USE OF FLY ASH AS ECO-FRIENDLY FILLER IN SYNTHETIC RUBBER FOR
TIRE APPLICATIONS

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In the Fulfillment

Of the Requirements for the Degree

Master of Science

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May, 2016

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Thesis

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ABSTRACT

In this study, the relationship between an eco-friendly filler, fly ash, and the properties of Styrene-Butadiene Rubber (SBR) - based compounds was investigated. Rubber compounds were produced by internal mixer and curing characteristics were evaluated. The total content of filler was constant and the content of fly ash increased from 0 to 10 phr. In the evaluation of the rubber compounds, the main focus was the mechanical properties and adhesion of the SBR compounds. Adhesion between these compounds and steel wire reinforcement was measured for assessing efficacy of adding fly ash to the rubber compounds in tire applications. There were two stages of this program: the first stage involved selecting the filler which could improve the mechanical properties (elongation at break, tensile strength, modulus at 100% strain and 2% strain level) of rubber compounds; the next stage involved combining precipitated silica with fly ash to improve the properties of rubber compounds. In order to gain better properties, ball mill treatment was used to change the morphology of the particles of fly ash by reduction to smaller size. The comparisons of untreated rubber compounds, ball mill treated rubber compounds, and rubber compounds containing different fillers were accomplished subsequently. In the result, the rubber compounds contained precipitated silica, carbon black and fly ash filler exhibited higher tensile strength, elongation at break, and adhesion and attributed to effective

filler dispersion as well as the reinforcing effect of silica. These conclusions were supported by the scanning electron microscopy (SEM) and swelling tests.

Key words: rubber compounds, fly ash, precipitated silica, carbon black, tensile test, hardness test, crosslink density, filler dispersion.

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CHAPTER I

INTRODUCTION

1.1. Objectives

The objectives of this thesis were the following.

1. To compare the influence of four different kinds of fly ash on the mechanical properties of rubber.
2. To find the optimized combination of rubber fillers for improving the mechanical properties and adhesion of rubber compounds.
3. To increase the reinforcing capability of fly ash by using ball mill treatment.
4. To identify the physical and chemical mechanisms for any rubber composite properties improved by fly ash filler addition.

1.2. Background

In this part, the background of the experimental materials, methods of research and scientific achievements were briefly reviewed. In addition, the relations between background and this project were also introduced.

1.2.1. Structure of tire

World-wide increase in demand for automotive ownership has resulted in an increasing market demand for pneumatic tires. Pneumatic tires are composed of external surface, called tread, under which resides a reinforcement belt, which is consists of a number of steel cords. Tread is the part which directly contacts the road surface, and thus, needs to be strong enough to avoid cracks or tears. In addition, reducing rolling resistance is very important for tread, because rolling resistance is related to fuel consumption with higher rolling resistance resulting in higher energy loss. Tread is made up of a rubber compound. There are two main types of rubber, synthetic rubber and natural rubber. Natural rubber is collected from mature rubber trees which have to be planted in damp and hot environments. Therefore, the production of natural rubber is limited and cannot satisfy the overall market need; this is why synthetic rubber was developed during World War II. Styrene Butadiene Rubber (SBR) is a kind of synthetic rubber which is polymerized by using the

monomers, styrene and butadiene. SBR has become one of the most important synthetic rubbers in the world because of its huge production.^[1] In tire applications, SBR rubber exhibits good abrasion resistance and stability, which is the reason why SBR rubber is usually used in tire tread.^[2] In the middle of the last century, the synthesis of Ziegler-Natta catalyst made it possible to produce Solution SBR (SSBR).^[3] SSBN is manufactured in hydrocarbon solution, with initiators by living polymerization which produces high molecular weight with narrow distribution. Because of its high molecular weight, the viscosity of SSBR is high, causing some difficulty in its processing. There are several methods to solve this problem; for example, adding branching agents to make branched molecular structure, and/or blending SBR with natural rubber to extend its properties. As another method in this research, treated distillate aromatic extract (TDAE) oil was added in order to increase the process ability. TDAE oil is a kind of product from crude oil, “treated” means further extraction of distillate aromatic extract oil.

1.2.2. Carbon black

Rubber compound fillers typically have multipurposes. Some fillers like carbon black and silica are used to improve the properties of rubber compounds by acting as reinforcement agent, on the other hand, some fillers such as calcium carbonates cannot increase the properties of rubber compounds, but are still used to reduce the

cost of the tire.. Absence of any fillers in the rubber compound, would result in soft and easy to break rubber material. Filler addition typically results in stiffer rubber resistant to abrasion and deformation. Among all kinds of rubber fillers, carbon black is the most traditional and commonly used reinforcing filler. Carbon black is collected from the carbon black oil furnace process ^[4]. There are various kinds of carbon black reactors, such as horizontal or vertical, rectangular or cylinder, etc. The internal atmosphere of carbon black reactors is isolated by a heat-resistant material in order to prevent the loss of heat. In this process, liquid fuel is used as raw material to produce carbon black. In the carbon black reactor, flame is produced by the fuel burner and natural gas or liquid fuels are used to produce the flame. Hot air is added into the flame to assist combustion. The temperature of the flame is about 1500°C depending on the requirements of the product. When the feedstock is preheated to about 250°C, it is delivered into the flame through the feedstock nozzle. Usually, the feedstock consists of hydrocarbons, such as aromatic compounds. The feedstock is often collected from the gasoline refineries. After the incomplete combustion of the raw material, carbon black can be formed at 1400°C. At this time, carbon black particles fly at high speed from flame zone to a quench zone where water is used to cool the carbon black down to 650°C. After that, carbon black and gas would pass through the heat exchanger to heat the feedstock, and they pass through primary and secondary filters to be collected as carbon black accompanied by separate gases. These gases can subsequently be used to heat the dryer in the later process ^[3].

The morphology of carbon black has been investigated for many years. Charles R. Herd, et al.,^[5] reported four models to describe different types of carbon black aggregation in Spheroidal, Ellipsoidal, Linear and Branched forms. The Spheroidal model represents the aggregation form of thermal black obtained from natural gas. Its particle size is large, and it has a low scale of aggregation. The ratio of the carbon element in thermal black is high, so thermal black has a purer form of the carbon elements than other kinds of carbon black. The other three types represent aggregation structures of different concentrations.

With the advance of experimental technology, scientists were able to observe the aggregation structure of carbon black directly. For example, the carbon black N234 pictures taken by transmission electron microscopy (TEM), revealing that the structure of N234 aggregation belongs to type 4 in Charles R. Herd's theory^{[5][6]}.

In the 2000 "Annual Book of ASTM Standards, Volume 9.01", carbon black classification was made by the standard D1765. Four-character nomenclature system was used to identify carbon blacks used for rubber fillers, as suggested by the ASTM D24 Committee on Carbon Black^[3]. In this system, the first letter represented the influence of carbon black on the cure rate of a typical rubber compound with that particular carbon black as filler. The second character in the nomenclature system indicated the average surface area of the carbon black, which was measured by using nitrogen surface area method^[3]. The third and fourth characters were usually from 0 to 4. They were arbitrarily assigned digits. Take the example of N234; the first letter

“N” meant that this carbon black does not have specific influence on the cure rate of the rubber compound. The second character “2” indicated that the surface area is about 100 to 120 m²/g (see Table 1-1) as given by the D1765 standard ^[3].

