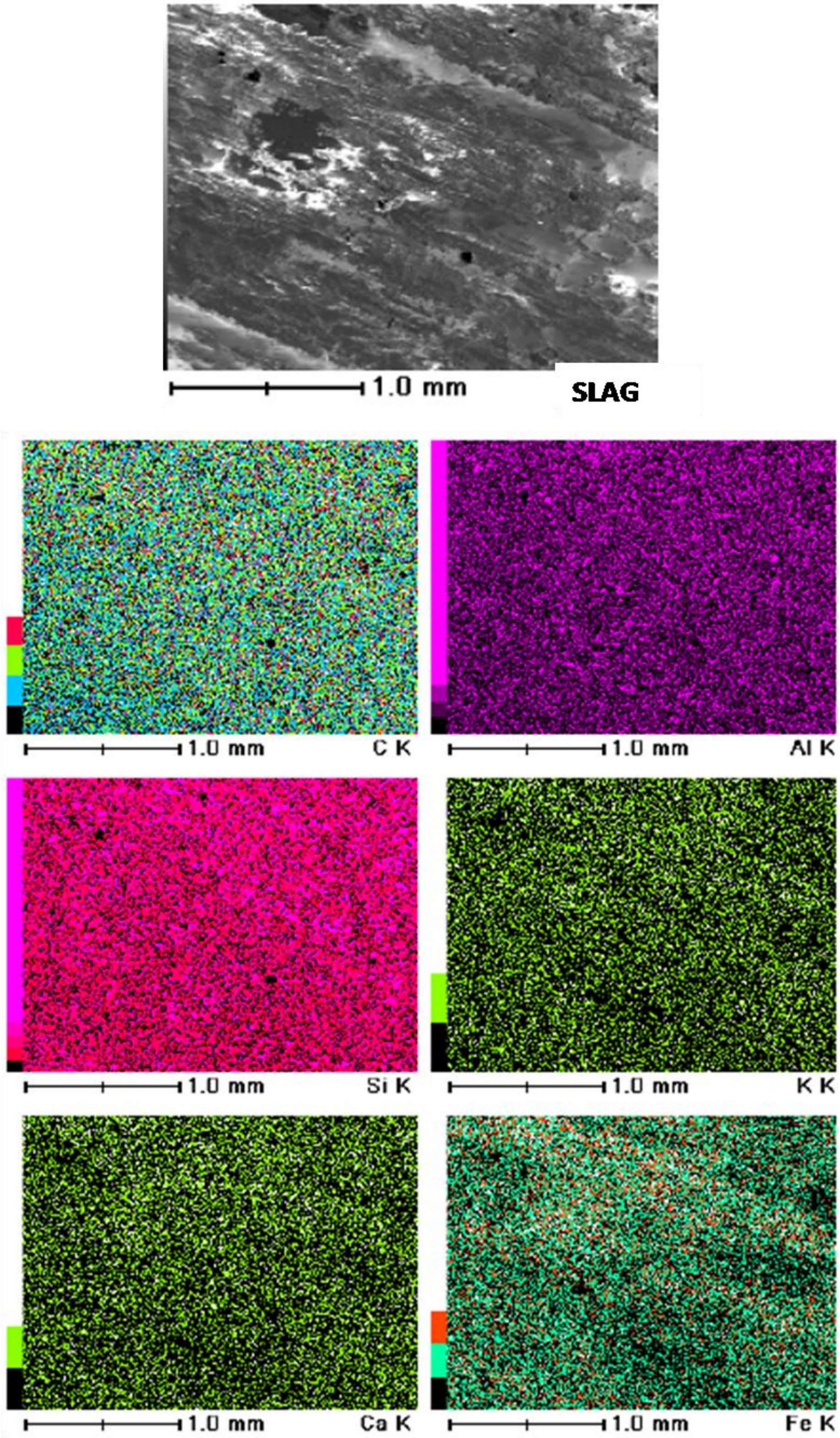
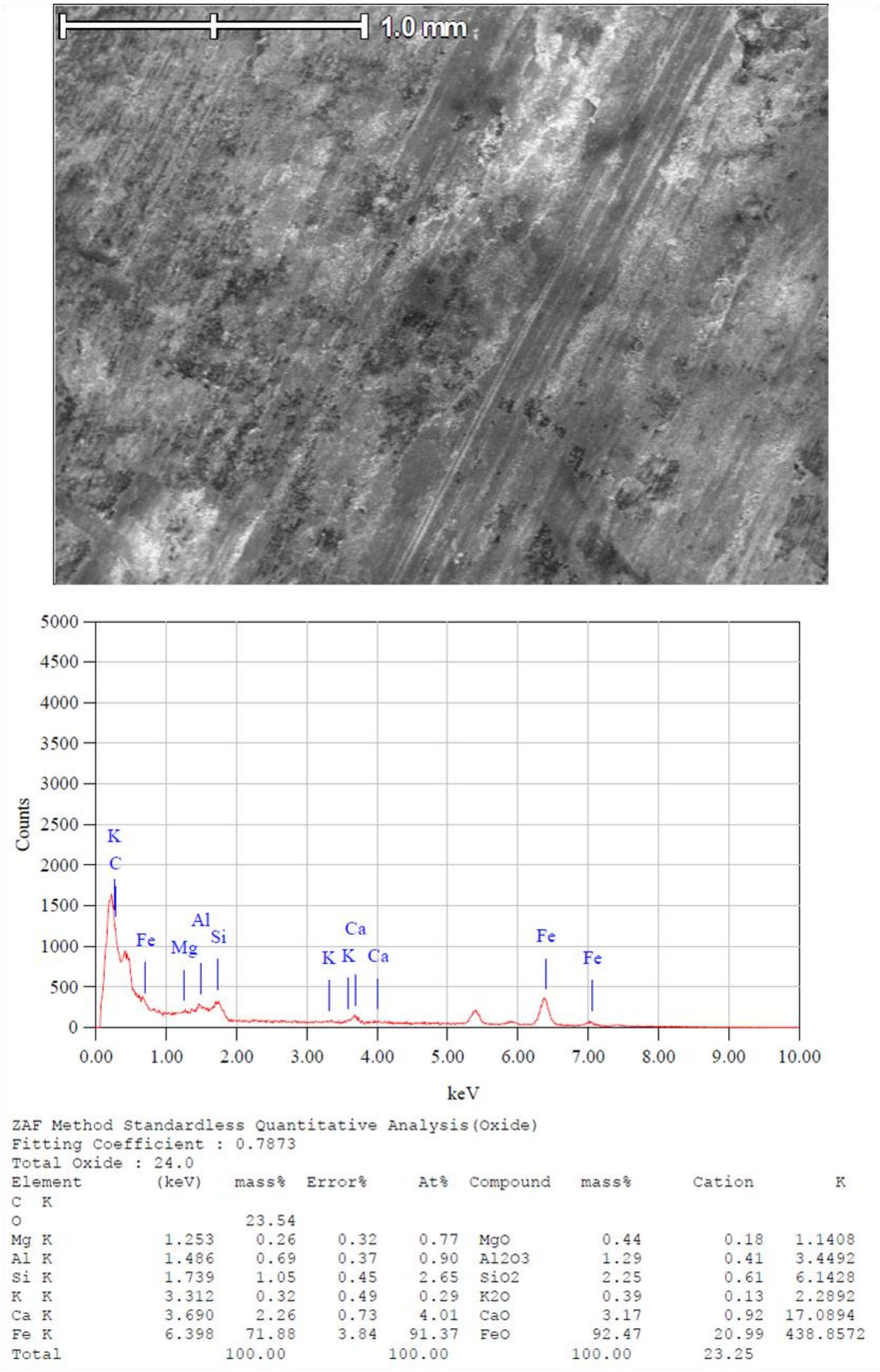


Figure 4.17(b): SEM and topography mapping of worn surface palm slag sample



```
ZAF Method Standardless Quantitative Analysis(Oxide)
Fitting Coefficient : 0.7873
Total Oxide : 24.0
Element        (keV)   mass%  Error%      At%  Compound   mass%      Cation        K
C  K
O                      23.54
Mg K           1.253    0.26    0.32     0.77  MgO         0.44        0.18   1.1408
Al K           1.486    0.69    0.37     0.90  Al2O3       1.29        0.41   3.4492
Si K           1.739    1.05    0.45     2.65  SiO2        2.25        0.61   6.1428
K  K           3.312    0.32    0.49     0.29  K2O         0.39        0.13   2.2892
Ca K           3.690    2.26    0.73     4.01  CaO         3.17        0.92  17.0894
Fe K           6.398   71.88    3.84    91.37  FeO        92.47       20.99 438.8572
Total                 100.00          100.00             100.00       23.25
```

Figure 4.18(a): SEM micrograph and quantitative analysis by EDS of worn surface of $CaCO_3$ sample

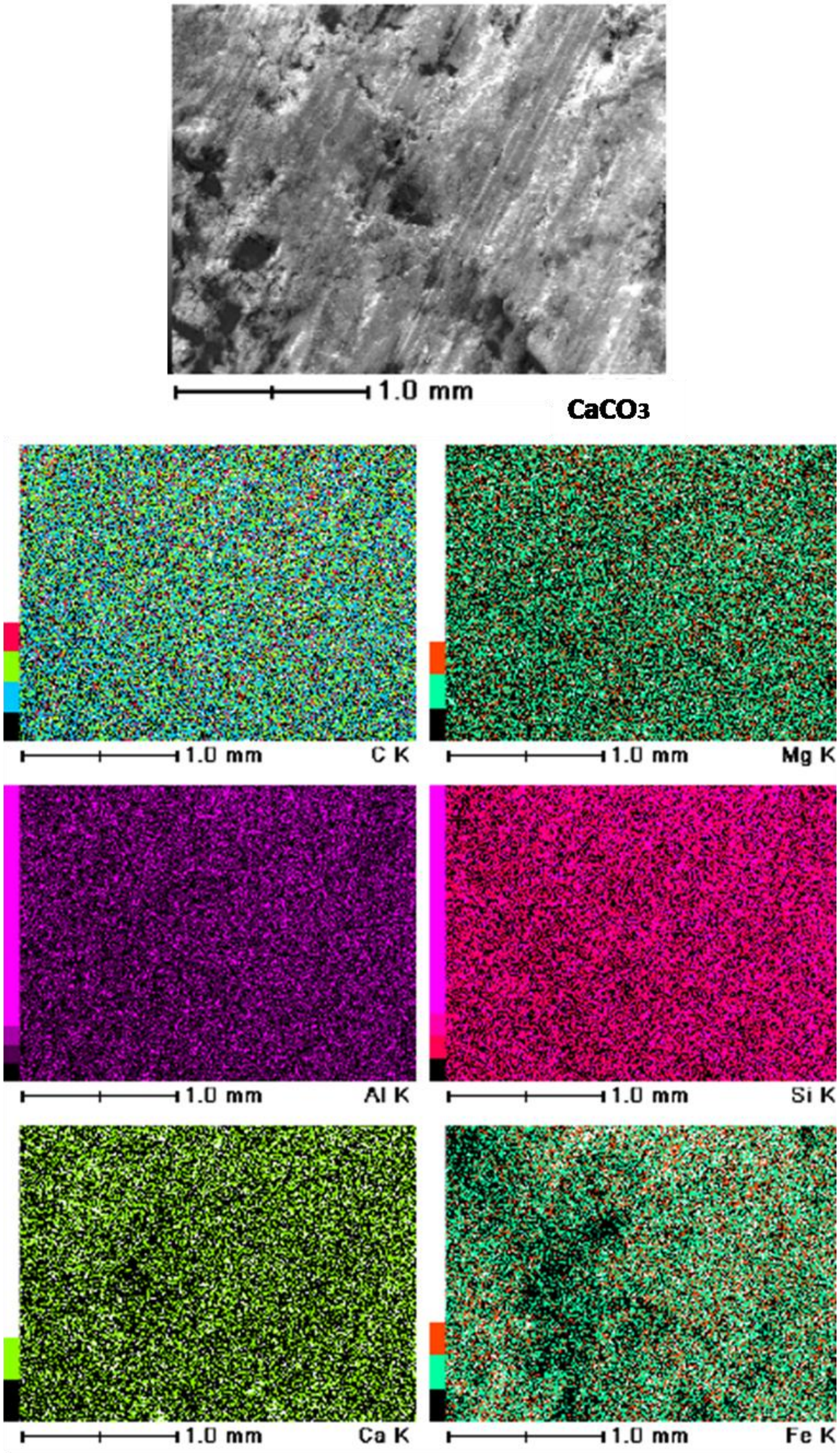
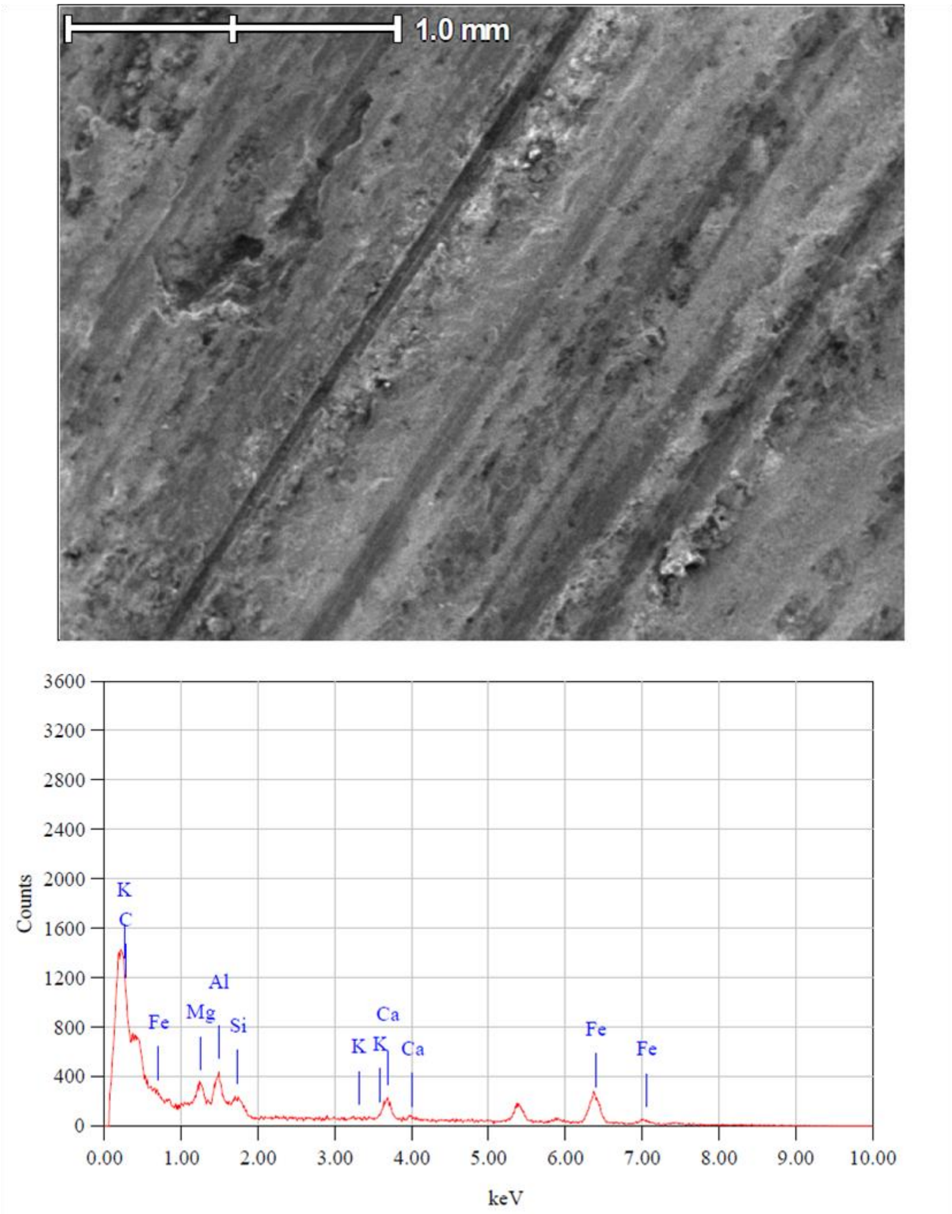


