

**EFFECT OF REPLACEMENT OF CALCIUM  
CARBONATE BY FLY ASH ON PROCESSABILITY AND  
THERMO-MECHANICAL PROPERTIES OF SOLID  
TIRE MIDDLE COMPOUNDS**

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Science in Polymer Technology

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## **DECLARATION OF THE CANDIDATE & SUPERVISOR**

I declare that this is my own work and this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgment is made in the text.

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## ABSTRACT

In this study, as the first step, the effect of partial replacement of  $\text{CaCO}_3$  with unmodified fly ash on the curing characteristics of the solid tyre middle compound and the properties of its vulcanizate was investigated. Fly ash and  $\text{CaCO}_3$  were first characterized. A series of solid tyre middle compounds with varying  $\text{CaCO}_3$  / fly ash loading were prepared in a laboratory-scale internal mixer. The total content of non-reinforcement filler was kept constant. Fly ash loading was increased from 0 to 60 pphr intervals with replacing  $\text{CaCO}_3$ . The dispersion level was evaluated using the  $\alpha$  view and SEM studies. Curing characteristics of the compounds were evaluated. Filler dispersion levels of the compounds and mechanical, rheological and physical properties of the respective vulcanizates were then focused. The unmodified fly ash filled rubber compound with optimum filler loading was selected based on the above properties.

In the second step of the study, the same studies were carried out with a smaller particle size (modified) fly ash filled NR compounds loaded with the selected filler loading.

It was shown that dispersion level was reduced with the addition of fly ash. Dispersion was improved with the incorporation of fly ash with reduced particle size and narrow particle size distribution. SEM studies showed a higher tendency of particle agglomeration with increasing loading of fly ash. It was found that  $M_H$  and  $M_L$  values of the rubber compounds were deteriorated with the increase of unmodified fly ash loading and the values were improved when fly ash with smaller particle size was used. However, no impact was observed on curing characteristics either with the replacement of  $\text{CaCO}_3$  with fly ash, its loading nor their sizes.

The hardness of the vulcanizates of the unmodified fly ash incorporated compounds was increased with the increase of fly ash percentage. Tensile strength, tearing strength, elongation at break and modulus showed a general reduction with the increase of unmodified fly ash except for tear strength, which had reduced only up to 45 pphr and shown a slight increase in 60 pphr of fly ash added sample. When the overall performance was considered, rubber compounds and vulcanizates prepared with 30 pphr fly ash loading showed the most comparable properties.

Studies carried out in the second stage, it was found that physical properties were improved with the use of fly ash with smaller particle size and narrow particle size distribution (0-53  $\mu\text{m}$ ) compared to unmodified fly ash incorporated compounds.

Rebound resilience values were reduced with the increase of the fly ash percentage. Dynamic mechanical properties such as heat build-up and blowout time were deteriorated with the addition of unmodified fly ash and results were improved with the use of small particles of fly ash. Tan delta value which depends on loss modulus and storage modulus shows a neutral role.

Based on the study, it was concluded that there is a potential to replace 50% w/w (i.e. 30 pphr) of the  $\text{CaCO}_3$  loading from the fly ash with smaller size particles without a significant adverse effect on the curing, physical, mechanical and rheological properties.

Keywords: rubber compounds, fly ash, calcium carbonate, compound properties, dispersion, solid tyre middle compound

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## LIST OF ABBREVIATIONS

| Abbreviation    | Description  |
|-----------------|--|
| 6PPD            | N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine |
| ASTM            | American Society for Testing and Materials         |
| BO              | Blow Out   |
| CTP             | N-(cyclohexyl-thio)phthalimide                     |
| DMA             | Dynamic Mechanical Analyzer                        |
| et al           | and others   |
| HBU             | Heat build-up                                      |
| MDR             | Moving Die Rheometer                               |
| M <sub>H</sub>  | Maximum Torque                                     |
| M <sub>L</sub>  | Minimum Torque                                     |
| NR              | Natural Rubber                                     |
| pphr            | parts per hundred of rubber                        |
| PVI             | Pre vulcanization inhibitor                        |
| Rpm             | Revolutions per minute                             |
| SEM             | Scanning Electron Microscope                       |
| SG              | Specific Gravity                                   |
| SIR             | Standard Indonesia Rubber                          |
| SMR             | Standard Malaysia Rubber                           |
| STR             | Standard Thai Rubber                               |
| t <sub>90</sub> | Optimum Cure Time                                  |
| TBBS            | N-tert-butyl-2-benzothiazolesulphenamide           |
| TGA             | Thermal Gravimetric Analysis                       |
| TMQ             | Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline   |
| t <sub>s2</sub> | Induction Time                                     |
| TSR             | Technically Specified Rubber                       |

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# 1. INTRODUCTION

## 1.1 Background

Local raw rubber and rubber product manufacturing industries earn approximately USD one billion contributing nearly 7% to the export earnings of Sri Lanka. The tire manufacturing sector composes the largest share of export turnover (60%) of rubber product exports in Sri Lanka which include solid tires, pneumatic tires, bicycle tires, three-wheel tires and a variety of smaller tire categories [1]. Currently, Sri Lanka is considered as the global leader in solid tires. Sri Lanka has developed into a center to produce solid industrial tires that are mainly for Transportation purposes within the airports, ports and warehouse. Out of world demand 20% is supplied by the Sri Lankan solid tire manufactures. USA named as largest importer while other countries like Italy, Germany and Belgium recommended as main importers of local tires [2].