Table 1-1. The relations between Second Character and Average N₂ Surface Area in the carbon black nomenclature system. ^[3]

Second Character	Average N ₂ Surface Area m ² /g
0	>150
1	121 to 150
2	100 to 120
3	70 to 79
4	50 to 69
5	40 to 49
6	33 to 39
7	21 to 32
8	11 to 20
9	0 to 10

As a kind of traditional reinforcing filler, carbon black has a great impact on the curing process and mechanical properties of rubber compounds. Carbon black has an influence on every aspect of rubber production, such as processing, vulcanization and properties. In the processing stage, carbon black significantly increases the viscosity of the rubber compounds. It is because carbon black has a hydrodynamic effect to reduce the volume fraction of the flow medium. When the rubber compound is in mixing or other similar conditions of shear flow, hydrodynamic effect would lead to increased shear strain, therefore, the viscosity would increase. After mixing, the

dispersion of carbon black in the rubber compound is also very important. The procedure of dispersion was divided into four steps, incorporation, deagglomeration, distribution and dispersion^[3]. In the first step, rubber molecules encapsulated the agglomerate of carbon black. In the next step, the size of the carbon black agglomerate was reduced under shear force and the carbon black distributed in the rubber matrix during mixing. During the final step, the filler network was formed by its dispersion in the rubber matrix. During vulcanization, carbon black can act as a catalyst, W. A. Wampler et al.,^[7] reported that carbon black had an influence on the cure rate when the vulcanization starts. For example, carbon black could significantly increase the cure rate for solution SBR and natural rubber. Some scientists reported that using carbon black as filler dramatically increased the tensile strength of SBR compounds^[8]. The mechanism of the reinforcement of carbon black has been investigated for many years and many models and theories have been reported. An interface model was reported by Yoshihide, Fukahori^[9]. Bond rubber is a part of the rubber matrix which directly contacts the filler. On the surface of carbon black, there were two layers of bond rubber. The first layer was called Glassy Hard (GH) - phase, which indicated that the molecules in this phase was constrained and fixed by the carbon black. The second layer was called Sticky Hard (SH) – phase. The molecule of rubber was relatively constrained by the carbon black, because the distance between this layer and the surface of carbon black was relatively far, compared to the GH-phase. In the SH-phase, the arrangement of molecules was

considerably loose, compared with the molecules in GH-phase, which meant molecules in SH-phase would be able to slide and deform.

Yoshihide, Fukahori, ^[9] proposed a model to illustrate why modulus and tensile strength of rubber compounds are increased by adding carbon black. In this model, rubber was under large strain, and the molecules in SH-phase oriented and extended in the direction of stretching. Compared with other molecules within the rubber matrix, the molecule in SH-phase was more oriented, and as a result, the orientation improved the tensile strength and modulus of the compound.

The production and use of carbon black may cause environmental problems. Annually, the production of carbon black is about 10 million tons ^[10]. Carbon dioxide is released into the atmosphere during the production of carbon black. Therefore, carbon black contributes to global warming. In order solve this problem, various methods were invented mainly in two different directions. One direction involving a new process to replace the old method of producing carbon black. For example, S. Rodat et al., ^[11] reported that carbon black can be produced by solar methane dissociation. The other direction involved replacing the carbon black with other eco-friendly fillers such as in this research, which involved partial replacement of the carbon black with silica and fly ash.

1.2.3. Silica

Besides carbon black, non-black fillers have been used in rubber industries for many years. The main non-black fillers are shown in Table 1-2 ^[12]. In order to control carbon emission, tire industries want to reduce the use of carbon black as rubber filler without decreasing the properties of tire.

Table 1-2. U.S rubber industry consumption of non-black fillers

Fillers	Fraction of total consumption
clays	54%
Silica and silicates	15%
Calcium carbonates	27%
other	4%

Among the non-black fillers, most of the calcium carbonates and clays are made from natural minerals, so their price is very cheap. The purpose of using these kinds of fillers is reducing the cost of the product rather than improving the tire properties. As for silica and silicates, they are synthetic fillers; in other words, their cost is more than those for natural materials. Some companies produced silica through the acid precipitation of sodium silicate ^[13]. In this process, sodium silicate and sulphuric acid were mixed, initiating a condensation reaction of silicic acid to produce an oligomer. The oligomers gradually grow. Finally, small particles form and phase separate. In general, silica is used for improving the properties of rubber

compounds and plays an important role as rubber filler, because the color of silica is white, black is not the only choice of the color of rubber product.

The reason why fillers can reinforce rubber compounds is complex. There are many theories, which use chemical and physical knowledge to explain the phenomenon of reinforcement. The main composition of precipitated silica is hydrated silica ($\text{SiO}_2 + \text{H}_2\text{O}$), which often appears in the form of silanol group ($\equiv\text{Si}-\text{OH}$). During mixing silanol groups react with rubber molecules because of the presence of hydrogen ion on silanol groups. A. Ansarifar et al.,^[14] reported that adding silica into rubber compounds can improve mechanical properties such as hardness, tensile strength and tearing energy. In addition, silica has a great influence on the protection of the environment due to lower CO_2 emission during its production as well as in its capacity to reduce rolling resistance in tires. Due to increasing environmental concerns, more and more tire companies are attempting to reduce rolling resistance and improve energy efficiency of tires. In these years, many scientists have found that the use of silica fillers can improve mechanical properties of rubber compounds and effectively reduce the rolling resistance in tires. For instance, P. J. Martin, P. Brown et al.,^[15] reported that when silica was used as filler in epoxidized natural rubber, lower rolling resistance and higher wet and ice traction were achieved. Silica also plays an important role in this research with mechanical and dynamic behaviors of silica rubber investigated as a potential filler in combination with carbon black as well as with fly ash.

1.2.4. Fly ash

Fly ash is a byproduct of the power generation industries neglected for many years as a potential filler in many different commercial products including the rubber compounds. In power generation, especially with thermal power stations, coal is generally used as the fossil fuel to combust and generate electricity. Fly ash is produced during this process. Before combustion in a boiler, coal is smashed into coal powder for effective combustion. In the boiler, the temperature during combustion is about 1500 degrees Celsius. After combustion, the residual particles are cooled down the solid particles are collected, and the inorganic part of these solid particles consist of fly ash^[16]. Annually, a large amount of fly ash is produced from the power stations all over the world. If fly ash is separated by the air and the wind, it will disperse everywhere. In that way, a serious air pollution problem would appear and the risk of getting pulmonary diseases would increase. To solve this problem, solutions have been proposed, with one of the main directions being the use of clean energy, such as solar energy, hydro energy and wind energy to replace the combustion of coal. However, for now, there are still some difficulties in disseminating clean energy. Take the example of solar energy; there are mainly three problems, the first one is the expense. In general, building and repairing a solar power station is quite expensive compare to the traditional power station if the scale is large. The second problem is efficiency. We all know that every day, there is abundant solar light which directly

irradiates to the ground surface of earth, but only limited but necessarily large surface areas can be utilized to generate solar-based electricity. This means that electricity generated by the solar power station cannot satisfy the needs of the society. The third problem is the production rate of the power station which is typically not stable when producing clean energy by using wind, water or sun light. This is because these power elements have strong relationships with the climate, which means that different amounts of power would be produced at different times. In order to solve these problems, Eric Hu et al.,^[17] reported that using solar energy instead of extracted energy to heat the feed water at power stations can improve their energy efficiency. Another direction is reusing the fly ash to prevent its pollution. Under this consideration, fly ash has been used for many applications. In construction industry, the fly ash is often used to produce concrete to improve its strength and permeation. Rafat Siddique et al.,^[18] reported that fly ash can be used as a part of self-compacting concrete, which has good deformability and segregation resistance. Isamu Yoshitake et al.,^[19] reported that fly ash can be used to be a part of recyclable concrete pavement. They report that recyclable concrete pavement containing high volume fraction of fly ash has similar flexural strength, compared to those containing low volume fraction of fly ash. Fly ash is also used as filler in rubber products. The main composition of the fly ash is silica. Our discussions above revealed that silica is also an important reinforcement filler in rubber industry. Therefore, just like the carbon black, fly ash can also be used as a reinforcing filler to improve the mechanical

properties of rubber compounds, as investigated over many years^{[20] [21] [22] [23] [24]}. Bahruddin et al.,^[20] reported that palm based fly ash can be used to improve the mechanical properties of thermoplastic vulcanizate. N. Sombatsompop, et al.,^[21] reported that when the content of filler is relatively small in the rubber compounds the reinforcing effect of fly ash was similar to the reinforcing effect of silica. S. Thongsang, et al.,^[22] reported that when fly ash was used as rubber filler, silane coupling agents could be used to modify its surfaces. Their results showed that silane treated fly ash would improve cure characteristics and mechanical properties. Fly ash can be combined with high fraction of precipitated silica as rubber filler, producing rubber compounds with optimal mechanical properties^[23]. Thomas K. Paul, et al.,^[24] reported that fly ash can increase the mechanical properties of styrene butadiene rubber. It was observed that fly ash has similar reinforcing effect in increasing rubber compound elongation, modulus and hardness when it was compared with carbon black filled styrene butadiene rubber. In this research, fly ash was investigated as a secondary filler along with carbon black and silica for possible improvements in mechanical properties of rubber compounds.