Figure 4.18(b): SEM and topography mapping of worn surface of $CaCO_3$ sample



```
ZAF Method Standardless Quantitative Analysis(Oxide)
Fitting Coefficient : 0.7007
Total Oxide : 24.0
Element         (keV)   mass%  Error%     At%  Compound   mass%       Cation        K
C  K            0.277    1.99    0.07   10.50  C           1.99         0.00   5.0880
O                       24.60
Mg K*           1.253    2.00    0.32    5.21  MgO         3.32         1.29   8.2682
Al K            1.486    2.74    0.38    3.22  Al2O3       5.19         1.59  12.8981
Si K            1.739    0.61    0.46    1.37  SiO2        1.30         0.34   3.2676
K  K
Ca K            3.690    5.82    0.75    9.20  CaO         8.15         2.27  40.2211
Fe K            6.398   62.23    3.98   70.51  FeO        80.05        17.39 346.3421
Total                  100.00          100.00            100.00        22.87
```

Figure 4.19(a): SEM micrograph and quantitative analysis by EDS of worn surface of dolomite sample

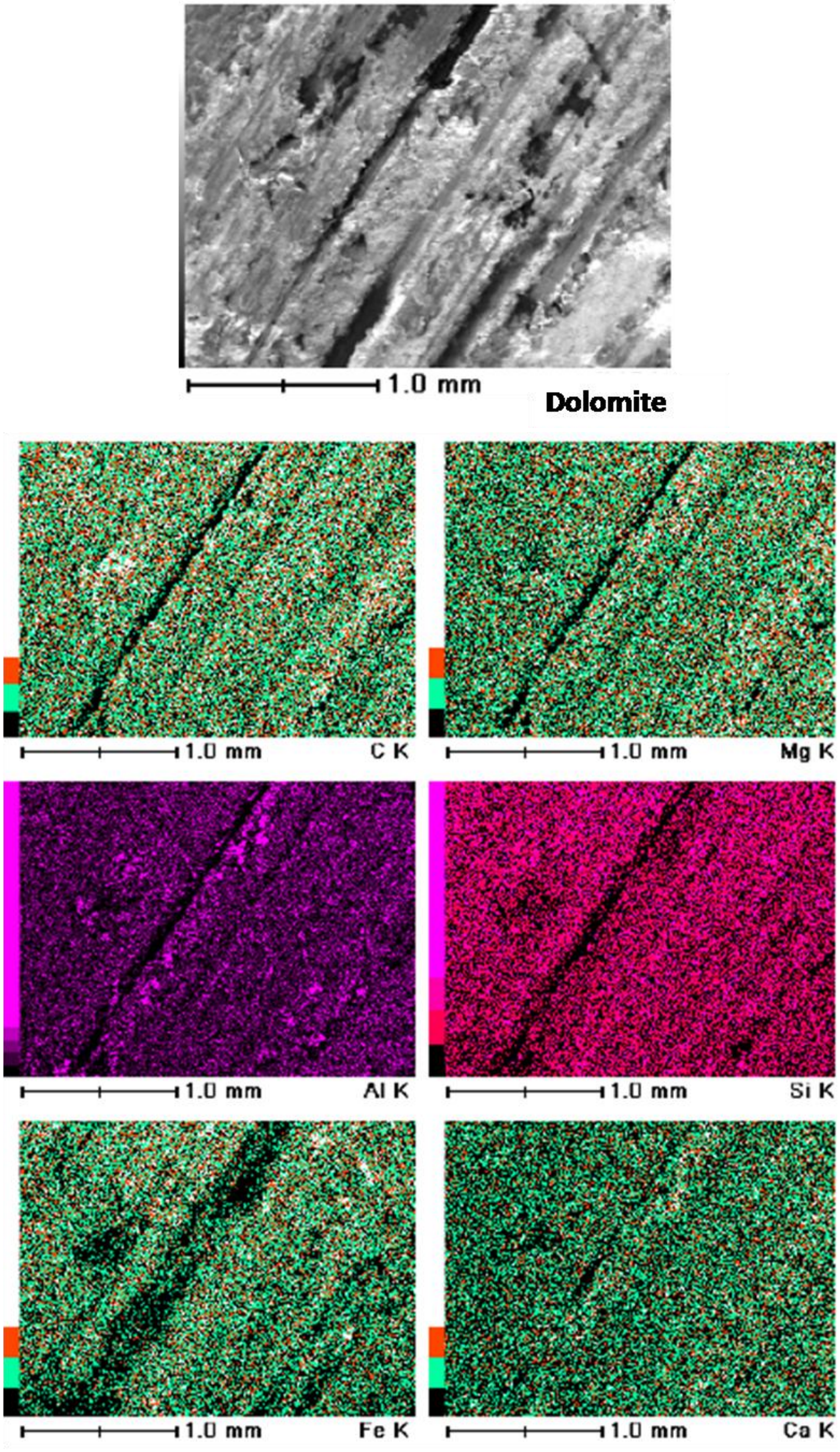


Figure 4.19(b): SEM and topography mapping of worn surface of dolomite sample

Figures 4.17(a) and (b) show the morphology of the worn surface and the elemental composition through elemental mapping using EDS on the worn surface of the palm slag filled brake pad. The figures clearly show that was more Fe than any of the other elements on the worn surface; the second highest amount was Si. Friction between the palm slag brake pad and the stainless steel plate produced debris, patches, scratches and friction film. The existence of well distributed traces of Fe and Si in elemental topography was due to the Fe from the steel plate, steel fibre and from the Fe and Si in palm slag itself.

Figures 4.18(a) and (b) show morphology of the worn surface and the elemental composition through elemental mapping using EDS on the worn surface of the $CaCO_3$-filled brake pad. The quantity of Fe still exceeded the quantities of all of the other elements on the worn surface followed by Ca. Debris, shallow scratches and a friction film also were observed. Again, the sources of Fe were steel plate and steel fibres, and the main source of Ca was the calcium carbonate filler.

Figures 4.19(a) and (b) show the morphology of the worn surface and the elemental composition through elemental mapping using EDS on the worn surface of the dolomite-filled brake pad. Similar observations were made, with Fe being the dominant element on the worn surface, followed by Ca, Al and Mg. Again, the Fe came from steel plate and steel fibres; the Ca, Al and Mg came from the dolomite filler that was used in this brake pad composite. Debris and deep scratches also were observed.

All of the observations described above show that there is correlation between wear rates and wear behaviours. The friction film that occurred on the contacting surfaces had an important influence on the wear rates. When stable friction films were formed readily, stable friction levels and low wear rates can be maintained as long as the friction film remains intact (Jacko et al., 1989). This also supported the wear rate results presented in Table 4.3.

4.4 Effect of Moulding Pressure on Mechanical Properties and Morphology during the Production of Palm Slag Brake Pads

Very few studies have been conducted to evaluate the effects of compression on the properties and morphology of composite materials during production of brake pads. This study deals mainly with the relationships between compression pressures during the production of palm slag brake pad and the resulting properties and morphology.

4.4.1 Effect of moulding pressures on the density of the sample

Figure 4.20 shows the density obtained by different compression pressures used in making palm slag composites for brake pads. It is obvious that the higher moulding pressures produced more compact palm slag composites. Subsequently, the increased of density make it possible to decrease the thickness of the compressed composite samples, as shown in Figure 4.21.

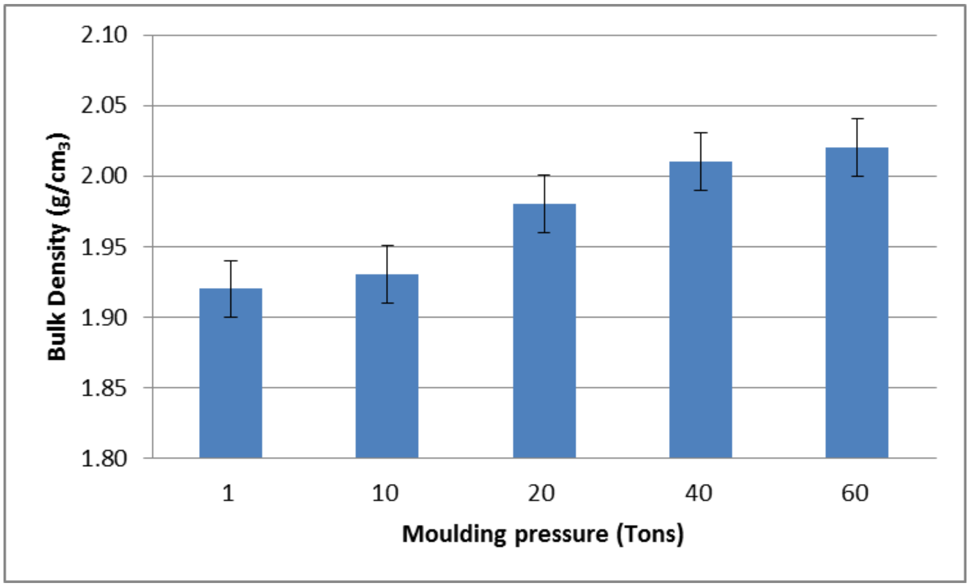


Figure 4.20: Density of palm slag composite at different moulding pressures

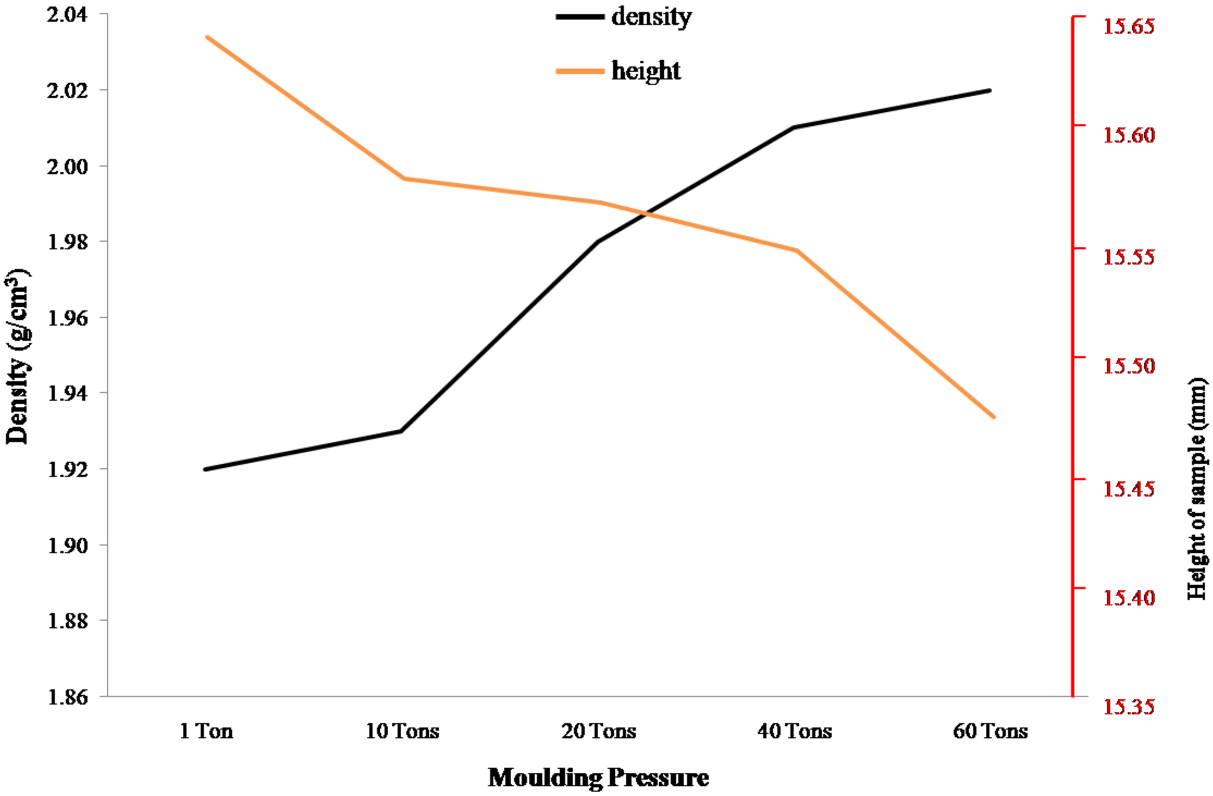
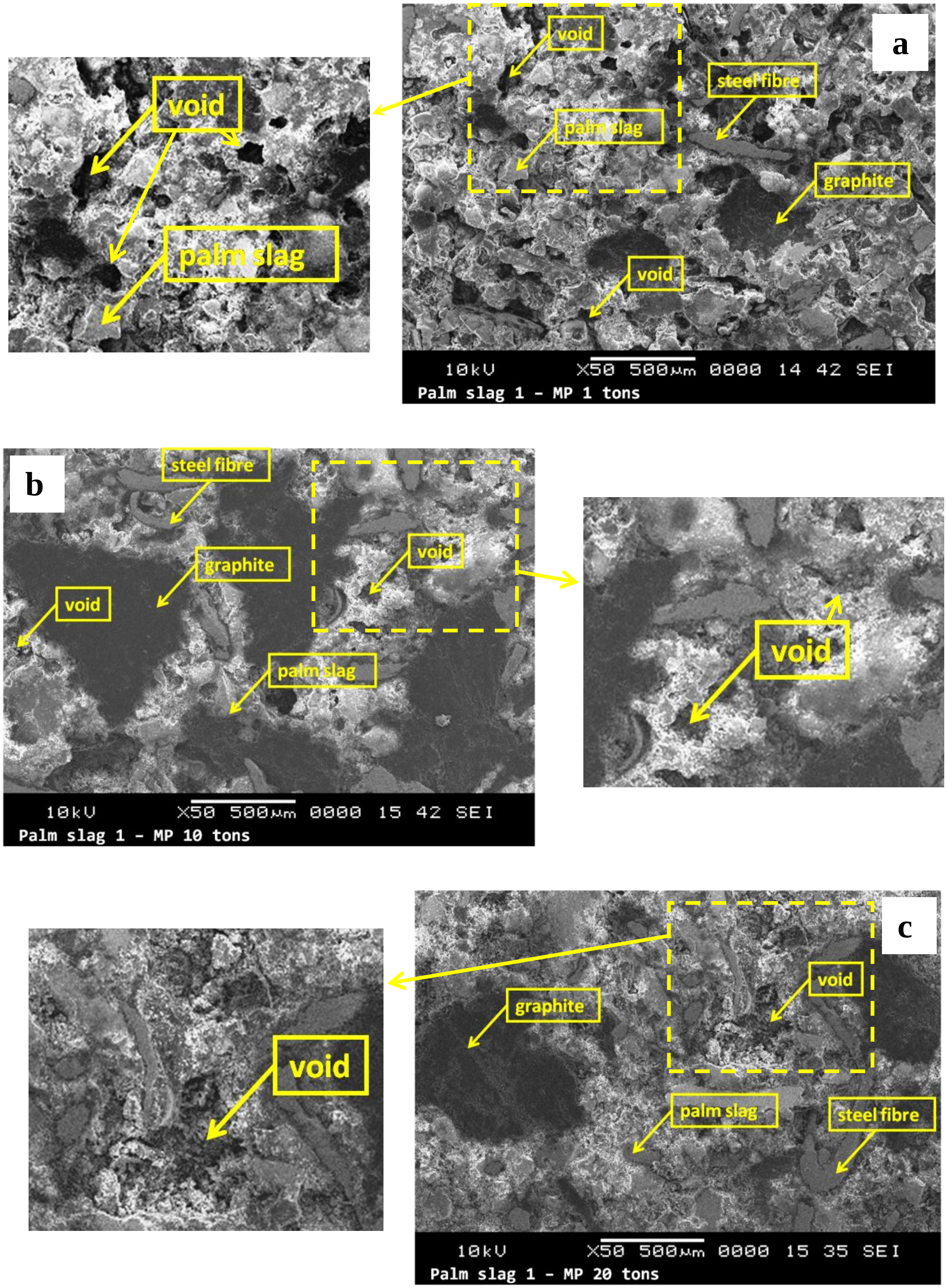