With the increased demand for solid tires together with the competitive market, a trend for low-cost products could be seen around the world. As a result, the rubber industry attempts to use various low-cost materials and efficient processes to meet the competitiveness. The filler being the major non-rubber component in a solid tire compound, replacement of conventional filler from a low-cost material has become a potential route to achieve the above objective. Most of the fillers investigated for replacement in solid tyre industry were eco-friendly materials generated as by-products in other industries [3, 4]. Those investigations have been carried out mainly focusing to cut down the material cost while maintaining the product performance and using them as cheap diluents. Clay and fillers derived from by-products or waste material were the main category of materials attracted in the field. The Use of these types of filler in product manufacturing is beneficial to the industry in term of its ultimate product cost and to the human being in term of environmental aspects.

In fact, not only for solid tyre, today a wide range of waste materials have been investigated as fillers in almost entire rubber product manufacturing industries. Out of these fillers, the majority is used as non-reinforcement fillers. Mainly  $\text{CaCO}_3$ , rice husk, wood dust, and rice straw are some of such fillers that have been

investigated in the rubber product manufacturing industry [5, 6]. Most of these studies have shown that the potential of partial replacement of  $\text{CaCO}_3$ , a widely used non-reinforcing commercial filler, with filler from agricultural and industrial wastes. However, most of the wastes are still needed to be pre-processed to use as a filler. Pre-processing steps include segregation, extraction, drying, particle size reduction, etc. Among most of the waste to which the attention is paid, fly ash requires minimum number of pre-processing steps as it free from the many pre-processing steps mentioned above [7, 8].

Fly ash is a by-product of the power generation industries. In power generation, coal is generally used as the fossil fuel to combust and generates electricity. Fly ash is generated during this process. After combustion, a part of these ash generated during the process is flown upwards and is collected by using electrostatic or other filtration equipment. These particles obtained are an inorganic material with very fine particles. This material records as fly ash. Annually, a large amount of fly ash is generated from the power stations worldwide as industrial waste, including in Sri Lanka. India, China, and the USA are the main fly ash generators in the world. Sri Lanka also generates approximately 300,000 tonnes of fly ash per annum [9].

A few percentages of fly ash are used for many applications, mainly in cement manufacturing. But this annual utilization percentage is much less, as shown in Figure 1-1. Utilization percentage is higher in developed counties like the USA, Canada, and Europe compared to Asian countries like India, China, and Sri Lanka. In India, more than 60% of production remains unutilized [9]. Currently, in Sri Lanka, more than 50% of fly ash remains without any usage.



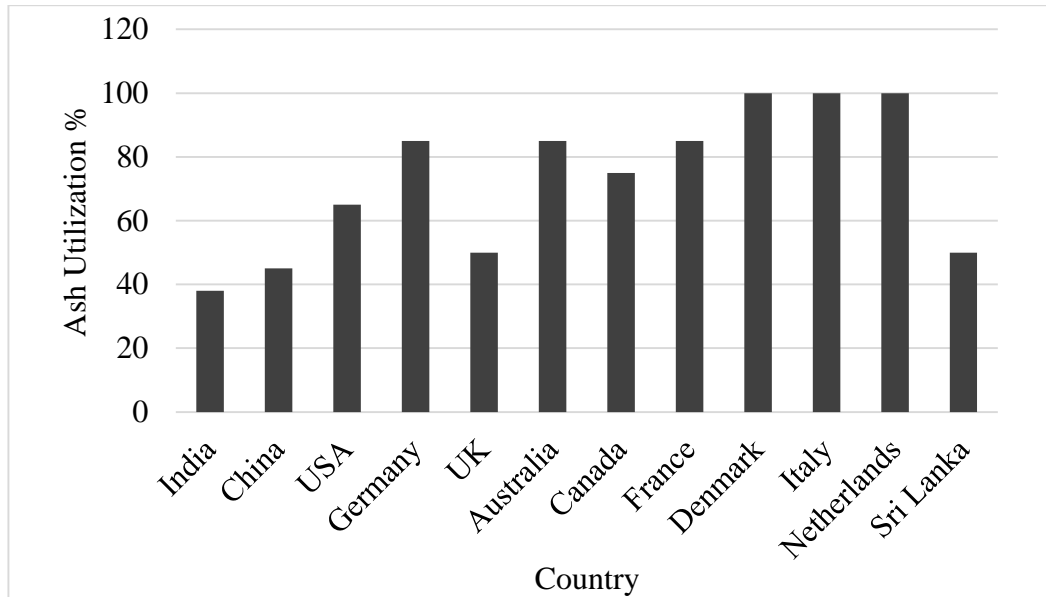


Figure 1-1: Fly ash utilization % with production

The balance amount remains unutilized and requires a disposal methodology. Fly ash disposal is carried out in mainly two methods in the world. They are wet disposal and dry disposal methods.

In the wet disposal method, fly ash is hydraulically conveyed as slurry and deposited in ash ponds, as shown in Figure 1-2. Even though this is not practiced in Sri Lanka, it is commonly used in other countries mainly in the USA [10].