1.2.5. Hybrid fillers

From the above, we deduce that carbon black clearly plays an important role in reinforcing rubber compounds, while possibly causing some environmental

problems. Additionally, we also deduce that the use of silica fillers help in reducing rolling resistance. However, silica without any surface treatment cannot be used as single filler in rubber compounds because it produces poor mechanical properties. For example, the rubber compound containing untreated silica exhibited lower tensile strength and modulus at 100% strain, when it was compared to the rubber compound which used silane treated silica as filler^[25]. As a result, some scientists and companies have tried to use hybrid filler recipes combining several kinds of fillers in rubber compounds. Wengjiang Feng, et al.,^[26] tried to partially replace carbon black fillers with precipitated silica without silane treatment. Their results showed that filler networking was weakened if a small amount of carbon black was replaced by silica. This was because filler-filler interactions were formed by hydrodynamic effect, with this effect on different fillers being weaker than on the same fillers. Thus, when the silica content was further increased the filler network was regenerated. This was because the silanol group is more and the silica is less compatible with rubber molecules in comparison to carbon black. In dynamic mechanical tests, Wengjiang Feng, et al.,^[26] also found that lower rolling resistance could be achieved by partially replacing the carbon black with a small amount of silica. This illustrated that filler network was weak and the energy loss during the destruction of filler network was reduced. Silica treated by silane coupling agent was also investigated for the application involving hybrid fillers. N. Rattanasom, et al.,^[27] reported that hybrid filler of carbon black and silane modified silica could reduce rolling resistance and

maintain tensile strength, when it was compared to the rubber compound which only used carbon black as filler. The explanation they provided was that blending of silica and carbon black would provide better filler dispersion and weak filler network. In order to reduce rolling resistance and maintain mechanical properties of rubber compounds, carbon–silica dual phase filler (CSDPF) was thus proposed. CSDPF is produced through a co-fuming process, in which silicon and carbon black are mixed to produce this unique filler. CSDPF has two phases, carbon black phase and silica phase, Meng-Jiao Wang, et al.,^[28] reported that CSDPF had higher rubber-filler interactions and lower filler-filler interactions when it was compared to carbon black and silica. Except for traditional fillers, some scientists reported that using the blends of low cost non-black fillers can also provide reinforcing effect on rubber compounds. For example, V. Raji Vijay, et al.,^[29] reported that the blends of silica and modified kaolin could improve the processing properties and mechanical properties of rubber compounds. In their research, they found that sodium salt of rubber seed oil could be used to modify kaolin while partially replacing silica with modified kaolin would increase filler-rubber interactions.

1.2.6. Adhesion

In general, the tire thread which consists of rubber compound must contact with the belt layer which is typically made up with steel cords, to improve the strength of

tires. Therefore, strong interaction or adhesion is required between the steel cord and the rubber compound. In the beginning, the method people used to improve adhesion involved physical attachments and bonding with ebonite. But, physical attachments were weak and ebonite began to fail even at moderate temperatures generated during tire operation. Then, in the middle of 18th century, the use of brass layer as interface between rubber and steel cord was invented to improve adhesion. After that, in the beginning of the last century, plating a layer of brass on the steel cord was commercialized^[30]. Thus, the use of brass layer has been one of the most traditional methods for increasing adhesion between the steel cord and the rubber compounds in tire industries. In addition, many other methods were also invented^{[30] [31] [32]}. For example, J. Giridhar, et al.,^[31] reported that adding NiZn and ZnCo would improve the corrosion resistance and aged adhesion retention properties. David A. Boscott, et al.,^[32] reported that partial epoxidation of double bonds within the rubber molecules would improve adhesion between the rubber and the brass layer. The brass layer is coated over the surface of the steel cord. N. A. Darwish, et al.,^[30] reported on using innovative adhesion promoters to enhance the adhesion between the natural rubber and brass-coated steel cords.

The formation of an interface between the rubber and brass-coated steel cords has been investigated for many years^{[33] [34] [35] [36] [37]}. The adhesion mechanism was divided into four stages. The first stage involved the formation of intermediate products with the use of accelerators^[38]. In other words, adhesion between the rubber

and the steel cords was initiated after the formation of active intermediate products, and by the reaction between the accelerator and the double bonds in the rubber molecules. Cyclohexyl benzothiazole sulphenamide (CBS) was typically used as the accelerator. CBS reacted with double bonds to produce mercaptobenzothiazole (MBT), which acted as the catalyst in decomposition of the CBS. Then mercaptobenzothiazole sulphenamide (MBTS) was produced from the reaction between CBS and MBT. MBTS will react with ZnO/S_8 to form the active sulphurating species.

In the second stage the accelerator fragments were absorbed on the surface of the steel cord and the stearic acid dissolved some zinc oxide on the surface of the brass layer^[38]. Then, MBTS or MTS was absorbed on the surface of the steel cords to form complexes.

During the third stage sulphur was inserted into the accelerator fragments and metal-sulphur bonds were activated to react with ZnO/S_8 to form a chelate^[38]. The result was that sulphur was inserted between the accelerator and the steel cord and X-S_y -steel cords complex was formed. X was a part of the accelerator.

In the fourth stage the X-S_y -steel cords complex decomposed and Cu_xS grows^[38]. The complex which was produced in the third stage breaks into two parts; one part was metal-Sulphur bond which connected to the surface of the steel cord, and the other part is $\text{S}_{y-1}\text{—X}$, which was an active radical for the crosslinking reaction of rubber molecules. In addition, copper was diffused to the surface of the steel cord

and contacted with the sulphur atoms on the surface. At this stage, Cu_xS is formed.

After that, Cu_xS would kept growing until the accelerator runs out. Then, rubber molecules would be trapped by this structure, crosslinking with sulphur atoms in Cu_xS , as a result. Thus the interaction (adhesion) between the rubber and the brass layer was formed.

After vulcanization, the crosslinking reaction between the rubber molecules and Cu_xS was finished, with rubber having established physical and chemical interactions with the brass layer ^[34]. The filler in the rubber compounds also had a great influence on the adhesion between the rubber and brass plated steel cord. Van-ooij et al ^[39] reported that silica could improve the adhesion between the steel cord and the rubber compounds, due to changing the content ratio of sulfur and copper. Silica reduces the content of sulfur and increases the Cu content in the adhesion layers, because of the anionic character of precipitated silica.

1.2.7. Ball mill treatment

Ball milling is commonly used as a method to improve the reinforcing effect of fillers. In general, ball mill treatment is used to reduce the particle size of filler and change the morphology of the filler particle. F.M. Mat Suki et al., ^[40] reported that when ball mill treated sago starch was used as a filler in natural rubber latex film, the mechanical properties of sago starch filled natural rubber latex was improved.

The reason is good filler dispersion and small particle size of sago starch. Siti Nadzirah Abdul Muttalib et al.,^[41] reported that ball mill treatment would improve the dispersion of attapulgite in the natural rubber/ attapulgite composites, thus increasing the tensile strength and the crosslink density of the resulting compound. In this research, the particle size and morphology of fly ash were changed by ball milling. The influence of the ball mill treatment on the mechanical properties and adhesion of SBR composites was thus investigated.