Figure 4.21: Comparison of density and height of the palm slag composite samples at different moulding pressures.

As shown in Figure 4.21, increasing the moulding pressure will increase the density and decrease the thickness of the composite. This can be attributed to the fact that the different materials, which were of different sizes and were used in the composite under compaction pressure, were subjected to sufficient force that plastic flow occurred, thereby increasing the density of the composite. The trend of this result was supported by Kawabe et al. (2011), in their mechanical and morphological studies on the compressive properties of brake materials. They found that the higher the moulding pressure was, the smaller the thickness or height of the specimen became. Guo et al.(2009), in their studies on the effect of the fabrication process of the carbon-carbon composite, also found that the moulding pressure had significant effects on density and compressive strength.

The different sizes of the various ingredients used in the brake pad are squeezed and push against each other in response to the application of high moulding pressure. Because of the movements of these particles, the gaps between the particles become smaller and this will result in decreased height and increased compaction of the palm slag composite, and it also will result in decreases in the sizes of the void. Even though this phenomenon is not easy to explain, it can be related to the classical bi-modal/ multi-modal packing effect.

In the multi-modal packing effect, small particles are used to fill in the pores in the packed structure obtained with large particle; then even smaller particles are used to fill in the remaining pores and this process is continued until most of the pores are filled (Rothon and Hancock, 2003).


a
void
steel fibre
palm slag
graphite
void
void
palm slag
10kV X50 500μm 0000 14 42 SEI
Palm slag 1 - MP 1 tons
b
steel fibre
graphite
void
void
palm slag
void
10kV X50 500μm 0000 15 42 SEI
Palm slag 1 - MP 10 tons
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Palm slag 1 - MP 20 tons

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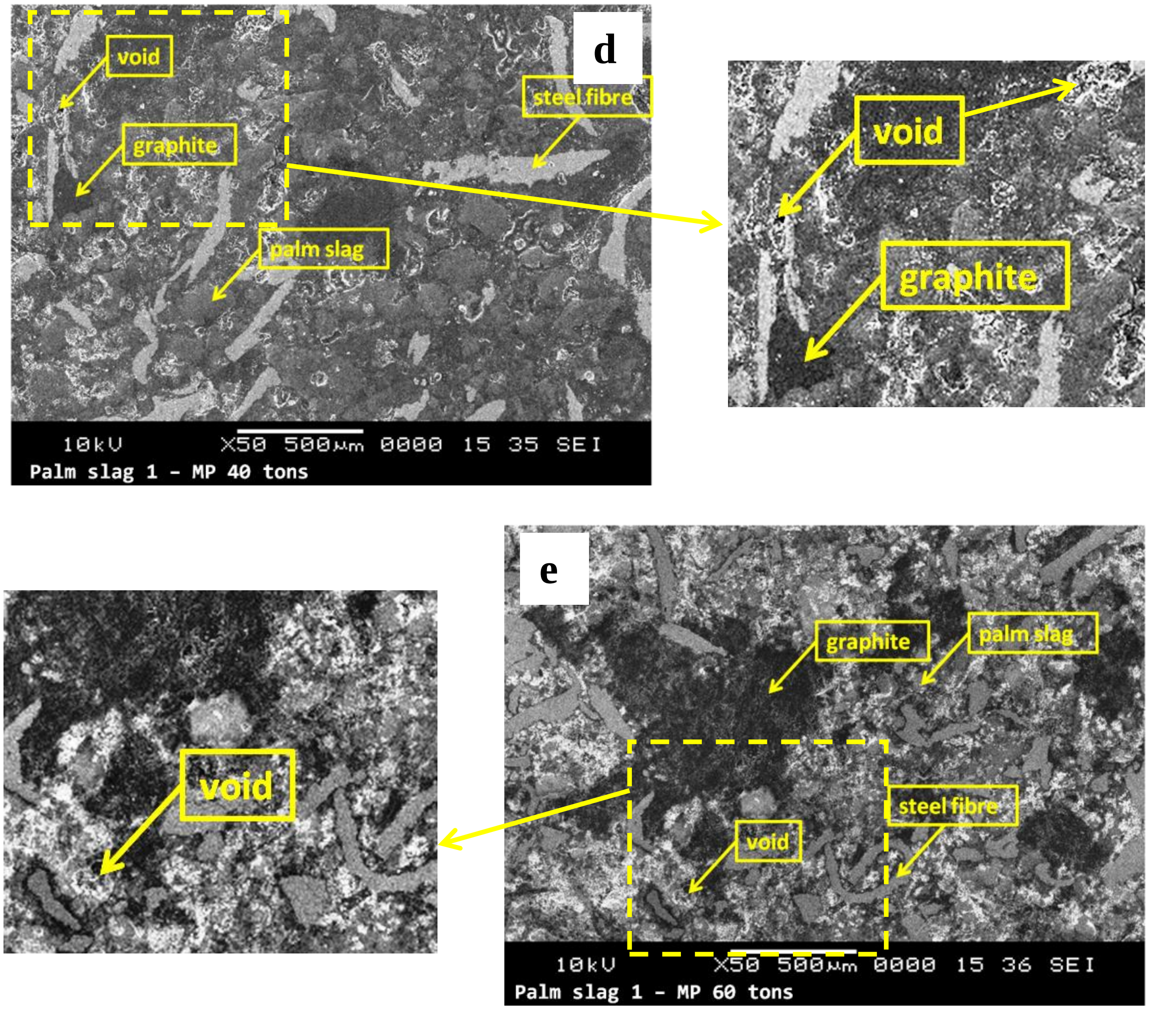


Figure 4.22: Microstructure of palm slag composite samples with different moulding pressure: a) 1 ton, b) 10 tons, c) 20 tons, d) 40 tons, e) 60 tons

These were proved further and supported by the observation of SEM micrograph as shown in Figure 4.22. The SEM micrograph clearly shows that, by using a 1-ton moulding pressure as shown in Figure 4.22 a), many large voids occurred. It was observed that increasing the moulding pressure will produce a more compact composite and, cause the amounts and sizes of the voids to become smaller. Figure 4.22 e) shows that the 60-tons, the highest moulding pressure used in this study, produced less voids and the one that existed were smaller than the voids occurred at the other pressures.

4.4.2 Effect of moulding pressures on the hardness of the samples

The hardness values of the composite are shown in Figure 4.23. It is apparent that hardness values of the samples increased as the moulding pressure increased. Rockwell type E measurement could not be obtained for the sample prepared by 1-ton moulding, due to its low hardness. The high hardness, i.e., a 61.1 Rockwell type E value, for the sample prepared by a 60-ton moulding pressure was a result of high compaction caused by the high moulding pressure. Increasing the moulding pressure will help the composite materials pack together more closely and eliminate voids.

This observation was supported by the previous finding by Elinn (1992) and Nash et al. (1995). They noted that it is important to keep porosity to a minimum to obtain compact, dense composite materials with increased mechanical properties. Zamri et al. (2011) in their studies of the influence of particle sizes and compaction pressure on surface hardness of aluminum composite fabricated via powder metallurgy also give a significant evident that the higher compaction pressure result in higher surface hardness.

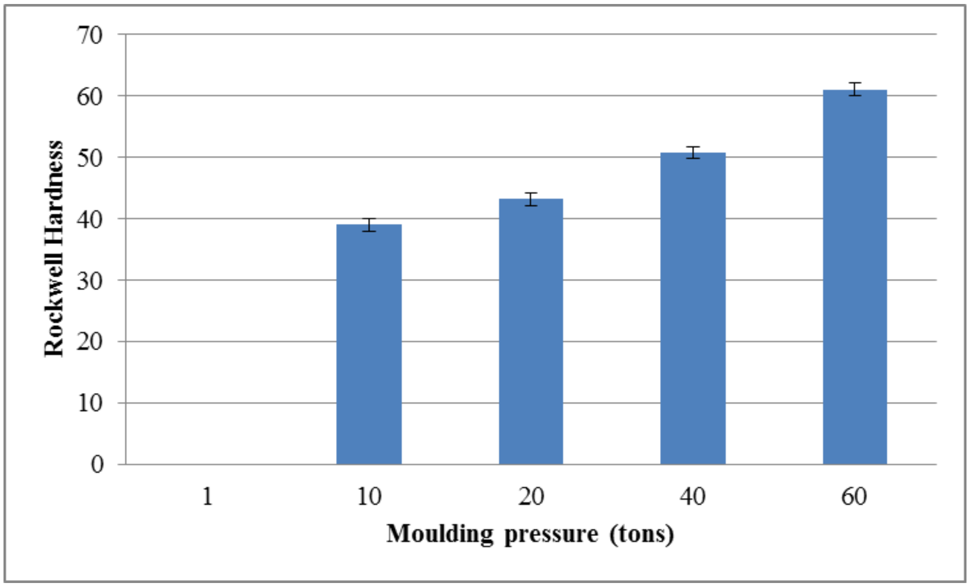


Figure 4.23: Rockwell hardness value of palm slag composite samples with different moulding pressures

In Figure 4.24 the effect of the different moulding pressure on density and hardness is shown. Even though previous studies have not shown any significant relation between hardness and density of the solid material, but the relation between them in composite form seems to be very significant when the composite is subjected to different moulding pressures. The higher the moulding pressure, the higher the density of the composite becomes, and the hardness values of the samples are increased as a result. The Rockwell hardness value for samples subjected to a moulding pressure 1-ton could not be obtained because the hardness was so low that it was undetectable by the Rockwell measurement.

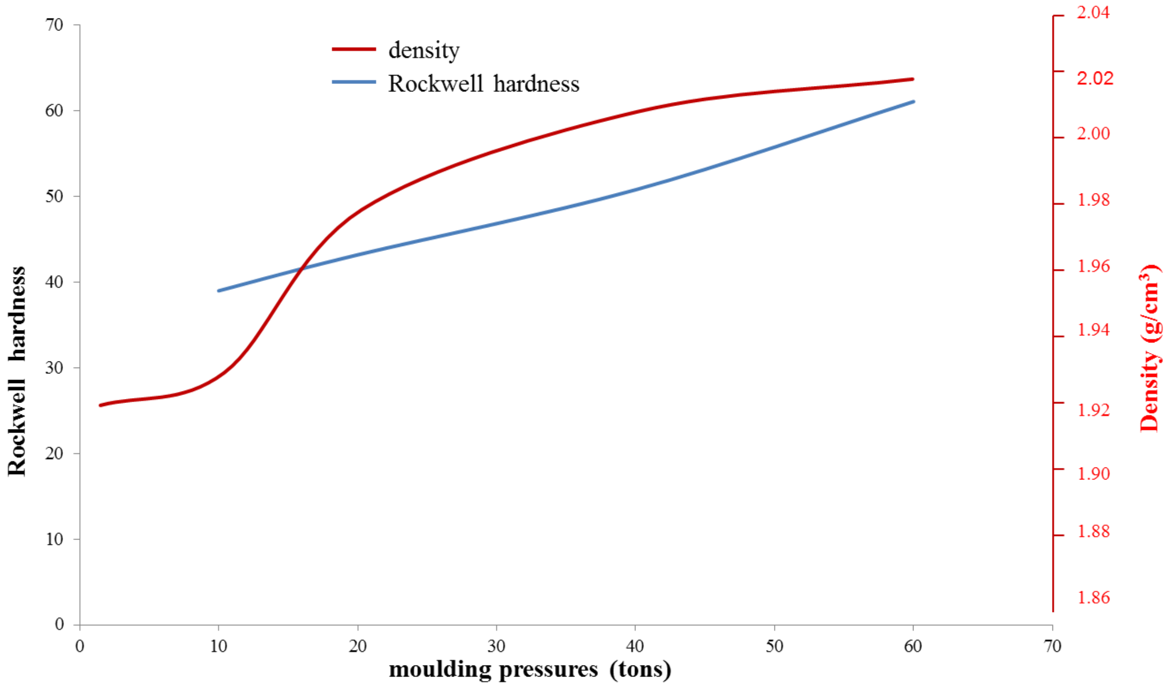


Figure 4.24: Relation between hardness and density of the palm slag friction composite at different moulding pressure.

To make this relation clearer, the direct correlation between hardness and density for the palm slag composite was again plotted in Figure 4.25. This Figure could be used as a master curve plot for palm slag friction composite sample. It is predicted that the higher moulding pressures, i.e., 80 or 100 tons, would result in the palm slag composite having even higher values of density and hardness.