Figure 1-2: Wet disposal method of fly ash

In dry disposal method, fly ash is conditioned and placed in landfills, (Figure 1-3). The main disadvantage of the dry disposal method is high dust production. Currently, this method is used to dispose of fly ash in Sri Lanka [10].



Figure 1-3: Dry disposal method of fly ash

Disposal of fly ash is expensive and creates environmental issues. This is a major problem for all countries which are not utilizing 100% generation of fly ash.

Fly ash could be considered as a material with a reliable supply and it could be used as a filler in many different commercial products. Research that could be found in literature revealed that fly ash has a potential for many industrial applications. Among them, majority was carried out in cement and concrete products. Few have been carried out in polymer product related research as filler for rubber compounds. However, still there is no potential application where fly ash is could be used in bulk quantities in Sri Lanka.

Among the polymer related products, solid tire compounds contain a significantly higher amount of fillers, so the possibility of using fly ash in solid tires could be investigated. For the use of low speed and high load running vehicles, solid tire made without an air cavity. Small resistance when starting, easiness for use and maintenance, full elimination from air leakages and punctures low maintenance, are some additional advantages of solid tires when compared with pneumatic tires. However, solid tire also requires durability, resistance for tearing and puncture and safety.

Solid tires can be classified according to their design, mainly three types. They are press on, cured on and resilient, shown in Figure 1-4.



Figure 1-4: Type of solid tires

The press on tires is strengthened by the band as well as the green tire is wounded on the band and cure the tire. According to the layers, there are two types one layer and two-layer press on tires. Cured-on tires also made on the customer specified rim and it is also having two types the same as press-on tires.

Resilient tires are strengthened by using beads. According to layer consistency, resilient tires are again differentiated into 3 categories. Resilient tire construction is defined according to product usage and considering other requirements. Tire construction is changed to cater to customer requirements, optimize the product price and optimize product performance. According to resilient tire construction, it can be categorized under the main three categories. They are three-layer, two-layer and two-layer high heel (Figure 1-5).

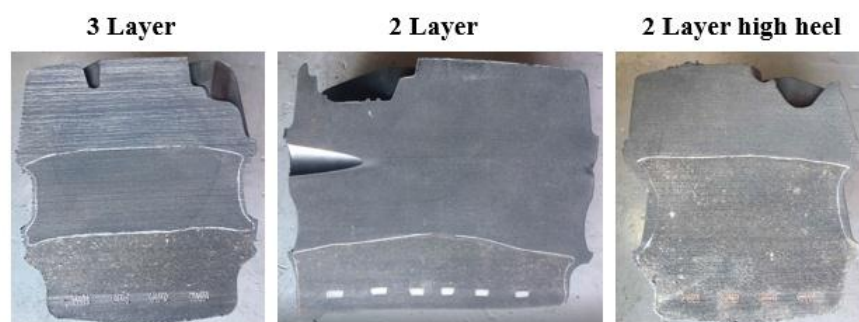


Figure 1-5: Layer configuration of resilient tires

The 3-layer solid tire consists of tread, middle and heel layers. Different layers give different features to the tire. The structure of a 3-layer tire is shown in Figure 1-6.

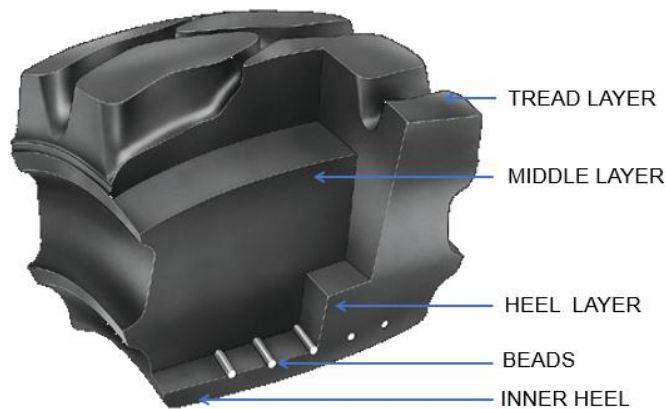


Figure 1-6: Structure of a three-layer tire

The main function of the tread layer is to the achievement of predicted service life, and therefore, it should be better wearing resistance. In addition, the tread layer should withstand tearing, cracking and survive in rough climatic conditions. Also, it should be resisting oils, grease, and other chemicals.

Better stiffness and proper deflection are the main functions of the heel layer. Stiffness is required to hold the tire with rim and steel reinforcement during usage of the tire.

Hold the tire to the rim and well grip between tire and the rim is the basic function of steel reinforcement. The number of beads and design is finalized by considering tire mounting and slipping. Tire mounting and slipping can be optimized by changing the steel reinforcement design.

Comfortability and low heat build-up are the main requirement of the middle layer. It should give low heat build-up during the usage by reducing the temperature rise and heat dissipation. Also rolling resistance is a key parameter and the middles layer contributes a major portion to control it.

Mainly tire thread needs high wearing resistance and tire heel require high strength, so fly ash could not be used for those layers due to non-reinforcing and wearing

issue in fly ash. The middle layer is fully covered and not touching outer surfaces. Then wear resistance is not needed for the middle layer, so non-reinforcing fillers can be used for middle compounding. Middle compounds do not require those properties and mainly they require low heat build-up property. Currently,  $\text{CaCO}_3$  and carbon black (CB) are used as fillers in middle compounds. Fly ash also could be a better alternative in middle layer rubber compounding due to its properties as filler.