CHAPTER II

EXPERIMENTS, CALCULATIONS

2.1. Experimental Materials

In this project, the main experimental materials were rubber, fly ash, other fillers and steel cords. The providers and composition of experimental materials were shown in this part.

2.1.1. Styrene butadiene rubber

Rubber used in this research is styrene butadiene rubber which was provided by the Lanxess Elastomers Company (Pittsburgh, PA), under the name BUNA VSL 5025-2 HM. The composition data published by the Lanxess Elastomers Company (Pittsburgh, PA) is shown in the Table 2-1.

Table 2-1. The composition of SBR ^[42].

Inspection method/ characteristic	Result	Unit
MO-AQ 254 LAB Vinyl content	50	% by weight
MO-AQ 255 LAB Volatile matter	Max. 0.75	% by weight
MO-AQ 246 LAB Oil content	27.3	% by weight
MO-AQ 243 LAB Styrene content UV	25	% by weight

2.1.2. Fly ash

We used four different kinds of fly ash in our experiments. Their names are Class F, Micron3, Pv14A and Pv20A, as provided by the Boral Co. (Canton, Georgia). The main differences among of these four kinds of fly ash are their chemical compositions and their particle size. The Boral Company (Canton, Georgia) has given the chemical composition data as shown in Table 2-2.

Table 2-2. Chemical composition of fly ash.

Ingredient (%)	Recipe	Class F	Micron 3	PV14A	PV20A
Silica	SiO ₂	65.71	52.27	56.2	35.87
Aluminum Oxide	Al ₂ O ₃	17.66	26.33	19.7	18.58
Iron(III) Oxide	Fe ₂ O ₃	2.57	4.20	4.5	6.97
Calcium Oxide	CaO	5.55	9.20	12.2	25.11
Magnesium Oxide	MgO	0.62	2.25	2.7	5.69
Sulfur Trioxide	SO ₃	0.31	1.32	0.48	1.75
Sodium Oxide	Na ₂ O	4.06	0.34	0.82	1.64
Potassium Oxide	K ₂ O	2.13	1.10	0.85	0.47

2.1.3. Other fillers

Other than the fly ash, two additional kinds of fillers are also used in this research. One is carbon black, N234, and the other is precipitated silica, Zeopol[®] 8745, provided by J.M. Huber Corporation (Edison, NJ). The composition of precipitated silica is shown in Table 2-3 with its typical properties shown in Table 2-4.

Table 2-3. Composition of silica ^[43].

Components	Weight fraction (%)
Synthetic amorphous silica	100

Table 2-4. Typical properties of silica ^[44]

Properties	Typical Values
Moisture (%)	5.5
pH	7
Density (kg/m ³)	200
Surface Area B.E.T (m ² /g)	180
Form	Granules

2.1.4. Steel cords

The steel cord in this research is 0.25+6+12x0.225HT. According to the nomenclature system ^[45] for steel cords, 0.25 means that the innermost layer contains only one strand and one filament, and the nominal diameter of the filament is 0.25 mm. The number 6 refers to the intermediate layer containing one strand and six filaments. The nominal diameter of every filament in the intermediate layer and the outer layer is 0.25 mm. The 12x0.225 designation means that the outer layer contains one strand and twelve filaments. The nominal diameter of every filament in this layer is 0.225 mm. The letters, “HT” refers to this steel cord having high tensile strength. Figure 2-1 shows the cross section structure for the steel cord. Properties of the steel cord provided by the supplier (Bekaert Company, Kortrijk, Belgium) are shown in Table 2-5 ^[46].

Figure 2-1 The cross section of steel cord.

Table 2-5. Parameters and properties of steel cord.

Test	Unit	Result
Cord diameter	mm	1.144
Lay length of intermediate layer	mm	7.48
Lay length of outer layer	mm	16.27
Linear density	g/m	6.173
Cord breaking strength	N	2323
Cord elongation at break	%	2.38
Cu content	%	63.52
Mass of brass	g/kg	4.02

2.2. Experimental methods

In order to investigate the properties of rubber compounds, eleven experimental methods were used. The details about experimental methods were introduced in this section.

2.2.1. Ball mill treatment

The ball mill used in this research is Retsch PM 100 Planetary Ball Mill (Retsch, Haan, Germany), shown in Figure 2-2. During the milling process, the fly ash was first added into the vial (a cylinder container) which had 21 balls for crushing and grinding the particles. The vial is placed on a base plate which could rotate in the direction opposite to vial rotation. The balls kept crushing the fly ash particles in this manner, resulting in size reduction and morphological changes for the fly ash particles. The total time of ball mill treatment was 60 minutes and the rate of rotation was 400 rpm.

Figure 2-2 The picture of Retsch PM 100 Planetary Ball Mill.

2.2.2. Observation of fly ash particles

The shape and size of the fly ash particles were characterized by using a Scanning Electron Microscopy (SEM) (Leitz Laborlux-12-POL-S optical microscope and Hitachim Tokyo, Japan Model-S2150). During preparation, the fly ash sample was placed on a conductive tape which was stuck on a steel holder and compressed air was used to remove excess particles. Because of its insulating property, the fly ash needed to be coated with a layer of silver. Before the test, compressed nitrogen was used to blow off the dirt on the surface of the sample. The fly ash particles were stuck to the surface

2.2.3. Rubber mastication and compounding

There were two steps for mastication and compounding of the rubber. The first step involved using an internal mixer (TYPE 808-1002-DTI, C.W. Brabender Instruments, Inc., South Hackensack, NJ), to masticate SBR and then mixing it with fillers and other chemicals for vulcanization. The second step involved using a two-roll mill (NO: 5438, Reliable Rubber & Plastic Machinery Co., North Bergen, NJ) for further mixing and improving process ability of the rubber compound. There were two recipes of rubber compounds containing carbon black/fly ash and silica/fly ash/carbon black: recipe A and recipe B. These recipes are shown in Tables 2-6 and 2-7, with the only difference being the type of fillers.

Table 2-6. Recipe A for the carbon black/fly ash rubber compound.

Function	Item-grad	phr
Rubber	Buna VSL 5025-2 HM	100
Reinforcing filler	Carbon black N234 and fly ash	50
Activator	Zinc oxide	3
Accelerator (CBTS)	N-cyclohexyl-2-benzothiazole	1.6
Vulcanizer	Sulphur	1.4
Asselerator	Stearic acid	2
Antioxidant and antiozonant	6-PPD	1
sum		159

Table 2-7. Recipe B of the carbon black/silica/fly ash rubber compound.

Function	Item-grad	phr
Rubber	Buna VSL 5025-2 HM	100
Reinforcing filler	Silica Zeopol® 8745 and fly ash Micron 3	50
Reinforcing filler	Carbon black N234	4
Activator	Zinc oxide	3
Accelerator (CBTS)	N-cyclohexyl-2-benzothiazole	1.6
Vulcanizer	Sulphur	1.4
Asselerator	Stearic acid	2
Antioxidant and antiozonant	6-PPD	1
sum		163

The purpose of using the recipe A was to investigate the effect of different concentration and types of fly ash on the mechanical properties of rubber compound. In recipe A, the total content of filler is fixed at 50 phr. There are two differences between the specimens. The first difference involves fly ash content, and the second difference involves the type of fly ash with the details shown in Table 2-8.

Table 2-8. Content of fillers in recipe A.

Carbon black (phr)	50	47.5	45	42.5	40
Fly ash (phr)	0	2.5	5	7.5	10
Total filler (phr)	50	50	50	50	50

The purpose of adopting the recipe B was to investigate if there were any synergistic effects related to the rubber compounds containing precipitated silica, fly ash and carbon black at the same time in hybrid form. The filler content in recipe B added up to 54 phr in the rubber compound used, in which the content of carbon was fixed at 4 phr and the content of fly ash and silica fillers changed with different specimens prepared. The details of such filler content changes for recipe B are shown in Table 2-9.

Table 2-9. Content of fillers in recipe B.