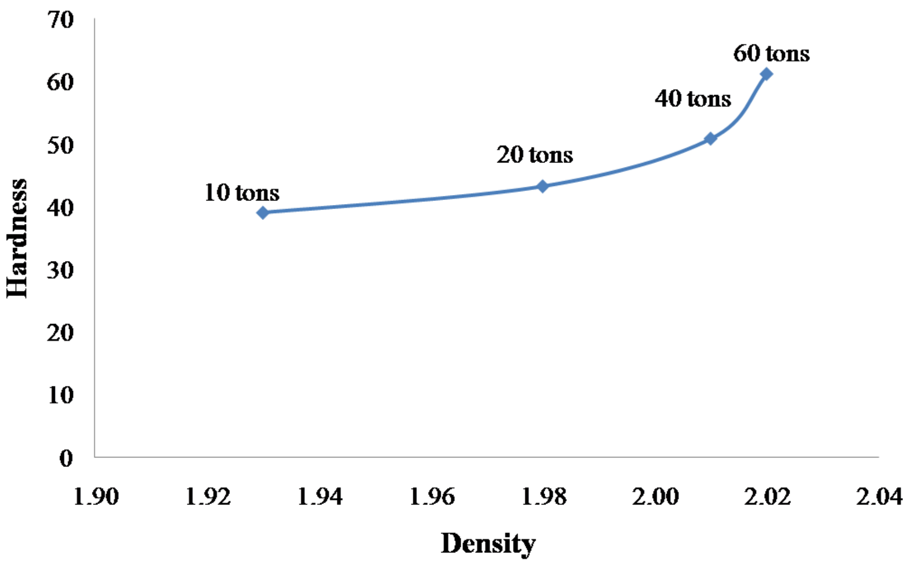


Figure 4.25: Correlation between hardness and density of palm slag composite samples.

4.4.3 Effect of moulding pressure on compressive strength of the sample

Figure 4.26 shows the compressive strength of the palm slag brake pad composite for different moulding pressures used during the process of making the brake pad composites. One can see that compressive strength exhibits a trend that is similar to that of hardness. Compressive strength of the brake pad increases with increased of processing moulding pressure and as the moulding pressure increased, the compressive strength seem to reach a plateau. Once again, the compactness of the composite material through the processing load can be seen clearly.

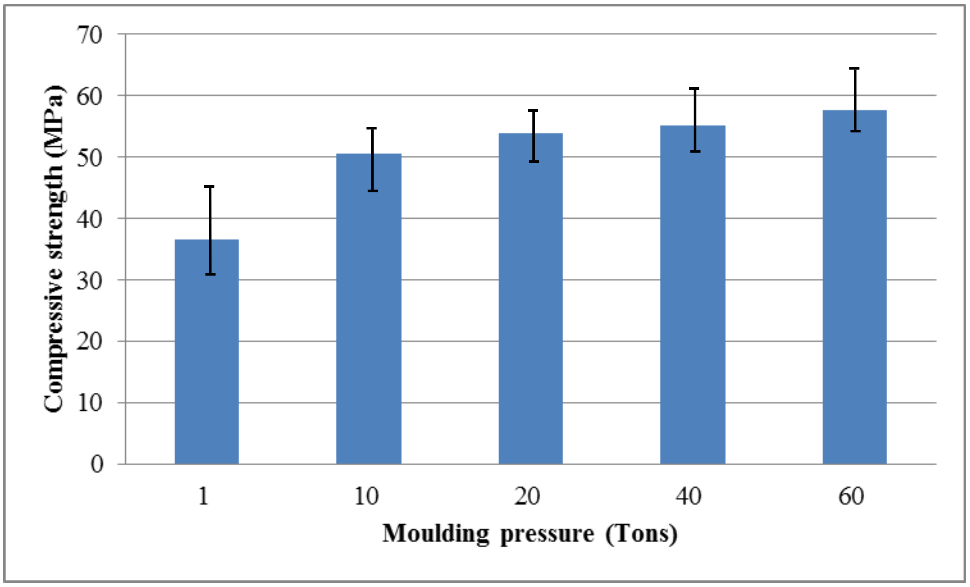


Figure 4.26: Compressive strength of the palm slag composite samples with different moulding pressure

The same trend also was observed with the modulus of the composite as presented in Figure 4.27. The higher the moulding pressure used in preparing the composites, the higher the modulus became, reaching a plateau at the highest pressures. This observation was due to the compactness of the composite product. Up to a certain limit of applied pressure, the compactness will reach its maximum point and remain at that point. At this stage, the mechanical properties of the product also reach their maximum limit, which explains the occurrence of the plateau.

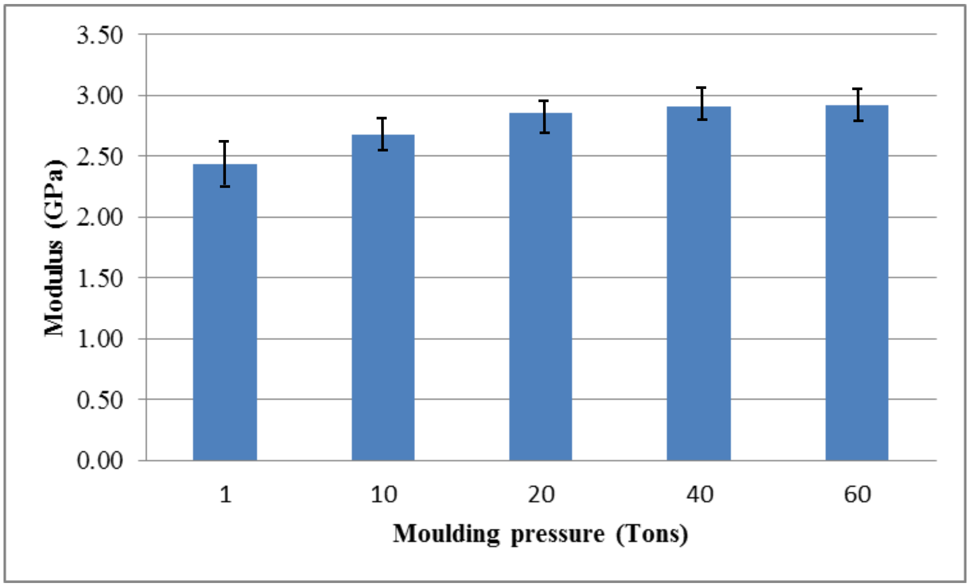


Figure 4.27: Modulus of the palm slag composite samples with different processing loads

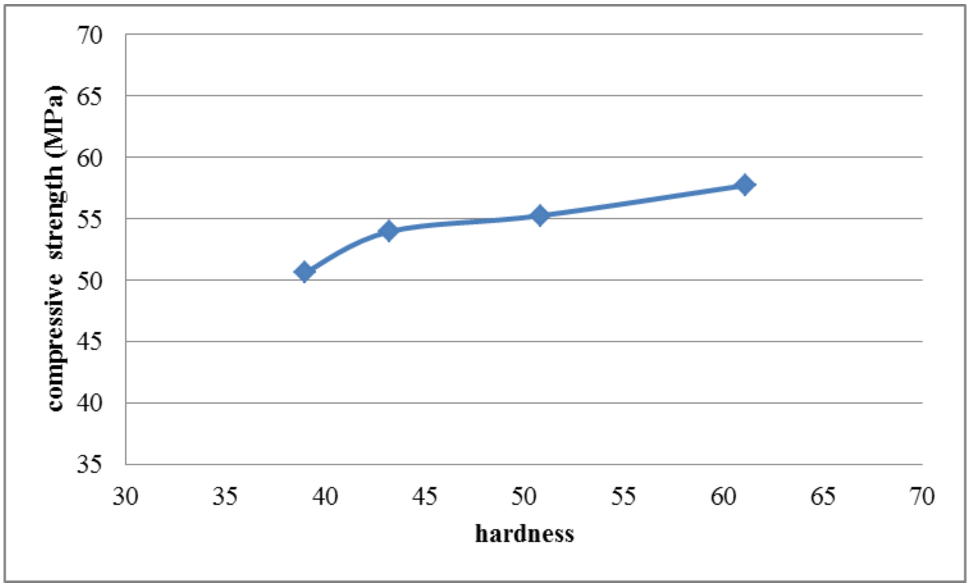


Figure 4.28: Relation between compressive strength and hardness

Figure 4.28 shows the relation between compressive strength and harness, and Figure 4.29 shows the relation between modulus and hardness. From the relations, it is shown that, even though higher moulding pressure can increase the hardness, the compressive strength and modulus reach a limit point and tend to become constant.

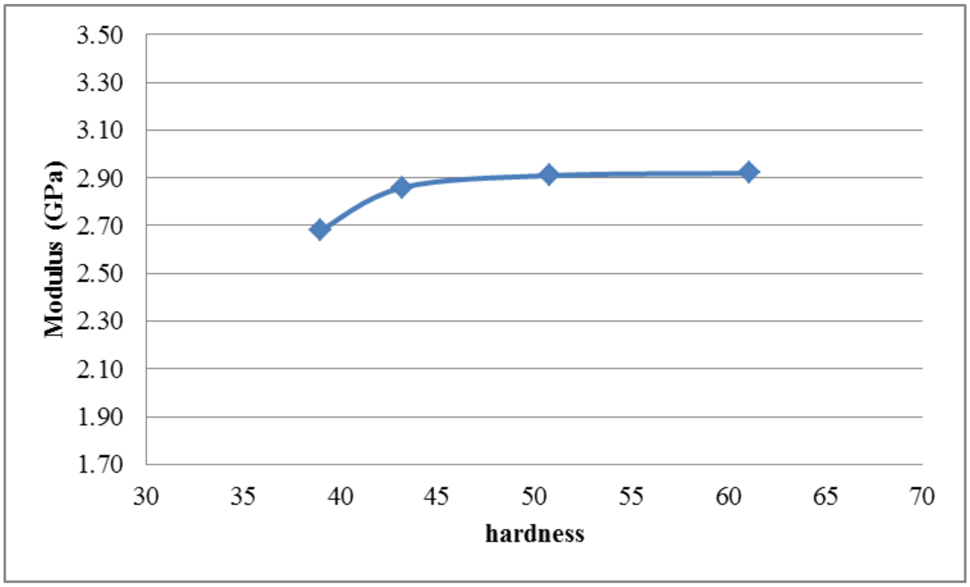


Figure 4.29: Relation between modulus with hardness

4.4.4 Wear Properties of Palm Slag Composite Samples

After sliding 1-km on the stainless steel plate, the weight loss of the brake pad composite was determined: then, wear volume and wear rate of the palm slag brake pad composites prepared at different moulding pressures were calculated and compared with the asbestos brake pad described in the literature by Chand et al. (2004). Figure 4.30 shows the weight loss of the palm slag composites prepared at different moulding pressures after sliding 1-km on the stainless steel plate. The results from Figure 4.30 clearly indicate that increasing the moulding pressure reduces the weight loss due to wear while sliding. In the test, less weight loss was observed for the composites that had been prepared at the higher moulding pressures. Thus, this lower rate of wear means that the composites had increased wear resistance. This is due to the increased that resulted from better compaction when applying higher moulding pressures.

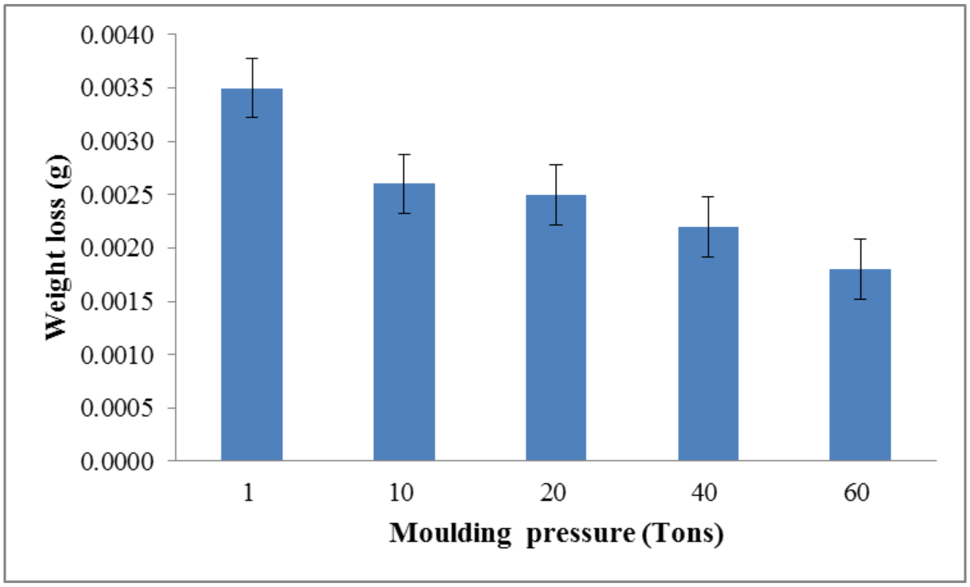


Figure 4.30: Weight lost after the 1-km wear test for palm slag composites prepared at different moulding pressures

The wear behaviour represented by wear volume and rate of the palm slag brake pad composite under 10 N for 1-km sliding distance is shown in Table 4.4. From the data shown in Table 4.4, one can see that the palm slag brake pad composite, especially with a processing pressure of 60 tons, possessed almost the same mechanical and wear properties as a conventional asbestos-based brake pad.

Table 4.4: Wear behaviour of palm slag composite samples under sliding wear condition

Sample	Density g/cm^3	Wear volume, $cm^3 \times 10^{-3}$	Wear rate, $m^3/m \times 10^{-13}$
Palm slag 10 tons	1.93	2.02	20.2
Palm slag 20 tons	1.98	1.77	17.7
Palm slag 40 tons	2.01	1.09	10.9
Palm slag 60 tons	2.02	0.89	8.9
Asbestos (Chand *et al.*, 2004)	2.22	0.72	7.2

4.4.5 Correlation between mechanical properties and wear rate

Further correlations were examined to obtain additional information on the relation between wear properties and mechanical properties. Figure 4.31 shows the correlation between wear rates and the density of the palm slag composite. Increasing density by using higher moulding pressures produced a good effect on wear behaviour. It was observed that wear resistance had a direct, positive relationship with the density of the brake pad composite. Generally, by looking at the regression line and the R^2 value shown in Figure 4.31, it can be seen that the correlation between wear rate and density has acceptable accuracy. Even though the R^2 value is lower than 0.9, it still close to 1.0, which represents perfect accuracy of the data.