Literature available on utilization of fly ash reveal that applications of fly ash in pneumatic tires with styrene and in natural rubber compounding have been investigated to a certain extent. However, they did not focus or discussed the effect of using fly ash on dynamic and viscoelastic properties. Considering these factors replacement of  $\text{CaCO}_3$  with unmodified fly ash for solid tire middle compound was carried out and the possibility to replacement of  $\text{CaCO}_3$  fully or partially was evaluated.

## **1.2 Research objectives**

The objectives of this research are the following.

1. To compare the curing characteristics of  $\text{CaCO}_3$  and unmodified fly ash filled solid tire middle compounds and thermal & mechanical properties of their vulcanizates
2. To identify the optimum  $\text{CaCO}_3$ : fly ash ratio for solid tire middle compounds
3. To study the effect of fly ash particle size and its distribution on product performance

## 2. LITERATURE REVIEW

### 2.1 What is filler

A filler can be considered as a solid material which is used to increase the weight, size or fill space. Initially, fillers were used to reduce the product cost. However, at present, fillers are used to improve many properties such as hardness, strength, resistance for wear, ability to process and in some cases, to improve the final product life. Therefore, filler selection highly depends on the product essential property. Fillers can be classified in different ways, as shown in following figure (Figure 2-1) [11].

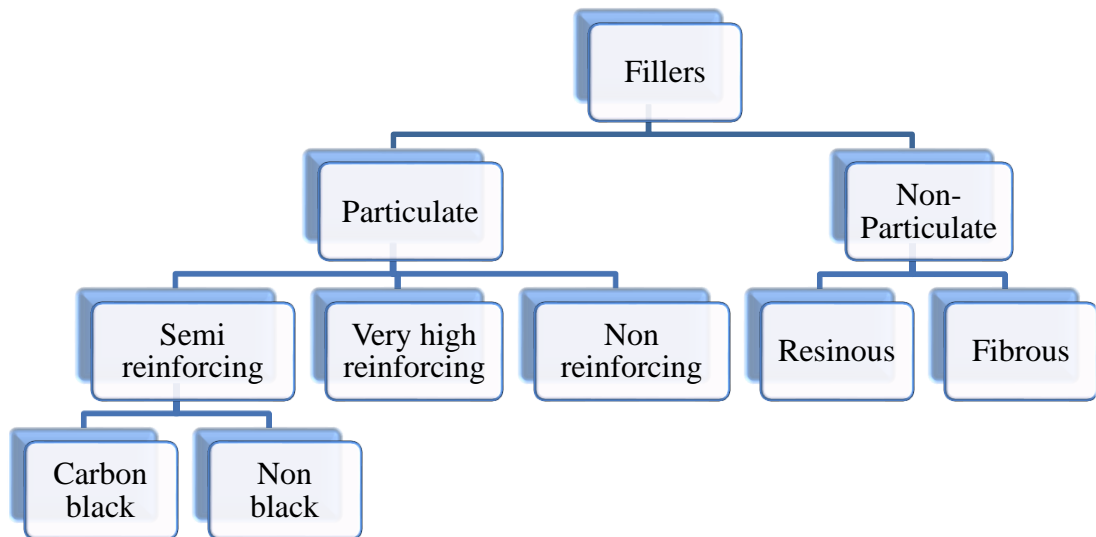


Figure 2-1: Filler classification

Filler properties depend on size of the particles, surface area, surface activity and shape of the particle. Combination properties of fillers with the elastomer depend on surface activities of both materials and the ability of elastomers to adhere to the fillers [3].

Smaller particles give, greater surface area for a given mineral concentration and therefore, effect of transfer of stress from elastomer to filler could be improved. Surface activity also called the bonding ability of the filler to matrix can be affected

by the compound's physical and mechanical properties. A general relation between filler particle size and reinforcement is given in Figure 2-2.