Silica (phr)	50	47.5	45	42.5	40
Fly ash (phr)	0	2.5	5	7.5	10
Carbon black (phr)	4	4	4	4	4
Total filler (phr)	54	54	54	54	54

During compounding in internal mixer, the rubber was masticated for 1 minute and fillers and the antioxidant were added together subsequently. The temperature was maintained at 80°C for 15 min during this process. After that, all the material in the chamber of the internal mixer would be taken out and placed in a refrigerator. The internal mixer was also cooled down by compressed air. During the next step the rubber was taken out from the refrigerator and placed into the internal mixer

chamber which was cooled down to 50°C. Stearic acid, zinc oxide, CBTS and Sulphur were then added into the chamber of the internal mixer and its temperature maintained at 80°C for 15 min subsequently. After that, all the rubber compounds in the chamber was collected and kept in the refrigerator. In the second step of rubber mastication and compounding, the rubber from the internal mixer was compounded in two-roll mill for 5 minutes. The rubber sheet produced in this manner was thus ready for vulcanization.

2.2.4. Methods of Cure characterizations

Differential scanning calorimetry (model Q-200 DSC; TA INSTRUMENTS, Woodland, California, USA) was used to determine the cure time for the rubber compound which was made according to recipe A. About 5 mg of sample was placed in the isothermal environment in DSC and the sample was maintained at 160°C for 30 min. After that, the plot of heat flow versus time curve would be obtained. The analyzing procedures is shown graphically in Fig 2-3. A base line was set by the minimal value of heat flow. The area between the heat flow line and the base line was integrated, and the time which corresponded to the 90% of the integrated area was T₉₀, which refers to 90% of the total cure time. Thus, the cure time is calculated using the equation:

$$\frac{T_{90}}{0.9} = \text{cure time} \quad (1)$$

Figure 2-3 Diagram of measuring cure time by DSC.

A moving die rheometer (MDR 2000, Alpha Technologies, Akron, Ohio, USA) was used for measuring the cure time of the rubber compound which was made according to the recipe B. 5 g of the sample was placed between two dies and its temperature was maintained at 160°C for 30 min. By measuring the maximum value of torque, the machine would calculate the time when the torque reach 90% of its maximum value. This procedure determined the 90% cure time designated as T90. The calculation for measuring the cure time is the same as in DSC measurement, so by using equation (1), the cure time can be calculated.

2.2.5. Compression molding for tensile tests

About 55 g of rubber was placed between two panels of the compression mold. The temperature was set at 160°C and pressure was set at 2.7 psi. The cure time was measured from the DSC and the moving die rheometer (MDR) instruments used. After curing, the rubber compound was cut into dumbbell samples. The sample width was 4.00 mm and the sample thickness was about 1.50 mm.

2.2.6. Swelling tests

In order to measure the crosslink density of the rubber compounds, a swelling method was used. The experimental equipment is shown in Figure 2-4. There are four parts of this swelling equipment. The first part, a magnetic stirrer with hot plate was located at the bottom. It provided heat and stirred the extraction solvent to prevent blasting boiling. Upon the first part, the second part was a flask which contained the extraction solvent. In this test, toluene was used as the extraction solvent. The flask was connected to the extractor which was the third part and contained a thimble in its chamber. The sample was cut to small pieces and placed into the thimble (the white container in Figure 2-4). The fourth part, a condenser, was located on the extractor. Water flowed through the condenser and flowed out. When the test began, toluene was boiled and the toluene gas traveled up to the condenser. , The gas was cooled down by the low temperature of water and dropped on the sample. The soluble components were thus dissolved into the solvent and

when the solvent was full in the chamber, the solvent and the soluble components were returned to the flask and ready for the next cycle. Therefore, during the swelling tests, the soluble components of sample were extracted by toluene.

The sample weight was measured after 48 hours of swelling test and the sample was taken out and weighted immediately. The swollen sample was then placed into an oven where the temperature was 100°C. In order to make sure that the sample was completely dried, it was kept in the oven for 48 hours, after which, the weight of the dried sample was measured. The crosslink density was calculated by the Flory-Rehner equation^[47]:

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = V_s \eta_{\text{swell}} \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right) \quad (2)$$

Where, V_r is the volume fraction of the rubber in swollen gel, and χ is the polymer-solvent interaction parameter. For SBR-toluene, χ is 0.31^[48]. η_{swell} is crosslink density of rubber (kmol/m³). V_s is the molar volume of toluene (in this research, 106.27 cm³/mol).

In order to calculate the crosslink density, V_r was calculated by the equation:

$$V_r = \frac{V_{\text{rubber}}}{V_{\text{solvent}} + V_{\text{rubber}}} = \left(\frac{m_3 - m_1 \times f}{\rho_{\text{rubber}}} \right) \div \left[\frac{m_2 - m_3}{\rho_{\text{solvent}}} + \left(\frac{m_3 - m_1 \times f}{\rho_{\text{rubber}}} \right) \right] \quad (3)$$

In equation (3), m_1, m_2, m_3 are the weights of the sample: m_1 was measured before swelling, m_2 was measured after swelling and m_3 was measured after drying. $\rho_{\text{rubber}}, \rho_{\text{solvent}}$ are the density of SBR and toluene. As for BUNA VSL 5025-2 HM and toluene, ρ_{rubber} was 0.94 g/cm³ and ρ_{solvent} was 0.867 g/cm³. f is the weight fraction of non-rubber components in rubber compounds. According to

the Table 2-6. and 2-7., in recipe A, the weight fraction of non-rubber components was 0.371, and in recipe B, the weight fraction of non-rubber components was 0.387.

Figure 2-4 Swelling test.

2.2.7. Tensile tests for the mechanical properties

The tensile strength, elongation at break and moduli were measured by the tensile tester (Model 5567 56P4494, Instron, Norwood, MA). The load cell used was

1kN and the specimens were tested using 500 mm/min crosshead rate. The machine would record the tensile force and changed length. The pictures of tensile tests are shown in Figure 2-5. From the results, tensile strength and elongation at break were directly obtained. The tensile strength represents the maximum value of stress during the tensile tests. The elongation at break refers to the fracture strain of the sample. As for the modulus, two kinds of moduli values, modulus at 2% strain and the modulus at 100% were calculated from the results. This is because in the practical applications, the deformation of tires is very small. Modulus at 100% strain is often used to represent the modulus of the rubber compound. These moduli are shown graphically in Figure 2-6. At small strain (0.5%-2%), there is a linear relation between the stress and the strain allowing the slope to be used to represent the modulus at 2% strain. When the strain was about 100%, the average value of the modulus was calculated using 100 points in order to reduce error. Strain range from 0.98-1.03 was used to represent the modulus at 100% strain.

(a)

(b)

(c)

(d)

Figure 2-5 Stages of tensile tests: (a) before the tensile test, (b) the sample is being stretched (c) sample is fractured, (d) sample for tensile tests.

Figure 2-6 Stress-strain curve from the tensile tests.

2.2.8. Measurement of dynamic properties

As mentioned earlier, rolling resistance is related to the energy loss during the usage of tire products. Wet grip is used to describe the ability of tire to prevent sliding during rotating. The Rolling resistance and wet grip of the rubber sample were measured by a dynamic mechanical analyzer (Model RSA3, TA Instruments), which was operated in the temperature ramp/ frequency sweep mode. Temperature was set from -50°C to 90°C , using a ramp rate of $3^{\circ}\text{C}/\text{min}$. Dynamic strain was 0.1% and frequency was 1Hz. The loss modulus (G''), storage modulus (G') and glass transition temperature were obtained from the results. In order to calculate the wet grip and

rolling resistance and glass transition temperature, the damping capacity ($\tan \delta$) was calculated using the equation:

$$\frac{G''}{G'} = \tan \delta \quad (4)$$

In general, $\tan \delta$ at 0°C and 60°C are used to describe the wet grip and rolling resistance [49] [50].

2.2.9. Hardness tests

The hardness of the rubber compounds was measured by the hardness tester (Shore Durometer Type “A-2”, Shore and represented in units of shore type A-2.