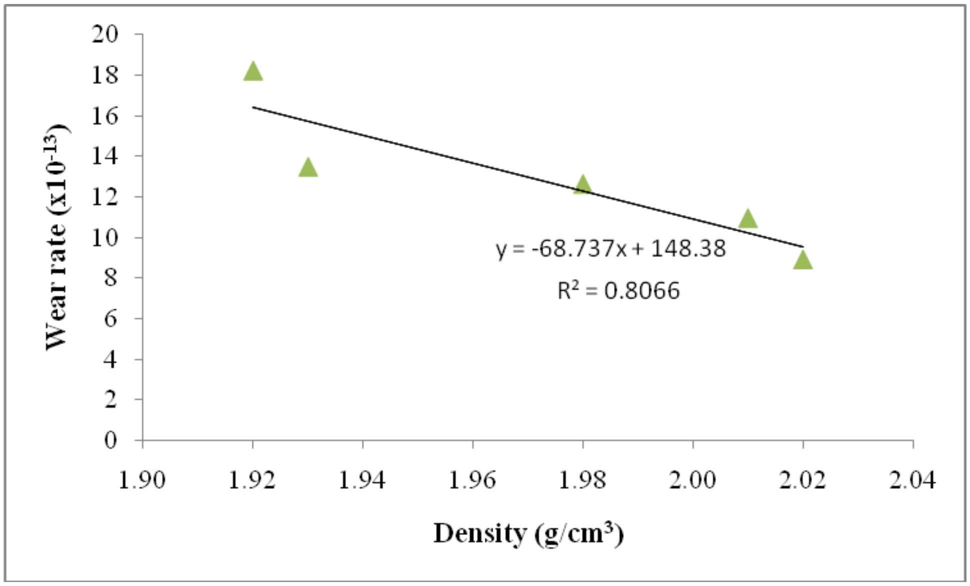


Figure 4.31: Correlation between wear rate and density of palm slag composite due to the different moulding pressures.

Subsequently improving the density would make the composite more compact and harder. From Figure 4.32, it can clearly presented that high hardness value will reduce the wear rate or increased the wear resistance. For the same reason, it was observed that using higher moulding pressure to the palm slag brake pad composites increase the compressive and modulus which were showed in Figure 4.33 and 4.34. The compaction give better mechanical properties to the composite; reduce the wear rate and increased the capability against friction or in other words increase wear resistance of palm slag brake pad composites.

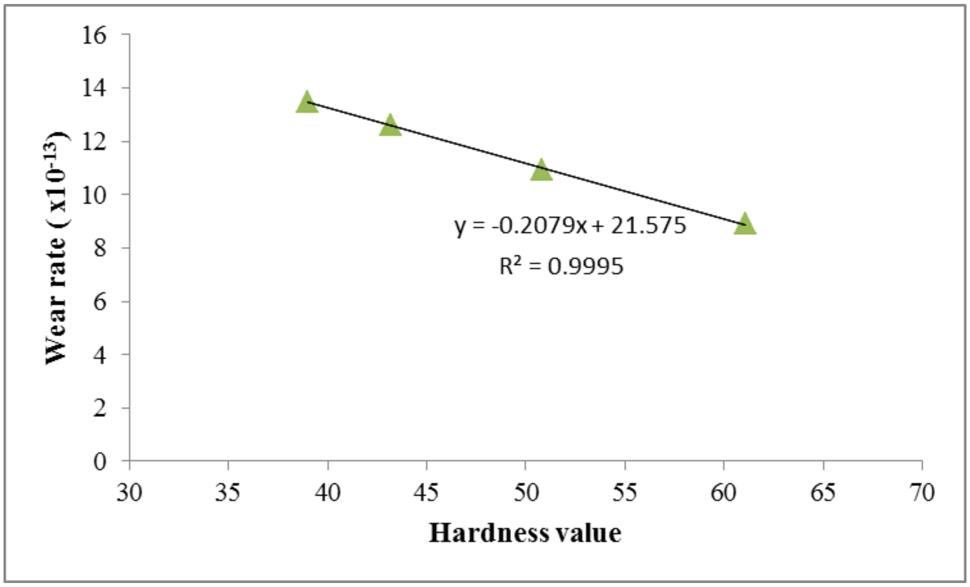


Figure 4.32: Correlation between wear rate and hardness of palm slag composite for different moulding pressures.

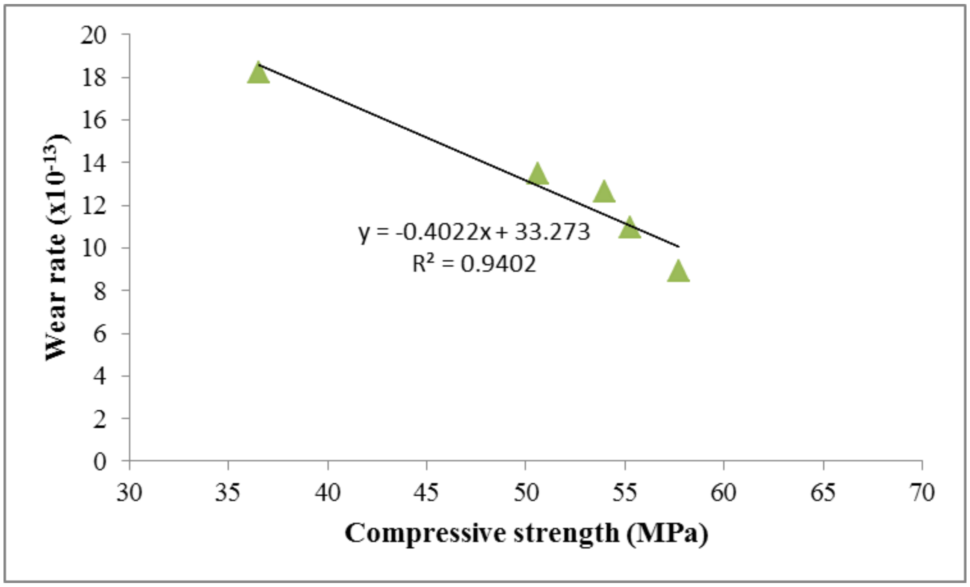


Figure 4.33: Correlation between wear rate and compressive strength of palm slag composite for different moulding pressures.

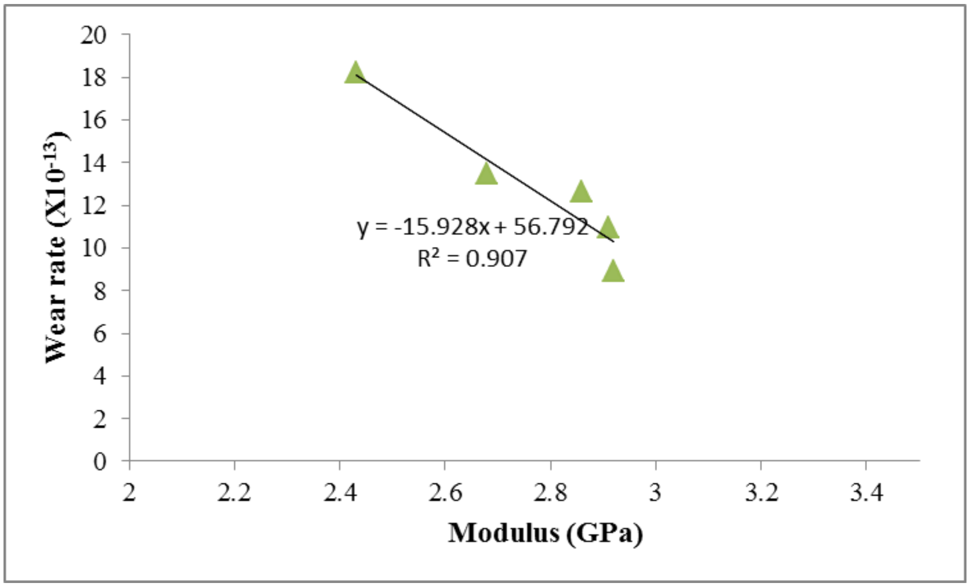


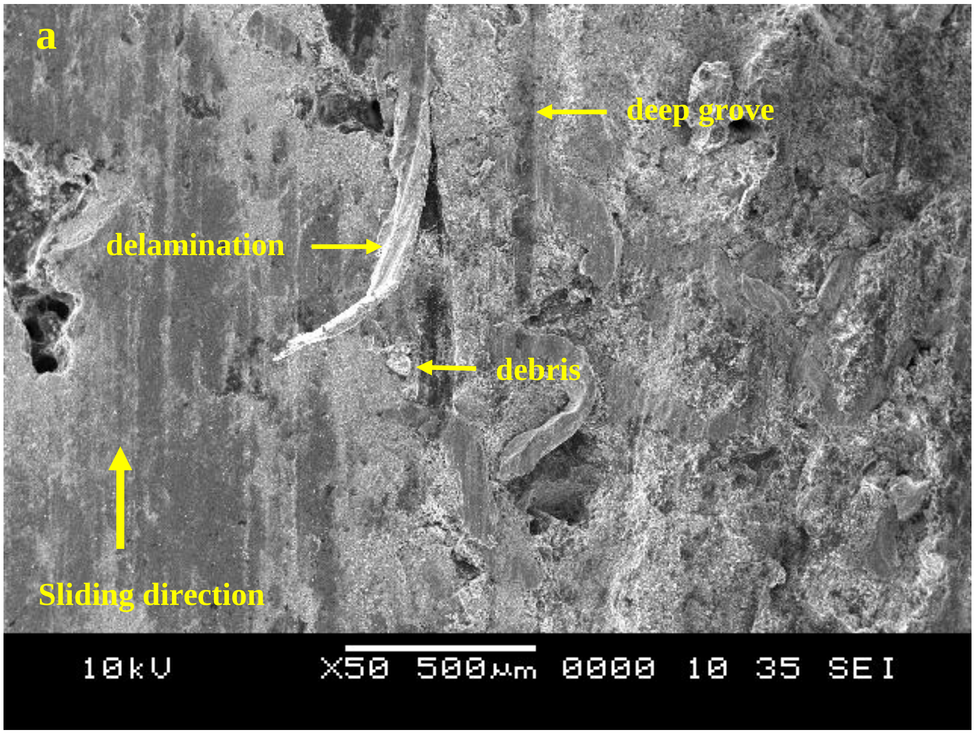
Figure 4.34: Correlation between wear rate and modulus of palm slag composite for different moulding pressures.

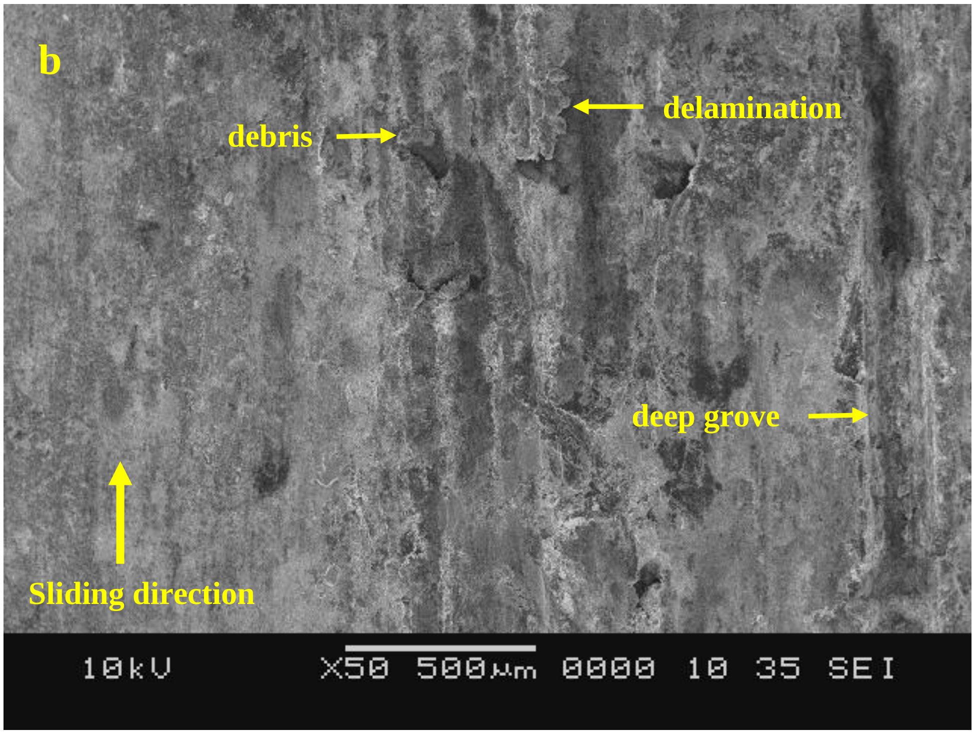
Due to the regression line and the R^2 values shown in Figures 4.32, 4.33, and 4.34, all of the data seem to be accurate and fit well and accurate. The R^2 values were greater than 0.9, indicating better than 90% accuracy of the correlation.

After the wear tests were performed, the worn surfaces of the palm slag brake pad composites were examined using SEM. The worn surfaces appeared to be rough on the microscopic scale and the texture was characterized as having peaks and valleys. Wear debris was generated during the braking test, and it essentially was a fine powder that was either released into the environment or trapped between the contact areas or in void areas. The wear debris accumulated and piled up against the contact areas. Subsequently, the contact areas increased in size and formed a friction layer due to the compaction of the trapped debris as can be observed in most of the SEM micrographs in Figure 4.35.

The micrograph of the worn surface of sample shown in Figure 4.35 shows that, the built-up friction layer only existed in a certain areas. Figures 4.35 (a) and (b) for example, show that the friction layer does not cover the metal fibres and graphite. The debris tends to fill the gaps and voids that occurred due to the low compactness that resulted from low moulding pressures.