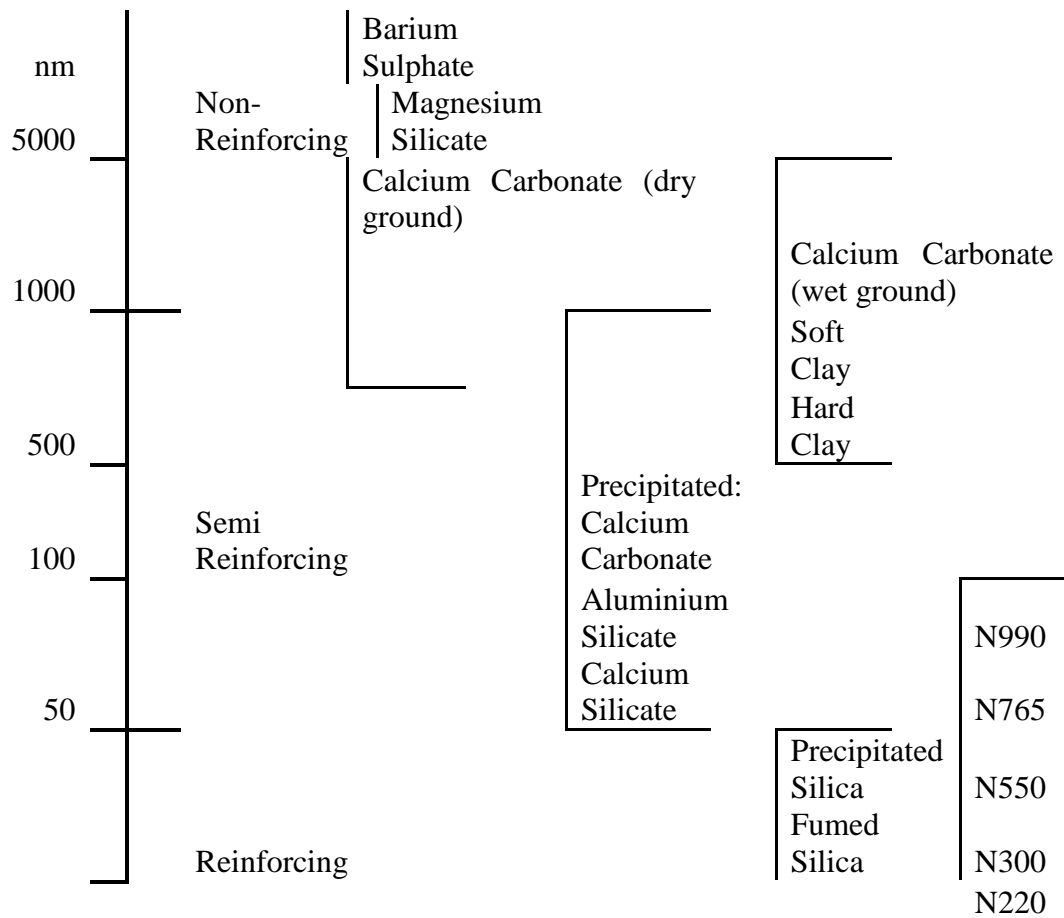


Figure 2-2: Filler classification considering particle size

Non-reinforcing fillers refer to fillers that unable to give any increment of the properties. Semi reinforcing fillers generally refer to the fillers with the ability for improvement of the tensile strength and tear strength of their composites, however. which unable to enhance the abrasion resistance. Reinforcing fillers which are the material which could improve all three properties, i.e. The tear strength, tensile strength and abrasion resistance [11]. Irrespective of their reinforcing ability fillers are categorised broadly into black fillers and non-black fillers (white fillers) as the colour of the product is directly depend on the colour of the filler particles.

Carbon black is the widely used black filler in the rubber industry while precipitated silica, fumed silica, alumina, clays, cellulose, magnesium carbonates and whitening fillers are known as non-black fillers [3].

### **2.1.1 Carbon black**

The powder form of carbon called Carbon black (CB). It contains a fluffy powder which is having the properties of extreme fineness, chemical stability larger surface area about 6-15 m<sup>2</sup> per gram. Incorporation of carbon black with rubber enhance the tensile strength, elastic modulus, fatigue life and abrasion resistance. Carbon black can be divided as furnace, channel, thermal, and lump black. That classification depends on its manufacturing method.

95% carbon black were made using furnace process. CB could be used as rubber reinforcing filler, black pigment and electrically conductive agent. Characters of particles like size, surface area, dispersion, shape, structure, surface activity and surface chemistry affect to the filler-elastomer reinforcement [3].

### **2.1.2 Silica**

Silica contains strong covalent bonds between silica and oxygen. Two types of silica are available for industrial use in the market. They are known as precipitated silica and fumed silica. Precipitated silica is manufactured by neutralization of sodium silicate solution by using concentrated sulfuric, carbonic acids or hydrochloric. Fume silica is produced by flame synthesis, includes combustion of silica molecules in liquid or vapour phase. Conditions for reactions are defined with respect to the required particle size. Silica doesn't have permanent structure. It consists of similar small primary particles. Due to hydrogen bonds between particles, silica clusters or aggregates forms. Structure of silica aggregates directly affected to reinforcement potential of the material. Precipitated silica has a three-dimensional network of agglomerates of primary silica particles. Those fillers can be divided into three groups called primary particles, agglomerates and aggregates. The lowest size particle is called primary particles and combining of those particles make a larger aggregate structure. Aggregates clustering or clumping need to procedure a larger



structure and it is called as agglomerates. The quality of SiO<sub>2</sub> fillers mainly defines according to specific gravity, oil absorption, particle size, and surface area [11].

Tires, shoes sole, and some rubber technical products, etc. are made using active silica. When compared with carbon black, silica could improve properties and gives the capability of making natural colored rubber products [11].

### **2.1.3 Alumina**

Alumina also called Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) is mostly used as engineering ceramics. Characteristics such as hardness, high stiffness, good wear resistance, high abrasion resistance, high compressive strength, good thermal conductivity affected to alumina's strong ionic interatomic bonding, extreme temperature resistance, high corrosive and environmental resistance show in alumina. Alumina are used in applications such as wear pads, seals or rubber applications which abrasion resistance and dimensional stability needed in high temperature [3].

### **2.1.4 Cellulose fillers**

Cellulose represents the main component of the plants like cotton and trees, which is the most available natural polymer. Due to properties like biodegradability, biocompatibility, availability in nature and low-cost, cellulose can be used for many applications such as coatings, packing, and papers. In the rubber industry, cellulose fiber is used as a reinforcement filler. Incorporation of these fibers into rubber phase improve strength, high stiffness and in solubility in water. The cellulose is used in many other applications such as cables, hose, belts, mats, and insulations [3].