2.2.10. Adhesion tests

Pull-out tests were carried out to measure the adhesion between rubber compounds and the steel cords. In this test, a special mold was used for curing the sample. The mold is shown in Fig. 2-7. There were three parts of this mold, the lid, middle part and the base. In Fig. 2-7, the left picture shows the middle part, the middle picture shows the base and the right picture shows the lid. Before curing, 5.5 g of rubber was placed in each mold slot and steel cord (0.25+6+12x0.225HT) was vertically inserted into the sample on both slots of the mold. Then the mold was placed between two panels of the compression mold. The temperature was set at 160°C

and time was set to the cure time which was measured using the DSC and MDR instruments. After molding, the sample for the adhesion tests was obtained. The picture of the sample is shown in Fig. 2-8. The right sample in Fig. 2-8 was cured but not subjected to adhesion tests. The left sample in Fig. 2-8 shows the result of a pull-out test with the steel cord already pulled out from the sample.

Figure 2-7 The compression mold for adhesion tests.

Figure 2-8 Pull-out (adhesion) test sample.

For the adhesion tests, the two sides of the sample were clamped on the tensile tester (Model 5567 56P4494, Instron, Norwood, MA). The load cell was 1kN and the crosshead rate used was 50 mm/min. When the experiment started, the steel cord which connected to the upper part of the sample was pulled out from the remaining part. The tensile tester would record the tension during the experiment. After the

experiment, the maximum force (F_{max}) was obtained from the results and the adhesion ratio was calculated using the equation:

$$\frac{F_{max}}{L} = Adhesion\ ratio \quad (5)$$

Where, L is the embedded length of the steel cord, as measured by a vernier caliper.

2.2.11. Measuring filler dispersion

The filler's dispersion in the rubber compounds was observed by using computerized axial tomography scan (SKYSCAN 1172, Bruker Allentown, PA) and Scanning Electron Microscopy (SEM) (Leitz Laborlux-12-POL-S optical microscope and Hitachim Tokyo, Japan Model-S2150).

For the computerized axial tomography scan (CT), a 0.5 mm aluminum filter was used resulting in 4 um resolution. The sample was cut into a cuboid form for these observations.

For the SEM observations, the rubber sample was immersed in liquid nitrogen for 20 min and folded to break and cut into small pieces. After coating with silver, the sample was observed using the SEM.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Morphology of fly ash

The fly ash particles without ball mill treatment are shown in Figure 3-1. Most of the particles were spherical before the ball mill treatment. By direct measurement, the mean size of the particles was obtained using these four pictures. The results are shown in Table 3-1. The results reveal that the Micron 3 particles group had the smallest particle size and Class F had the biggest particle size.

Figure 3-1 Pictures of four kinds of fly ash: (a) untreated Class F, 5.0kV, X1000, (b) untreated Micron 3, 5.0kV, X1000 (c) untreated Pv14A, 5.0kV, X1000 (d) untreated Pv20A 5.0kV, X1000.

Table 3-1. Mean sizes of untreated fly ash.

Fly ash	Class F	Micron 3	Pv14A	Pv20A
Mean Size (μm)	6.0	1.7	2.2	2.3

Figure 3-2 shows the morphology of the fly ash particles after ball mill treatment. The mean size of the particles was calculated using the SEM pictures, as

shown in Table 3-2. After ball mill treatment, the shapes of most fly ash particles were changed from regular sphere to irregular shapes and the particle size was reduced. Class F particles were still the biggest particles and Micron 3 had the smallest mean particle size.

Figure 3-2 SEM pictures of ball mill treated fly ash particles: (a) treated Class F, 5.0kV, X1000 (b) treated Micron 3, 5.0kV, X1000 (c) treated Pv14A, 5.0kV, X1000 (d) treated Pv20A 5.0kV, X1000.

Table 3-2. Mean sizes of treated fly ash.

Fly ash	Class F	Micron 3	Pv14A	Pv20A
Mean Size (μm)	3.8	1.0	1.3	1.3

3.2. Cure characterizations

The T90 (time to 90% cure) values for the rubber compounds containing carbon black and various fly ash are shown in Figure 3-3. “UNT” refers to the untreated fly ash. “ball” refers to the ball mill treated fly ash. “Class F”, “Micron 3”, “PV14A” and “PV20A” refer to the fly ash Class F, Micron 3, PV14A and PV20A. Addition of fly ash increased the cure time, we think, due to two reasons: first, carbon black acted as a catalyst in the vulcanization of rubber and increased the cure rate ^{[3][7]}. Second, we note that the main composition of fly ash is silica and during vulcanization, silica reacts with zinc oxide ^{[1][3]}. The production of reaction between silica and zinc oxide is zinc sulfide (ZnS) ^[51]. We again note that, zinc oxide is used to react with stearic acid to produce the intermediate of the vulcanization. Therefore, the amounts of accelerators and zinc oxide were reduced due to the introduction of silica by fly ash into the compound.

Figure 3-3 T90 (time to 90% cure) of rubber compounds of recipe A with various fly ash loadings.

As for the rubber compound which involved recipe B, the T90 is shown in Figure 3-4. “50Si, FA UNT+4CB” and “50Si, FA ball+4CB” refer to the rubber which involved recipe B. “UNT” refers to the rubber compounds containing untreated fly ash, and “ball” refers to the rubber compounds contained ball mill treated fly ash. It was obvious that as the content of fly ash changed, the T90 did not change much and just fluctuated. The reason is again the fact that the main composition of fly ash is silica which causes retardation of vulcanization as explained above. We note that silica fillers are also added in recipe B separately in rather large amounts (40 to 50 phr, see Table 2-9), thus inducing additional retardation in vulcanization. Compared with the rubber compound recipe A, the cure time of the rubber compound recipe B was higher, which was because the content of silica in recipe B rubber compound was higher, and more accelerators were absorbed or reacted by the silica.

Figure 3-4 T90 (time to 90% cure) of rubber compounds of recipe B with various fly ash loadings.

3.3. Crosslink density of silica/carbon black/fly ash rubber

The crosslink density of the rubber which involved recipe B is shown in Figure 3-5. An increasing amount of fly ash below the 10 phr level resulted in increases crosslink density. This improvement in crosslink density can be explained by the synergic effects of the hybrid filler used (fly ash, silica and carbon black). When a small amount of fly ash was added into the filler system, the dispersion of all of the fillers likely improved. On the other hand, the crosslink density declined at higher contents of fly ash when using either untreated or ball mill treated fly ash. This was because the fly ash particles would aggregate with silica and other fly ash particles,

and the forming of crosslinking network was affected by such aggregated structures. Compared with the untreated fly ash, ball mill treated fly ash did not improve the crosslink density at intermediate loading levels (i.e., 7.5 phr, Fig. 3-5), because the morphology of fly ash particles altered by ball milling made it easier to form agglomerate structure with silica, as observed on the fracture surface shown in section 3.8.

Figure 3-5 Crosslink density of rubber compounds of recipe B with various fly ash loadings.

3.4. Results of the tensile tests

Results of the tensile tests for the carbon black/fly ash rubber compounds are shown in Figure 3-6. “UNT” refers to the rubber compounds containing untreated fly ash and “ball” refers to the rubber compounds contained ball mill treated fly ash. Compared with the rubber compound which contained untreated fly ash, the

compound with ball mill treated fly ash had higher tensile strength, which indicated that ball mill treatment improved the reinforcing effect of the fly ash by reducing the particle size and increasing the interface area between the fly ash and the rubber. Except for the rubber with Micron 3 class particles, the tensile strength of other rubber compounds decreased overall as the content of fly ash increased. As the content of fly ash increased, the fly ash particles would aggregate. In addition, the large particle size of the untreated fly ash may have caused initiation of local tears and inclusions under tension. Among the four kinds of fly ash used, Micron 3 had higher tensile strength at various concentrations possibly due to its small particle size and high fraction of silica.

Figure 3-6 Tensile strength of rubber compounds of recipe A with various fly ash loadings: (a) Class F (b) Micron 3, (c) Pv14A (d) Pv20A.