Detailed studies of the SEM micrographs revealed that the following wear mechanisms were involved and observed during the wear test, i.e., abrasion, delamination, adhesion, and groove formation. The abrasion wear mechanism is always characterized by the presence of ploughed marks on the friction layers. This wear mechanism was observed in all cases of the wear test for all of the different moulding pressure used, as shown in Figures 4.35 a), b), c), d), and e). A similar observation was reported by Talib Ria et al. (2008), Sterle and Urban (2006). This phenomenon is due to the hard particles, which exist as a third component between the friction material and brake disc, ploughing into the wear surface.


a
deep grove
delamination
debris
Sliding direction
10kV X50 500µm 0000 10 35 SEI


b
delamination
debris
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Sliding direction
10kV X50 500µm 0000 10 35 SEI

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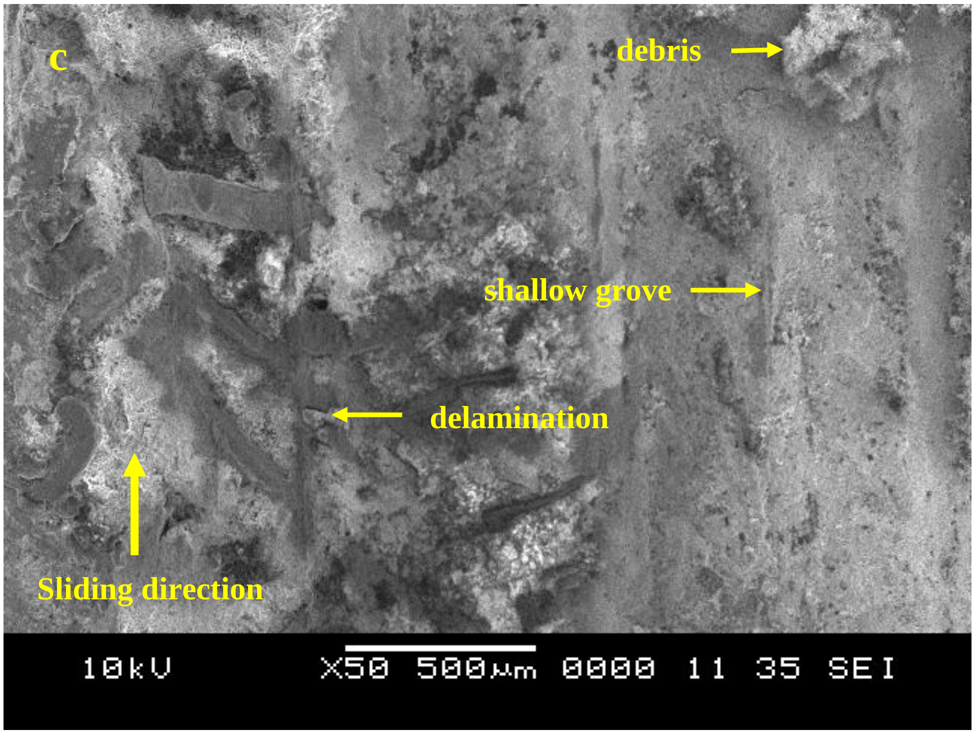
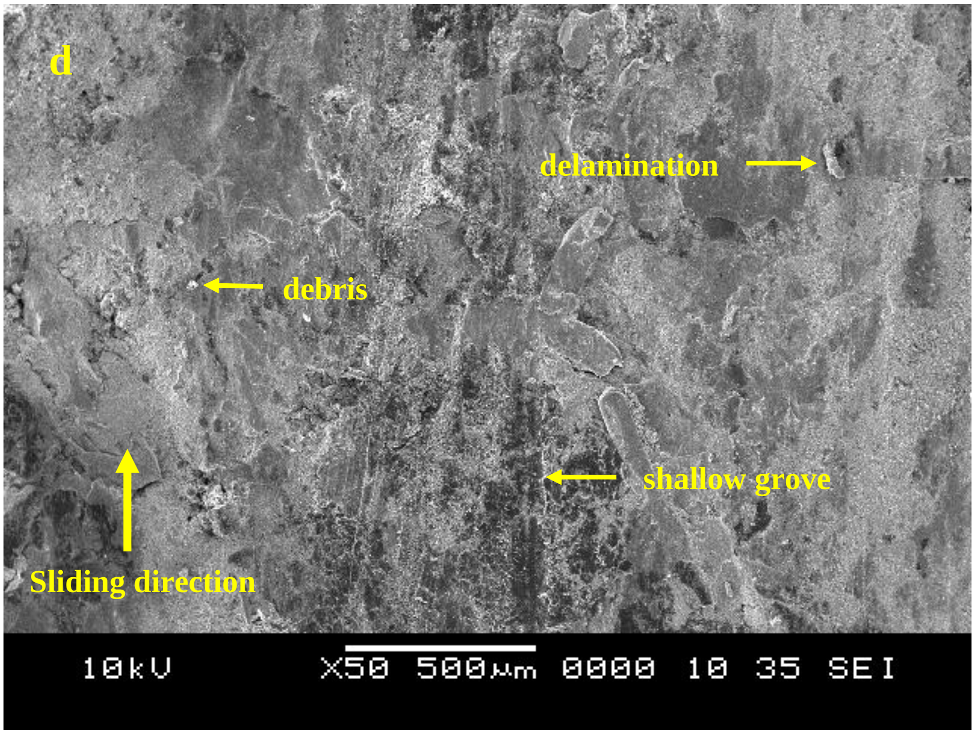

c
debris
shallow grove
delamination
Sliding direction
10kV X50 500µm 0000 11 35 SEI


d
delamination
debris
shallow grove
Sliding direction
10kV X50 500µm 0000 10 35 SEI

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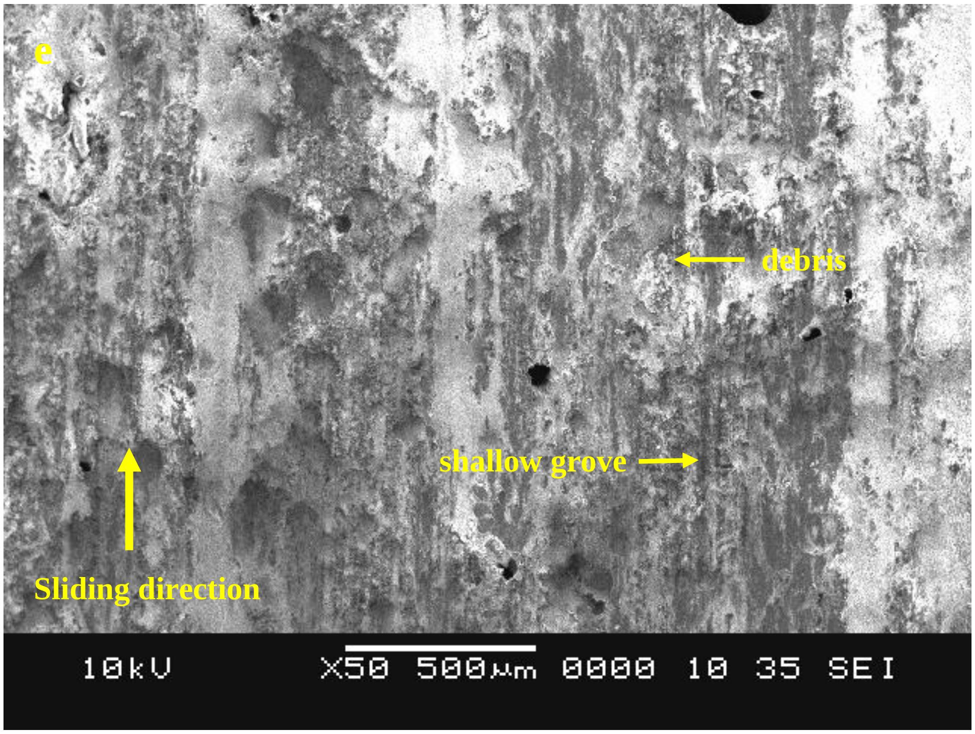

Figure 4.35: Post-wear test microstructure of worn surface palm slag brake pad samples prepared with different moulding pressure: a) 1 ton, b) 10 tons, c) 20 tons, d) 40 tons, e) 60 tons.

Delamination wear is a phenomenon that can be observed when the particles that make up the surface of the brake abrasion peel off from the worn surface. More severe conditions show that there are fibres in the brake pads that are pulled out of their original positions. Figures 4.35 a), b), and c) clearly show the delamination wear mechanism. Because of the wear particles such as pulled-out steel fibre form groove that can be observed in Figures 4.35 c) and d).

This situation first was postulated by Suh (1973) who found that, in the early stage of sliding, the morphological changes of the sub-surface showed the process of plastic deformation, followed by the formation of micro voids and micro cracks. As sliding progresses, the micro cracks propagate parallel to the surface. Finally, the wear surface flakes off, subsequently producing delaminated sheets.

Another wear mechanism that is involved is adhesion, which occurs when the contact area grows to form patches due to the compaction of wear debris trapped between the sliding surfaces. A thin film will continuously form smear and shear, flattened on the sliding surface as the braking progresses as shown in Figure 4.35 e). The composition of this friction film is somewhat akin to that of the ingredients from the friction material and brake disc.

4.5 Effect of Palm Slag Filler Size on the Morphology and Properties of Composite Samples

4.5.1 Morphology of different palm slag sizes in composite samples

The palm slag utilized in this study was crushed and sieved with a standard mesh sieve column on a mechanical shaker and then divided into three (3) ranges of particle sizes. The ranges used in this study are shown in Table 4.4. The SEM micrographs clearly illustrated the irregular shapes and rough surfaces of the crushed palm slag, as well as some porous features. (See Figures 4.36 (a), (b), and (c)).

Table 4.5: Ranges of the particle sizes of the palm slag

Material	Size ranges
Palm slag 1	< 300 µm
Palm slag 2	300 – 600 µm
Palm slag 3	>600 µm – 2 mm

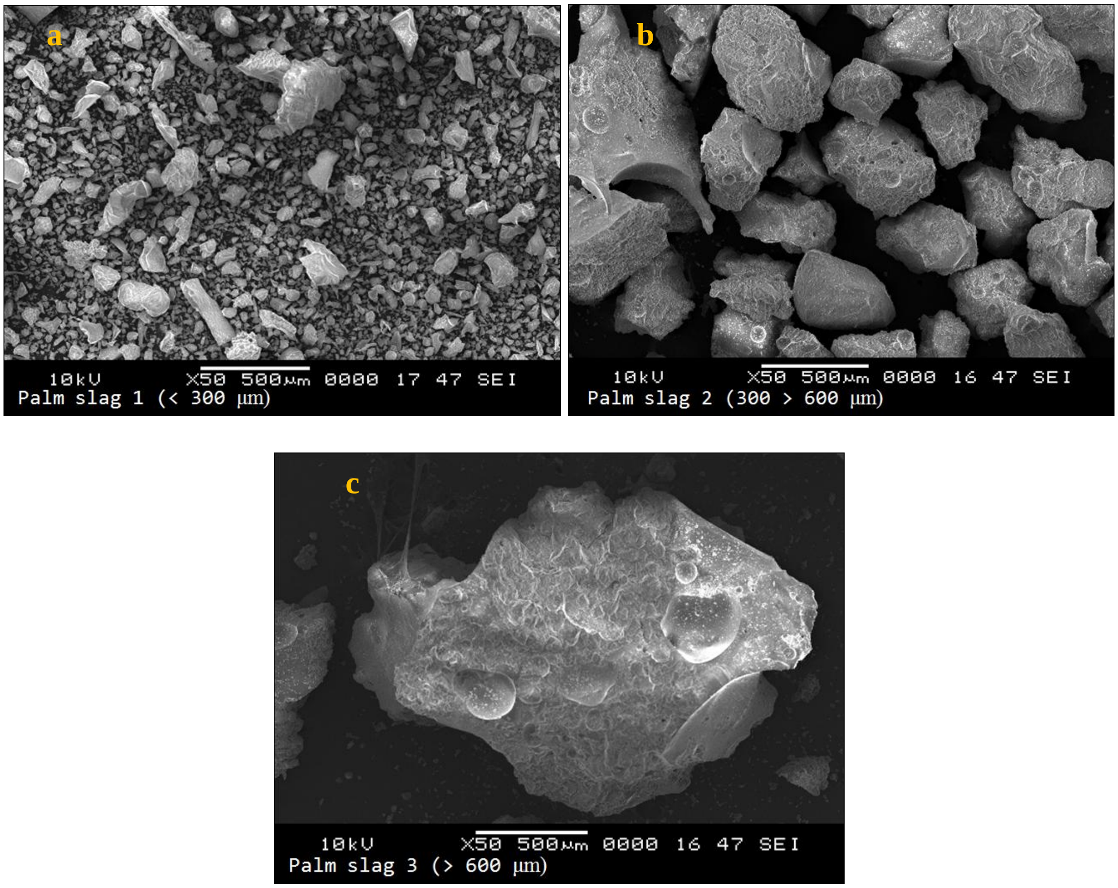

Figure 4.36 : SEM micrograph of (a) palm slag 1 (< 300 µm), (b) palm slag 2 (300-600 µm) and (c) palm slag 3 (> 600 µm-2mm)

Microstructures of the brake pad composites made with the three (3) different particle sizes are shown in Figure 4.37. The figure shows that the palm slag particles and other materials were well distributed in the composites and no obvious agglomeration of a material was evident.

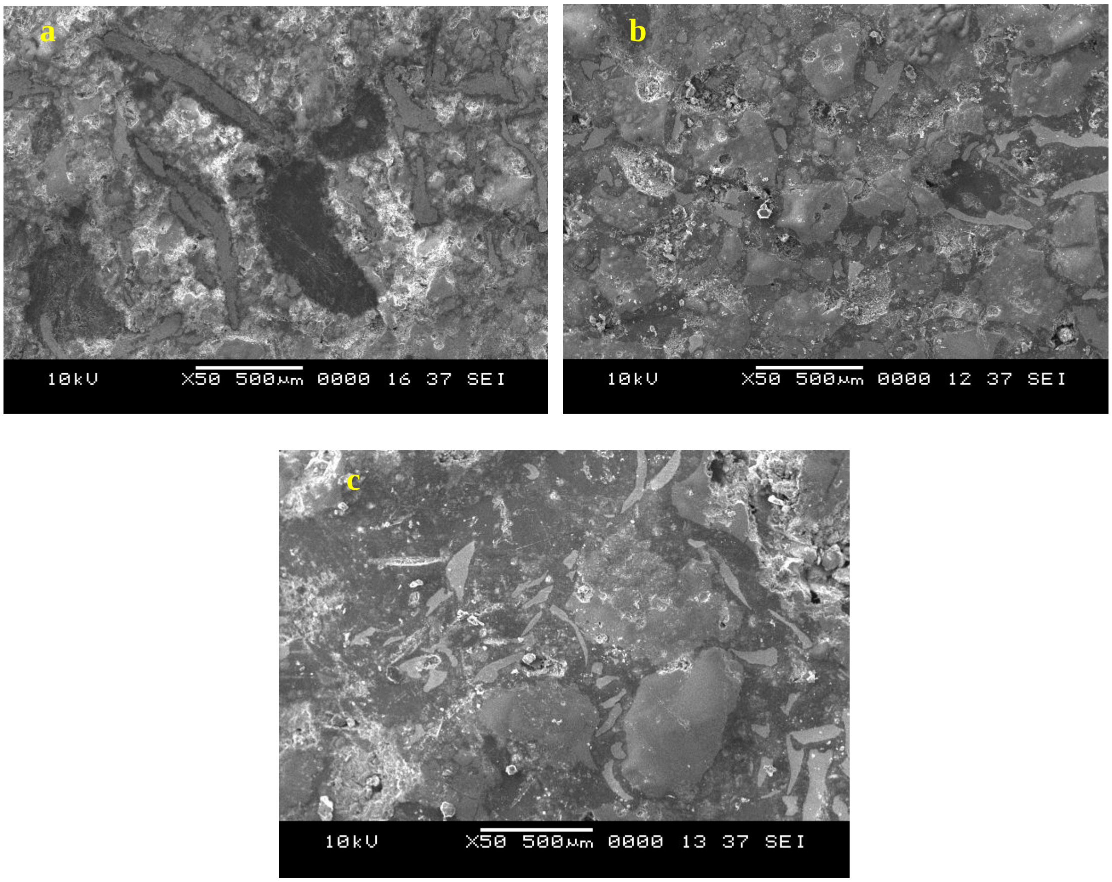

Figure 4.37: SEM micrograph of palm slag composites; a) palm slag 1(< 300 µm), b) palm slag 2 (300-600 µm), c) palm slag 3 (> 600 µm-2mm).