### **2.1.5 Clay**

Clay could be considered as one of cheapest filler and has poor reinforcing capability due to higher particle size and less surface activity. Clay is used to reduce compound costs and to improve both physical and processing properties of the rubber compounds. According to the particle size and stiffening, clay can be graded as hard clay and soft clay. Hard clay reinforces rubber and imparts high tensile modulus, tensile properties, stiffness and abrasion resistance to the compounds. Soft clay

reinforces rubber imparts low physical properties. Clay particles are modified with silane coupling agents before added to rubber to improve the adhesive bond between clay particles and rubber, increased tensile modulus, tensile strength and improve the performance of rubber compounding [11].

### 2.1.6 Calcium carbonate

Calcium carbonate is divided into two groups, such as natural limestone (wet / dry) and precipitated calcium carbonate. Ground natural calcium carbonate contains low aspect ratio and low surface area. Those factors gave disadvantages like reduction property of adhesion between polymer & filler, abrasion and tear resistance. However, they could be used at more loading with slight harm to softness of compound, elongation and resilience of the compound.

Precipitated calcium carbonate is produced by controlled carbonization of a dilute solution of calcium hydroxide. It contains a higher surface area. Different crystal forms and crystal shapes can be achieved by changing concentration of reactions, temperature and time [11].

### 2.1.7 Fly ash

Fly ash is small particles exist in powder form. The fly ash consists of inorganic, incombustible matter present in the coal, percentages are given in Table 2-1 and Figure 2-3. Fly ash composition analysis was carried out at the Lakvijaya power station in Sri Lanka [12]. More than 20 fly ash samples were tested by using different shipments of Coal and, Coal was imported from South Africa.

Table 2-1: Percentage of composition in fly ash

| Composition    | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO | SO <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO | P <sub>2</sub> O <sub>5</sub> | TiO <sub>2</sub> | K <sub>2</sub> O | Na <sub>2</sub> O | MnO <sub>2</sub> | Undetermined |
|----------------|------------------|--------------------------------|-----|-----------------|--------------------------------|-----|-------------------------------|------------------|------------------|-------------------|------------------|--------------|
| Percentage (%) | 47.7             | 30.3                           | 7.7 | 4.1             | 3.7                            | 1.8 | 1.6                           | 1.6              | 0.7              | 0.2               | 0.1              | 0.5          |

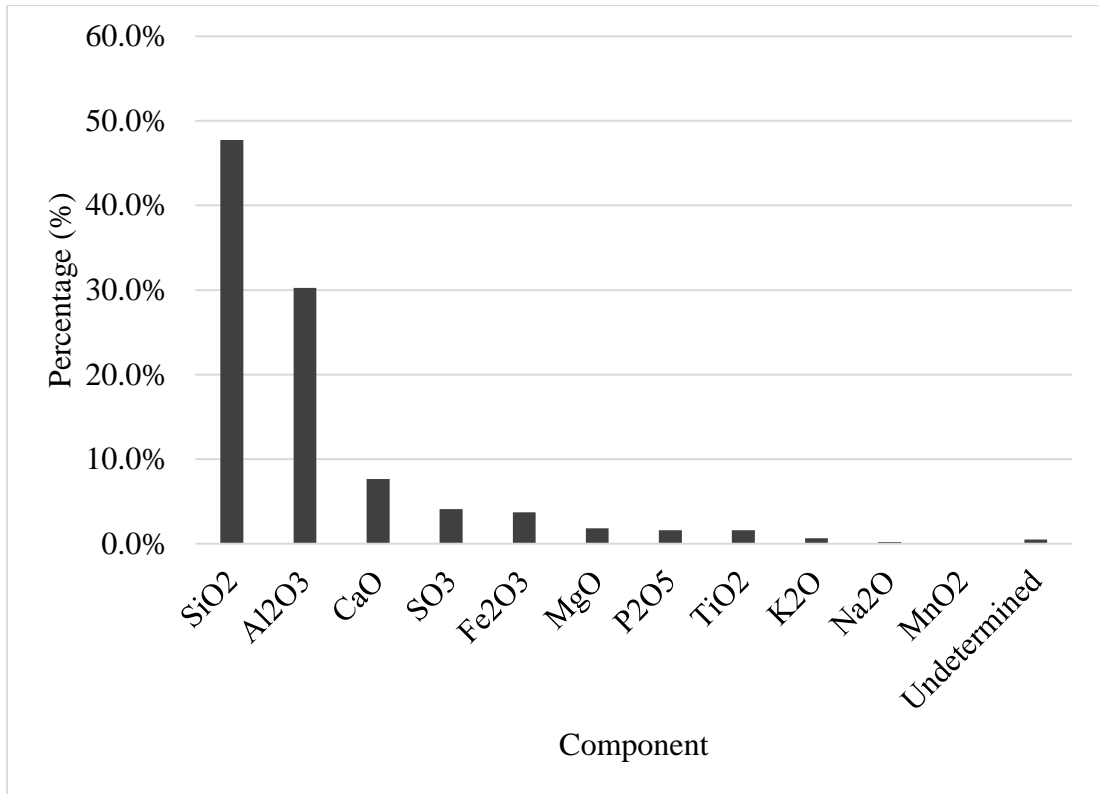


Figure 2-3: Composition of fly ash

### 2.1.8 Filler characterization

Filler characterization results could be used for selecting materials for rubber compounding by considering the required properties of the final product.