The elongation at break for rubber compounds which involved recipe A is shown in Figure 3-7. As the content of fly ash increased, the elongation at break improved. This can be explained by the fact that the interaction between fly ash and rubber molecules is comparatively weak when it is compared to the interaction between carbon black and rubber molecules. This means that the rubber molecules

remained relatively flexible when the fly ash was added so that the rubber compound was easier to deform when the content of fly ash was increased. Ball mill treatment improved the interfacial area between the rubber and the fly ash, which resulted in increased restriction in rubber molecule movements. However, the dispersion of fly ash also improved as the particle size was reduced. Therefore, besides rubber with Class F, there was not much difference in elongation at break for the rubber compounds which contained ball mill treated and untreated fly ash. On the other hand, ball mill treatment could improve the elongation at break for rubber with Class F fly ash at high concentration. This was because the large particle size would result in the distinct separation between the rubber phase and the filler phase and flaws were easier to take place causing elongation at break to be smaller when the untreated Class F was added to the rubber compound.

Figure 3-7 Elongation at break of rubber compounds of recipe A with various fly ash loadings: (a) Class F (b) Micron 3, (c) Pv14A (d) Pv20A.

The modulus at 2% strain of carbon black/fly ash rubber compound is shown in Figures 3-8 and 3-9. As the content of fly ash increased, the modulus at 2% strain decreased. This behavior can be explained by the Payne effect under cyclical loading with small strain amplitude ^[52]. The modulus, which depends on the strain amplitude, is affected by the breakage and reformation of filler aggregates. There is a big

difference between the polarity of carbon black and silica molecules. Therefore, the interaction between fly ash and carbon black was weaker than the interaction among the carbon black particles resulting in reductions in 2% modulus as the fly ash content increased.

Figure 3-8 Modulus at 2% strain of rubber compounds of recipe A with various fly ash loadings: (a) Class F (b) Micron 3, (c) Pv14A (d) Pv20A.

(a)

(b)

(c)

(d)

Figure 3-9 Modulus at 2% strain of rubber compounds of recipe A with various volume fractions of fly ash: (a) Class F (b) Micron 3, (c) Pv14A (d) Pv20A.

Figures 3-10 and 3-11 show the modulus at 100% strain of carbon black/fly ash rubber compound. Obviously, the modulus at 100% strain reduced as the content of the fly ash increased. This behavior can be attributed to two reasons: The first reason is that the large particle size prevented the formation of crosslinking network during vulcanization. The second reason involves the fact that rubber – filler interactions get weaker as the fly ash content is increased. Remembering that the main

composition of the fly ash is silica and metal oxide, low reinforcing effect is obtained as silica has poor compatibility with rubber and metal oxide has nearly no reinforcing effect on rubber. As the percentage of fly ash was increased above 10%, there was a bigger decline of the modulus at 100% strain, which was also attributed to the agglomeration of the fly ash particles.

In Figures 3-9 and 3-11, for each kind of fly ash, trendlines (according to the five points of moduli values from 0 to 10 phr) and the linear equations are shown. The slope was negative because modulus decreased as fly ash increased. The values of slope were between -0.30 — -0.80, which indicated that the fly ash particles had poor interaction with rubber molecules instead of non-interactions. If there is no interaction between fly ash and rubber molecules, the values of slope were far more than 1.

(a)

(b)

(c)

(d)

Figure 3-10 Modulus at 100% strain of rubber compounds of recipe A with various fly ash loadings: (a) Class F (b) Micron 3, (c) Pv14A (d) Pv20A.

(a)

(b)

(c)

(d)

Figure 3-11 Modulus at 100% strain of rubber compounds of recipe A with various volume fractions of fly ash: (a) Class F (b) Micron 3, (c) Pv14A (d) Pv20A.

Figure 3-12 shows the tensile strength of the silica/fly ash/carbon black rubber compound. In Figure 3-12, “50Si, FA UNT+4CB” and “50Si, FA ball+4CB” refer to the rubber which involved recipe B, “50CB+FA UNT” and “50CB+FA ball” refer to the rubber which involved recipe A. “UNT” refers to untreated fly ash and “ball” refers to ball mill treated fly ash. In order to make a comparison among the recipes, the tensile strength of the compound which contained Micron 3 and carbon black was

used as a comparison. Compared with the carbon black/fly ash rubber, the silica/fly ash/carbon black rubber exhibited higher tensile strength, especially for the compound which contained untreated fly ash, silica and carbon black. The synergic effect of hybrid fillers could be used to explain this phenomenon. During rubber compounding, fly ash particles would improve the distribution of the silica and carbon black. Noting that Micron 3 already induced a synergic effect in the carbon black/fly ash rubber results reported earlier, it maintains such synergic effect on further improving the tensile strength of the rubber compounds. We note that, for the carbon black/fly ash rubber, ball mill treatment improved the tensile strength as shown in Figures 3-6 and 3-12. For the silica/fly ash/carbon black rubber, however, ball mill treatment reduced the tensile strength. This behavior can be attributed to the distinct characteristics of fillers; in carbon black/fly ash rubber compound, the carbon black-fly ash interaction is weak because of different polarity. The surface chemistry of carbon black and silica particles is shown in Figure 3-13. The surface of silica is mainly covered by silanol groups mentioned in section 1.2.3. On the other hand, the main composition on the surface of carbon black is carbon and a small fraction of the surface consists of hydrocarbon and oxygen-containing groups^[3]. In addition, the quasi-graphitic crystallites form the aggregation structure of carbon black and the unit structure is a graphite-like hexagon^{[53][54]}. Thus different chemical components on the surface result in the weak interaction between carbon black and fly ash particles. However, in silica/fly ash/carbon black rubber, the fly ash-silica interaction

was strong because the main composition of the fly ash was silica, and silica particles prefer to form strong filler-filler interactions with adjacent silica particles ^{[3] [14] [21]}.

Therefore, Silica preferred to aggregate with ball mill treated fly ash particles.

Figure 3-12 Tensile strength at 100% strain of rubber compounds with various fly ash loadings.

Figure 3-13 Schematic of silica and carbon black particles.

Elongation at break and modulus at 100% strain for rubber compounds with various fly ash loading are shown in Figures 3-14 and 3-15. Elongation at break increased and modulus at 100% strain decreased for the silica/fly ash/carbon black rubber compound as the content of fly ash increased. This behavior is attributed to the crosslink density of the rubber compounds. Figure 3-5 reveals that crosslink density increases at low concentrations of untreated fly ash, resulting in improved modulus and decreased elongation at break. However, as the content of fly ash was further increased, the crosslink density decreased, so that elongation at break increased and modulus decreased. At high concentration of the fly ash, there was not much difference between the rubber with untreated fly ash and the rubber with ball mill treated fly ash. But at low concentration of the fly ash, there was a big difference of modulus at 100% strain. Obviously, the modulus improves with untreated fly ash instead of ball mill treated fly ash, indicating that ball mill treatment increases the size of aggregated structure.

Figure 3-14 Elongation at break of rubber compounds with various fly ash loadings.

Figure 3-15 Modulus at 100% strain of rubber compounds with various fly ash loadings.

The modulus at 2% strain is shown in Figure 3-16. The modulus of the silica/fly ash/carbon black rubber was higher than that for the carbon black/fly ash rubber,

which could be explained by the Payne effect. It was well known that silica would form filler-filler networks in rubber compounds, so that the filler-filler interactions were stronger in the silica/fly ash/carbon black rubber compound. The influence of fly ash particles on the filler networks is shown Figure 3-17 (real particle size is different from the particles shown in Figure 3-17). As the fly ash content increased, the filler network was interrupted and filler-filler interactions were reduced contributing to the decrease in modulus at small strain levels. When used at small concentration, increasing ball mill treated fly ash resulted in the decline of the modulus at 2% strain. This phenomenon indicated that the addition of ball mill treated fly ash broke the formerly-formed silica network and initiated weak filler-filler interactions with silica.