Based on the results of various earlier studies, finer particles seem to contribute to improved properties under the sliding wear condition better than larger particles. For examples, Friedrich (1993) and Xing and Li (2004) confirmed that fine particles of glass and spherical silica produced better properties than their coarser particles. However, the opposite effect was reported by Friedrich (1986), Durand et al. (1995) and Ravi Kumar et al. (2011).

In our palm slag studies, the opposite size effect was observed. Figure 4.38 shows the density of the different palm slag filler size brake pad composites at 60 tons of processing pressure. It can be seen that the palm slag brake pad composite that had the largest particles also had the greatest density, which meant that it was the heaviest brake pad among the three. This observation can be explained by looking at the theoretical arrangement of different sizes of particles. Materials with small particles will put themselves into the spaces between large particles. This situation seems to complement each other. The present of voids will be minimized. Particles in the composite structure will be made more compact. As a result the brake pad composites will have a high density.

This result was supported by fact that particle size distribution was one factor that influenced the density of the powder product during compaction, and bi-modal particle blends can pack to higher densities than mono-sized particles (German, 1994).

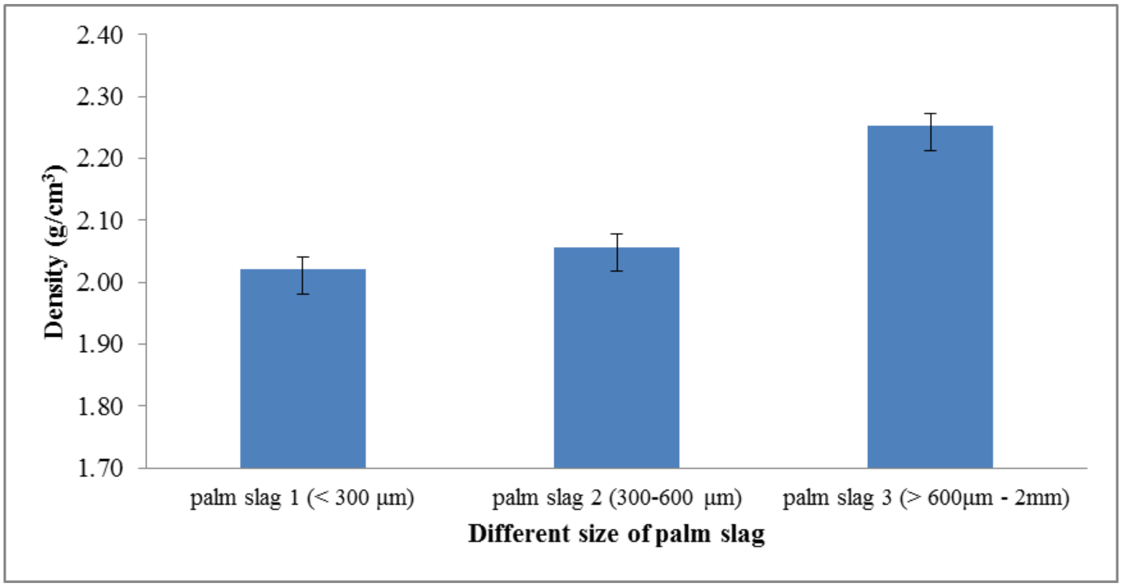

Figure 4.38: Density of palm slag composites prepared with different filler size.

Similar trends also were observed for the mechanical properties, such as hardness and compressive strength. Figures 4.39 and 4.40 show the effect of filler size on the hardness and compressive strength of the brake pad composites. The hardness increased when the particles size of the palm slag increased. By comparing the particle size of palm slag with the particle size of other materials used in this brake pad composite, it clearly was shown that the lager the sizes of the different materials used, the higher the maximum packing density becomes, which tends to improve hardness and compressive strength of the brake pad composite.

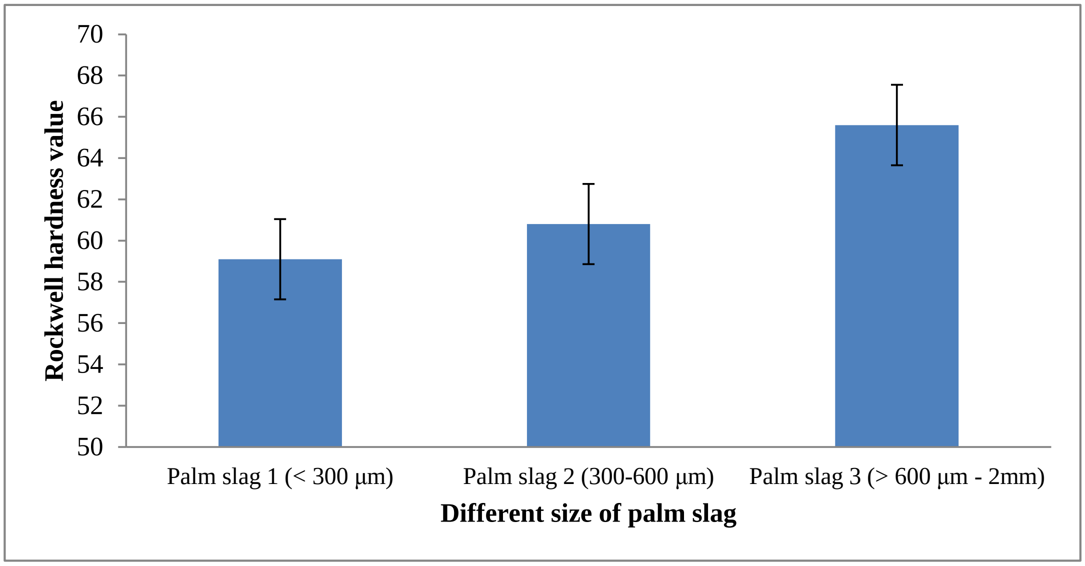

Figure 4.39: Surface hardness of the different sizes of the filler in the palm slag composite samples

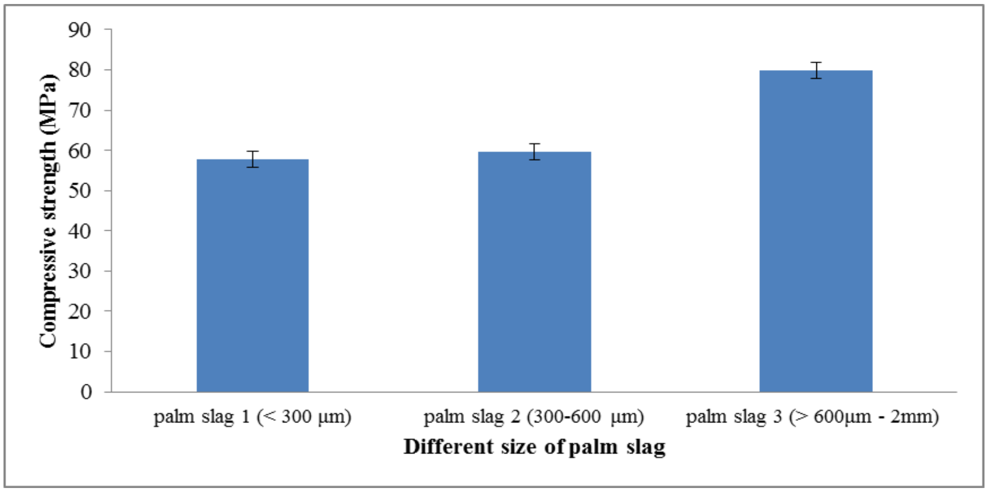

Figure 4.40: Compressive strength of the different size of the filler in the palm slag composites

4.5.2 Effect of the size of the palm slag particles on wear rate

From Figure 4.41, it can be inferred that the particle size also is one of the factors that influences wear properties. As the size of palm slag particles became coarser, the ability to withstand the brake friction becomes higher. This was observed when coarser palm slag particles were used in the brake pad composite, since the wear rate of the composite decreased. Therefore, the wear resistance was greater for the coarser filler particles. This might be due to the fact that the probability for the coarse particles the surface bonding is higher than that of the small particles. As a result the interfacial strength of the coarse particles would be higher than the small particles thereby preventing particle pull out. The small particles had small surface bonding and this factor made the interfacial strength weaker and more susceptible to particle pull out.

The above mentioned observation was supported by the work of Ravi Kumar et al. (2011), and Sudarshan and Surappa (2008) in their studies of aluminum composites reinforced by different particle sizes of fly ash.

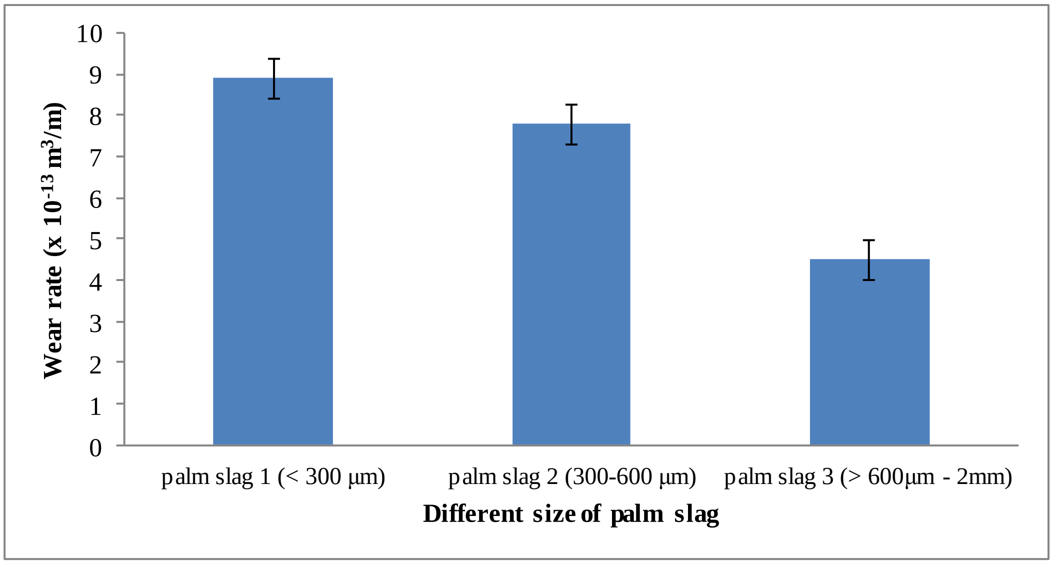

Figure 4.41: Effect of different sizes of palm slag particle on wear rate for a constant braking load of 10 N

4.5.3 Correlation between wear rate and properties

Although some reports have claimed that there is no correlation between wear properties and composite hardness (Lappalainen et al., 1989), other studies have stated that there is a correlation, in fact there is a direct correlation between these properties (Kawai et al.,1998, Chung and Greener, 1990). The finding from this study showed a direct, inverse linear correlation between hardness and wear rate. Figure 4.42 shows that the composites' wear rates decreased as their surface hardness increased. This was due to the mutual correlation factors between compaction, density and hardness. Increased compaction of the materials in the brake pad composite will result in increased density and, consequently increased hardness. A similar correlation was observed between wear rate and compressive strength as shown in Figure 4.43. Both Figures 4.42 and 4.43 shows very good correlations because the data points were very close to the regression line. The R^2 value also confirmed that the values were greater than 0.9.

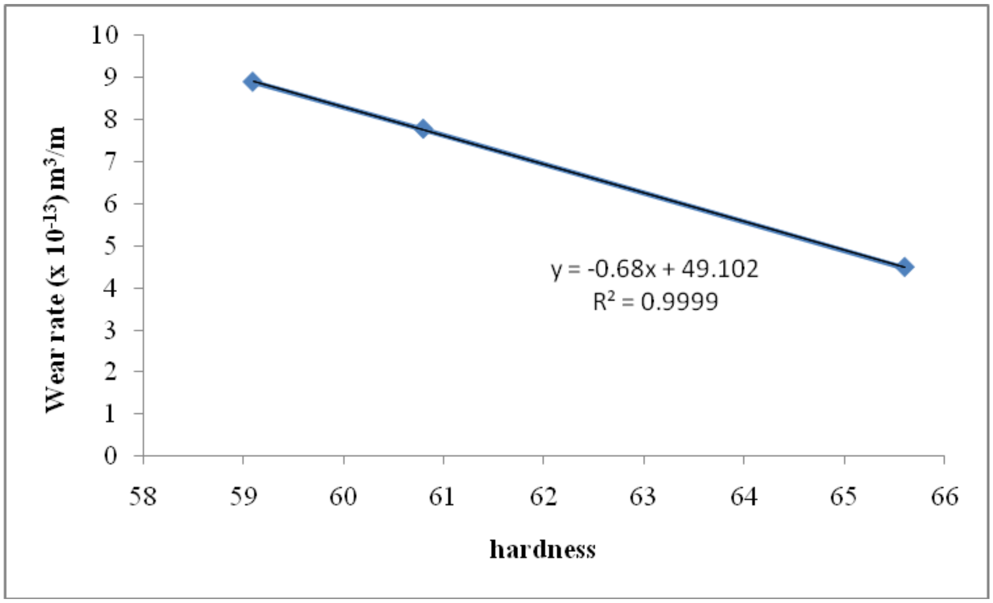

Figure 4.42: Correlation between wear rate and surface hardness.

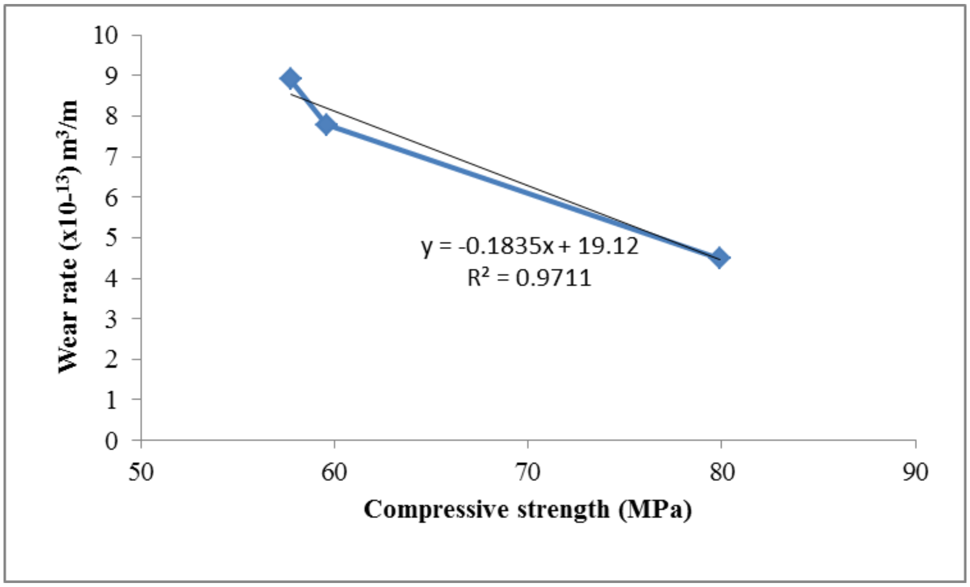

Figure 4.43: Correlation between wear rate and compressive strength.