#### 2.1.8.1 Particle size distribution

One of basic property in filler characterization is particle size which influences the properties of rubber composites. Smaller particles support to increase reinforcement, abrasion resistance and enhance the tensile strength. However, fillers with finer particle sizes takes more mixing time and energy. To indicate the fineness level, filler surface area could be used. Fillers having larger particle sizes results the lower in cost. However, they offer poor reinforcement to the rubber composites. Like the average of particle size, the particle sizes distribution is also an important filler parameter. Particle size distributions directly influence the rubber properties. Particle size distribution can be narrow or broad or even bimodal.

### **2.1.8.2 Specific gravity (SG)**

The compound is a mixture of different materials with different chemical compositions, shapes, and sizes. Some are different phases of the same material. Each type of material could have different particle density. Therefore, when determining the particle density of fly ash, the average particle density of the combination of these materials was taken and could be adapted to a specific density.

### **2.1.8.3 Moisture content**

Moisture content in a filler is affected for rubber mixing, vulcanization process and product performances. High moisture availability of filler increases the energy requirement for mixing. Also, it creates a lot of difficulties for operators and introduces especially safety and product performance issues.

### **2.1.8.4 Porosity**

Porosity is a fundamental property of fillers. It could be influenced by the measurement of surface area providing a total surface area larger than the external value. Density of the aggregates is reduced with increase of porosity. That enables the rubber to load more fillers without changing specific gravity. It will result an enhance the modulus & conductivity of the compound in fixed filler percentage.

Fillers with above mention characteristics are incorporated with various natural rubbers: Solid tire industry mainly uses technically specified rubber.

## **2.2 Technically specified rubber (TSR)**

TSR (Technically Specified Rubber) is also referred to as a block rubber. Widely used industrial grades of TSR could be divided into four main types, which are TSR5, TSR10, TSR 20 and TSR50 Compound. TSR is classified based on several factors, such as ash content, dirt content, availability of volatile matters, color, and viscosity or portion of chemical contents, stearic acid, etc. Most of TSR producing country launches the same TSR standards following the international ISO standards. However, TSR is marketed in different names representing the country of

manufacture. For instance, STR (Standard Thai Rubber) uses for Thailand products, SIR (Standard Indonesia Rubber) symbol is used for Indonesian TSR and SMR (Standard Malaysia Rubber) used for Malaysian TSR [13]. Similarly, Sri Lanka produces SLR grades. TSR 20 is produced mostly from field coagulum or lower grade of the ribbed smoked sheet (RSS) and or unsmoked sheets. They offer outstanding performance in processing, physical properties and mechanical properties. It has reduced viscosity and better rubber mixing characteristics than ribbed smoke rubber. It helps to optimize the mixing time. Like in most of the other dry rubber product manufacturing applications, TSR is also filled with a variable filler types considering the application. Irrespective of the type of TSR or the application, filler dispersion in the matrix influences the final performance of the product. Therefore, filler dispersion needs to be considered for a better mixing.

### **2.3 Performance of fillers derived from agricultural and industrial waste in the rubber industry**

#### **2.3.1 Limestone dust waste as filler in natural rubber**

Pongdhorn et al studied the possibility to use of limestone dust waste as a filler in natural rubber. Initially, the basic properties of limestone dust were characterized. Limestone dust was mixed with natural rubber and compound properties were determined. In addition to limestone dust, precipitated  $\text{CaCO}_3$  and nanoprecipitate  $\text{CaCO}_3$  added compound samples were prepared and tested by them.

Limestone dust was little affected by the processability of the compound. Also, limestone was negatively affected by the mechanical properties of the compound such as tensile strength, tear strength and abrasion resistance of cured samples. According to Pongdhorn et al, with an increase in the filler loading, mechanical properties were weakened in limestone and precipitated  $\text{CaCO}_3$  added compounds. However, incorporation of Nano precipitated  $\text{CaCO}_3$  incorporated compounds has yielded better results with increasing the filler loading. It has been reported that reinforcement of rubber compound could not be achieved in limestone dust waste and precipitated  $\text{CaCO}_3$  due to low specific surface area when they are used as fillers.

Consequently, they could be used as a non-reinforcing filler. But nanoprecipitate  $\text{CaCO}_3$  acted as a semi-reinforcing filler since it has a greater specific surface area and improved the properties of its rubber vulcanizates to a certain level [14].

### **2.3.2 Ground rice-hull ash as a filler for rubber**

Haxo and Mehta studied the possibility to use of ground rice hull ash replacing carbon black (CB) as a filler for rubber. From their study, it has been found that ground rice hull ash can be used as filler for rubber which is moderately reinforcing. The process is a new burning process where a controlled burning process is used to make a composition of 85-90% amorphous silica and 10-15 % carbon. In that process, the most of organic compounds of rice hulls are removed and amorphous silica is kept intact. Resultant ash is then ground to obtain the fine particle in 0.1- 2.0  $\mu\text{m}$ .

An important property of this filler is not affecting the vulcanization characteristics and aging of rubber compounds adversely. Also, as this is mainly made of silica, it has a good capability to respond to the effects of silane coupling agents. In conclusion, they have shown that rice hull ash is a potential substitute for CB when used alone or partially [4].