Figure 3-16 Modulus at 2% strain of rubber compounds with various fly ash loadings.

Figure 3-17 Schematic representation of filler networks.

3.5. Dynamic mechanical properties

As mentioned in section 2.2.8., it is acknowledged that Tan delta ($\tan \delta$) values at 0 °C and 60 °C are correlated to the wet grip and rolling resistance. Our measurements for the rolling resistance and wet grip behavior of the rubber compounds are shown in Figure 3-18 and 3-19. Compared with the carbon black/fly ash rubber, both rolling resistance and wet grip are reduced when silica/fly ash/carbon black rubber compounds are used. This indicates that silica has an influence on reducing the rolling resistance and wet grip. As the content of the fly ash increased in the carbon black/fly ash rubber compound, the rolling resistance decreased, as attributed to increased silica by fly ash usage. In silica/fly ash/carbon black rubber, rolling resistance was independent of the fly ash content, as silica was already present as a main component of the rubber compound. As for the wet grip, the addition of fly ash slightly improved wet grip due to the fact that the addition of fly ash interfered with the filler network, so that the rubber molecules were flexible, and wet grip increased. The glass transition temperature (T_g) is shown in Figure 3-20. The rubber compounds which involved recipe B exhibited lower glass transition temperature, compared with recipe A, which could be explained by the similar reason for the higher elongation at break of recipe B. The poor silica-rubber interaction resulted in the flexible rubber molecules, so the glass transition temperature was decreased. As the fly ash content of fly ash increased, glass transition temperature

did not change much, and ball mill treatment also had no obvious effect on glass transition temperature.

Figure 3-18 The $\tan \delta$ at 60°C with various fly ash loadings.

Figure 3-19 The $\tan \delta$ at 0°C with various fly ash loadings.

Figure 3-20 Glass transition temperature with various fly ash loadings.

3.6. Hardness

The hardness of the rubber compound recipes A and B are shown in Figure 3-21.

At small concentration of fly ash, the hardness of silica/fly ash/carbon black had higher hardness than the carbon black/fly ash rubber, as attributed to the Payne effect; in other words, strong filler-filler interaction of silica resulted in the high hardness. Such filler-filler interactions were reduced with increasing fly ash, and the hardness was reduced. As for the carbon black/fly ash rubber compound, the hardness is independent of the fly ash content, which could be explained by the fact that fly ash interrupted the interaction between carbon black particles and also formed new filler-filler interactions among its own particles.

Figure 3-21 Hardness of rubber compounds with various fly ash loadings.

3.7. Adhesion tests

Figure 3-22 shows the adhesion ratios (equation (5)) of the rubber compounds. Compared with recipe A rubber, the silica/fly ash/carbon black rubber exhibited a higher adhesion ratio, which indicated that silica had an influence on improving the adhesion between the rubber and the steel cord. The ball mill treatment has a similar effect on adhesion when it is compared with the tensile results, indicating that ball mill treatment would improve the dispersion of filler in the carbon black/fly ash rubber. However, in the silica/fly ash/carbon black rubber, ball mill treatment had the reverse influence on adhesion. This may be due to the fact that ball mill treated fly ash absorbs silica and causes other fly ash particles to form large aggregation structure. As the content of fly ash increased, adhesion decreased, because the

particle size of the fly ash was large while silica occupied only about 50% of the fly ash. As for the carbon black/fly ash rubber, at small concentrations of fly ash, the adhesion was slightly improved by the ball mill treated fly ash, but adhesion was further decreased as the content of fly ash was increased. We note that the silica in fly ash was effective in improving adhesion when used in small amounts. When the concentration of fly ash was high, however, the influence of the silica in fly ash was blocked by flaws it may create in the rubber compound caused by the aggregation structure.

Figure 3-22 Adhesion ratio of rubber compounds with various fly ash loadings.

3.8. The dispersion of filler

The Figures 3-23 and 3-24 show the dispersion of the rubber filler. Ball mill treated fly ash aggregates with other silica and fly ash particles. The aggregated structure of the untreated fly ash particles was much smaller in comparison to the structure observed with the ball mill treated fly ash particles. This phenomenon was considered earlier when tensile and adhesion test results were discussed and related to the aggregated structures of the fillers used.

(a)

(b)

(c)

(d)

(d)

(f)

Figure 3-23 SEM picture of fracture surface: (a) 2.5 phr fly ash(untreated)+47.5 phr silica+4 phr CB, X1000, (b) 2.5 phr fly ash(ball mill treated)+47.5 phr silica+4 phr CB, X1000, (c) 2.5 phr fly ash(untreated)+47.5 phr silica+4 phr CB, X5000, (d) 2.5 phr fly ash(ball mill treated)+47.5 phr silica+4 phr CB, X5000, (e) 2.5 phr fly ash(untreated)+47.5 phr silica+4 phr CB, X10000,(f) 2.5 phr fly ash(ball mill treated)+47.5 phr silica+4 phr CB, X10000.

(a)

(b)

Figure 3-24 CT picture of fracture surface: (a) 2.5 phr fly ash (untreated) + 47.5 phr silica+4 phr CB, (b) 2.5 phr fly ash (ball mill treated) +47.5 phr silica+4 phr CB.

CHAPTER IV

CONCLUSIONS

Based on our experimental and analytical studies, we can make the following conclusions:

1- In four kinds of fly ash, Micron 3 exhibited higher tensile strength and elongation at break. The reason was that Micron 3 had the smallest particle size and high fraction of silica which had reinforcing effect on the rubber compounds.

2- Ball mill treatment changed the morphology of the fly ash particles. The fly ash particles changed from regular balls to irregular particles. The ball mill treatment could improve the mechanical properties of the carbon/fly ash rubber, as attributed to the increased interface area and reduced particle size of the fly ash. However, ball mill treatment had the reverse influence on the silica/fly ash /carbon black rubber compound, as attributed to the aggregation of the ball mill treated fly ash particles and silica.

3- Cure time was increased by adding fly ash into the carbon black/fly ash rubber compound because of the retardation effect from silica during vulcanization.

4- Tensile strength was improved as silica partially replaced the carbon black, due to the synergic effects of hybrid filler usage. When a small amount of fly ash was added, this synergic effect was further improved. At small concentration of fly ash, the silica/fly ash /carbon black rubber exhibited high tensile strength and elongation at break.

5- The rolling resistance and wet grip of the silica/fly ash /carbon black rubber are lower than those with carbon black/fly ash rubber, but adding fly ash would improve the wet grip of the silica/fly ash /carbon black rubber. Thus silica/fly ash /carbon black rubber compound exhibited lower energy consumption and service safety. For the carbon black/fly ash rubber compound, however, adding fly ash reduced rolling resistance. Thus, fly ash addition is expected to reduce energy consumption with the carbon black/fly ash rubber compounds.

6- Modulus at small strain and hardness were improved by partially replacing the carbon black with silica, as attributed to the enhanced filler-filler interactions.

7- Adhesion between brass coated steel cord and rubber was improved by using silica as the main part of filler in rubber compounds. In addition, fly ash would result in decreased adhesion.

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APPENDIX

Table 1. The densities of four kinds of fly ash

	Class F	Micron 3	Pv14A	Pv20A
Density (g/cm ³)	2.55	1.78	2.35	2.78

Table 2 The densities of rubber compounds with recipe A

FA content	CB content	density(g/cm ³)
0.00	50	1.1362
2.50	47.5	1.1396
5.00	45	1.1429
7.50	42.5	1.1463
10.00	40	1.1497

Table 3 Volume fraction of fly ash in filler

phr of fly ash	phr of rubber	Class F	Micron 3	PV14A	PV20A
0.00	159	0	0	0	0
2.50	159	0.007026	0.010066	0.007624	0.006445
5.00	159	0.014094	0.020191	0.015294	0.012928
7.50	159	0.021204	0.030376	0.023008	0.019449
10.00	159	0.028355	0.040621	0.030768	0.026009