SEM studies of the worn surface were conducted with JEOL equipment. Figure 4.44, 4.45 and 4.46 were obtained from the worn area of the brake pad composites of palm slag 1, 2 and 3, respectively. It was noted that the mechanism of friction layer formation with grooving, abrasion, adhesion and delamination occurred during the wear test. Figure 4.44, for example, shows that the friction layer continuously formed smear and shear on the sliding surface as the braking progressed. The abrasion wear mechanism was manifested by the presence of a smooth and smear friction layer that exist as third component on the composite surface due to the small particles of most of the materials in the brake pad composite. In addition, small grooves also were observed due to the pull out of small particles.

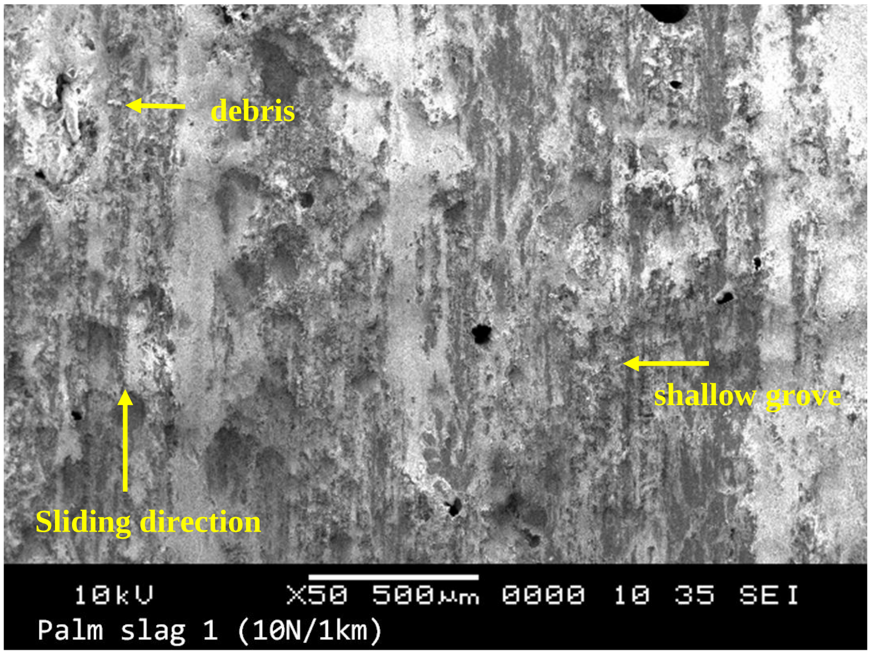

Figure 4.44: Worn surface of palm slag 1 (< 300 µm).

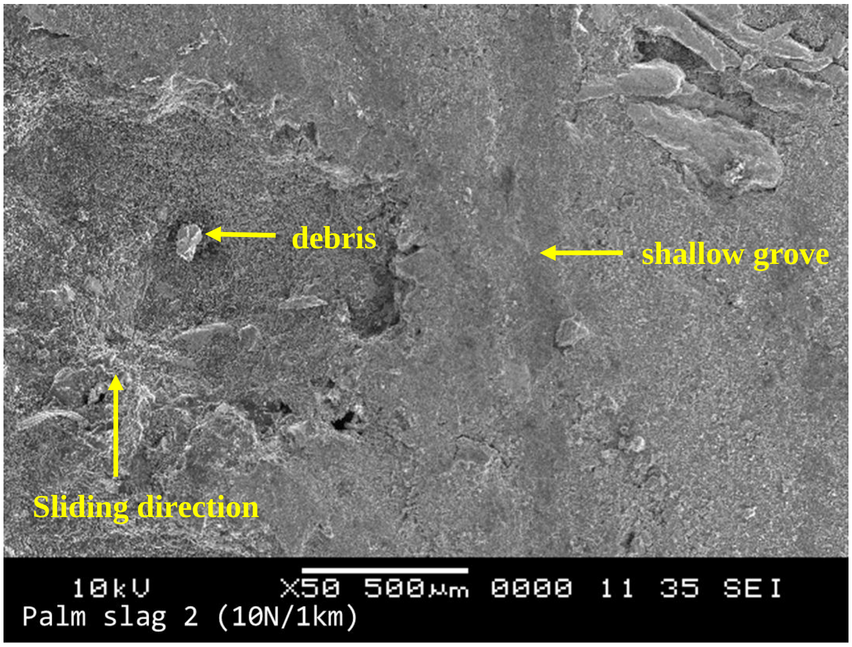

Figure 4.45: Worn surface of palm slag 2 (300 – 600 µm)

Figures 4.45 and 4.46 provide a different perspective from Figure 4.44 in that there was more debris and deep grooves on the friction surface. Small flakes of materials were pulled out from the surface. The larger sizes of the pull-out particles resulted in larger grooves on the surface.

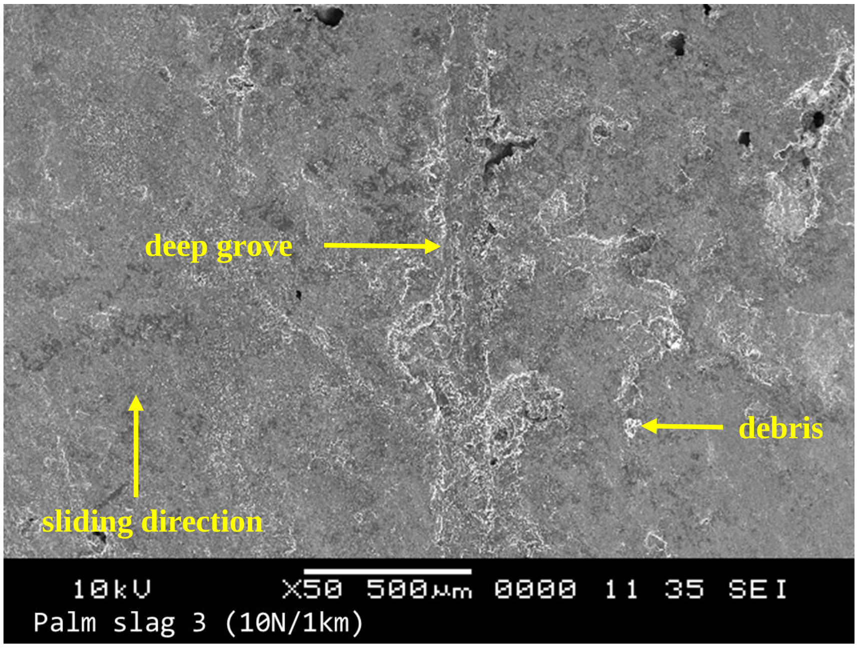

Figure 4.46: Worn surface of palm slag 3 (>600 µm – 2 mm)

4.5.4 Effect of sliding distance on wear rate

Sliding distance was one of the major factors that influence the wear rate of the composite. Figure 4.47 shows the influence of sliding distance on the wear rate for a constant load. It can be seen that the wear rate of the palm slag composite decrease as the sliding distance increased. It also was observed in the early stages of the test that the wear rate of the composite was high resulting in large mass losses. After a certain sliding distance, the wear rate of the composite seemed to become constant, which could be related to the linear increase of mass loss as the sliding distances were increased.

A longer sliding distance allows more time for the compact debris and contact plateaus to form. During the early stage, the rough surfaces of the brake pads rubbed against each other and produced more debris, resulting in high weight loss. After a certain time or distance, the surface becomes smoother because of the formation of the compact debris layer and the formation of contact plateaus, thereby increasing the possible area of contact between the pad and the disc. Further, as the contact area increased and the surface was worn smooth, contact increased. This is believed to result in increased wear resistance which was manifested as the constantly decreasing wear rate, as shown in Figure 4.47.

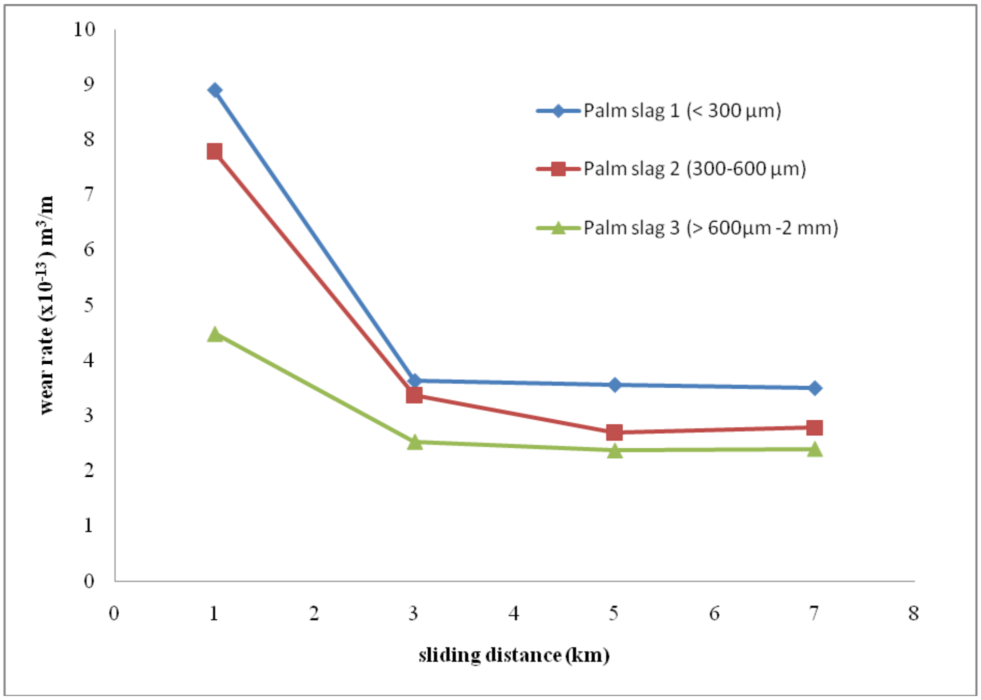

Figure 4.47: Effect of sliding distance on wear rate for the different particle sizes of palm slag at a constant braking load of 10 N

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION FOR FURTHER RESEARCH

5.1 Conclusions

Based on the mechanical properties, wear properties and morphology, this research indicated that palm slag can be used effectively as an alternative to other fillers in brake pad composites. Comparisons with other fillers showed that palm slag has significant potential for becoming an alternative material for use as the filler in brake pad composites. The densities of the palm slag composites also indicated that they were suitable for use in brake pads due to their light weight, even when compared with asbestos.

The major conclusions derived from this study are:

- The thermal characterization of the raw materials was given an evidence of the potential and suitableness of palm slag to become an alternative fillers used in brake pads. Palm slag with phenolic binder was very stable which only 18-20% mass loss occurring in the temperature range of 100 – 850^{o}C
- The moulding pressures have a significant effect on the properties of the brake pad composite products. Composites with higher density and hardness were produced by higher moulding pressures.

- Even though higher moulding pressures produced higher density and hardness, it was observed that the compressive strength and modulus reached a limit point after which they tended to remain constant.
- Wear rate decreased from 2.02 to 8.9 $m^2/m \times 10^{-13}$ as moulding pressure increased from 1 to 60 tons. The wear rate of palm slag composite sample, 8.9 $m^2/m \times 10^{-13}$ at the highest moluding pressures, 60 tons was comparable to that commercial asbestos brake pad composite.
- The trend of opposite size effect was observed, with particle size exhibiting an inverse relationship with the mechanical properties of the brake pad composites. The largest particle size of palm slag filler in composite; 600µm - 2mm, provided the highest value of density, hardness and compressive strength. The larger the particle of palm slag also show the increased in the wear properties.
- These studies also showed that the higher the particle size of palm slag filler the lower the wear rate of the composite will be. There also was an inverse correlation between hardness and compressive strength of the brake pad composites with the wear rate. The higher the hardness and compressive strength, the lower the wear rate, which means that the composite that have higher hardness and compressive strength will give higher wear resistance.
- Morphological studies on worn surfaces showed that the major wear mechanisms throughout the braking process was abrasion, adhesion, grooving and delamination. It also showed that the friction layer was discontinuous and did not cover the whole surface. The sizes of the grooves depended on the sizes of the pull-out particles.

- The correlation between composite properties and its wear rates were very good with the R2 values were greater than 0.9, indicating more than 90% correlation accuracy.
- In general, the trend of wear rate with sliding distance tended to become constant and linear after the initial stage.

Possible reasons for all of the above mentioned conclusions are the compaction behaviour of the composite and the interfacial strength between the particles and the matrix. The larger palm slag filler particles provide a better opportunity for the composite to become more compact, and more small particles were pulled out from the matrix because the interfacial strength between the particles and matrix became weak due to the small surface bonding area.

5.2 Recommendations for further research

The development and validation of a friction material involve a significant amount of testing in the laboratory and on the road. On-road brake tests with real-world conditions normally are the final tests that are performed to evaluate and validate the formulation. Thus, vehicle testing on a test track is the ultimate measure for the overall assessment of the performance of the brake pad composites. Further investigation of the performance and wear of the developed brake pads should be conducted for actual real-world road conditions.

Further investigation also is needed to establish the effects of load, braking distance, and braking time on wear properties.

5.3 The Future

Expect existing compounds to continue to evolve with ever-wider operating temperature ranges and longer lives. Increased use of improved NAO ceramic pads, true ceramic pads, and other exotics as costs come down will be given more attention. On the street, increasingly sophisticated ABS computers will permit more aggressive pad materials without the traditional dust and wear penalties previously associated with them. Phenol-formaldehyde, the current bonding resin for pad materials, may be superseded by silicon-based resins with increased high-temperature stability. Regenerative braking-wherein brake energy is used to help recharge the electrical system on electric cars or hybrids-may cause radical changes in future brake systems as manufacturers pull out all the stops in a quest to perfect the longest-lasting, best-stopping, widest-temperature compounds. Developments in the use of waste materials, new friction materials and new binders will be the focus.

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APPENDIX

- **Patent Search Letter**
- **Malaysian Patent Filed Letter**
- **Front Page for Patent Specification PI No. 2012004523**
- **Special Award Certificate**
- **Related Papers –SCORPUS**