### **2.3.3 Properties of rice straw filled standard Malaysian rubber**

Alnaid et al studied the standard Malaysian rubber which was used to determine the property change with adding rice straw. Two different sizes of rice straw were used by them. Rheological and physical properties have been analyzed.

According to the results, torque was increased in rice straw added samples. Alnaid et al described that it is due to the rice straw that can enhance the stiffness of the composite when added to the matrix. It was reported that scorch time also decreased because of the resistance exert on the rubber matrix mobility then vulcanize took fewer time to achieve the onset time of rice straw loaded vulcanizates with increase in the rice straw percentage.

In these experiments, with the rice straw loading and size, significant variations could be obtained in the swelling percentages. A higher swelling percentage was shown with the coarse size rice straw while fine size gave a lower value. As per the

study of Alnaid et al, there is a tendency to agglomerate, which results rise in the voids availability in rubber compounds. The results show that the rice straw loaded rubber resulted in better modulus, hardness, and crosslinking density and in reduction of physical properties(tensile, elongation at break) [5].

## **2.4 Performance of fly ash waste in non-rubber applications**

### **2.4.1 Use of Nano fly ash for enhancing properties of concrete**

Kodippili focused on the use of fly ash as a cement additive and the possibility to improve properties by using Nano level particle size of fly ash. The gravimetric determination was performed, and it shows 79% silica availability in fly ash. XRD analysis has confirmed the availability of minerals which are favorable for cement hydration reactions. Kodippili has replaced the cement in the mortar by fly ash in each stage of grinding by different percentages. According to Kodippili, grinding of fly ash alone was not a better way to produce the nano size fly ash particles, may be due to the agglomeration. Fly ash nanoparticles used samples did not show better results than large particles used samples, the same results were obtained. Early strength was increased in 225.5 nm particle used samples. Flexural and compressive strengths were reduced by increasing the percentage of fly ash. Flow properties of mortar were improved with adding fly ash to the mixer and optimum cement replacement by fly ash was 10% [15].

### **2.4.2 Sulfur absorbents for cleaning of flue gas**

To remove SO<sub>2</sub>, calcium hydroxide treated fly ash was tested and currently in use [16].

Properties of the fly ash is improved by unburned carbon left in the fly ash samples which is considered as the agent adding main surface area to fly ash. According to the study minerals should be removed efficiently from unburnt carbon of fly ash prior to the activation to have a better sample for gas phase environmental application [16].

Unburned fly ash has a capability to adsorb mercury. Amount of carbon in fly ash taken from the combustion of bituminous coals and coal blends with anthracites has a relationship with mercury content. Primary sites are absorbent centres in carbon surface. When an adsorbate molecule adsorbs on a primary site that molecule becomes a secondary centre to adsorb more molecules [16].

It has been observed that particle aggregated, and thermal activated fly ash shows better results in adsorption for toluene vapours [16].

### **2.4.3 Fly ash used for wastewater treatment**

Due to major chemical components such as alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon as well as physical properties such as porosity, particle size distribution and surface area fly ash can be used in wastewater treatment. fly ash has been widely used as a low-cost adsorbent for the removal of heavy metals, Inorganic component, Organic component and dyes [16].

## **2.5 Performance of fly ash used in rubber applications**

### **2.5.1 The use of fly ash fillers in rubber**

Rubber compounding, processing and physical properties of cured samples were tested with adding fly ash into natural rubber by Richard et al. They This study has evaluated the effect of fly ash, their loading and particle size with other fillers and without filler in the performance of their rubber composites.

In their study, Wallace's rapid plasticity test was done at 100 °C to compare the processing. According to results, fly ash filled compound was not giving any negative impact to flow properties. Oscillating Disc Rheometer (ODR) testing was carried out for curing characteristic evaluation and results show that  $M_L$  of fly ash added sample gave the minimum value which is indicating better processability. Fly ash added compounds and the non-fillers compound showed the same behavior on curing, no significant difference could be observed in  $T_{S2}$  and  $T_{90}$ .  $M_H$  value of fly ash added compound was increased by increasing fly ash pphr in their study. They



confirmed the cured rubber hardness is increased with increasing the filler percentage.

By using fillers in all-natural rubber samples tensile strength was decreased ~~in~~ according to their results. Tensile strength was reduced by increasing the fly ash percentage and increasing the fly ash particle size. Tensile strength of finer fly ash added compound has better resulted than the same of higher particle size fly ash added compounds and it is about 50% strong. Tear strength has been also reduced when adding fillers, but it has not been considerably affected either with the particle size or its percentage.

They have also evaluated the Elongation at the break when adding fillers with their percentage. It was also reduced by adding fillers and increasing the filler percentage. Finer particle added samples have shown better elongation at break results than higher particle size added compound samples. They have shown that Modulus of elasticity was also increased in filler added compounds than non-filler compound, but no change with particle size.

According to their study, addition of the fillers increases the hardness an increase of the filler loading. The density of fly ash added samples obtained lower compound density compared to other filler added compounds, due to lower relative density of fly ash [17].

### **2.5.2 Use of rubber and bentonite added fly ash as a liner material**

A set of test series with rubber and bentonite loaded fly ash was done in Cokca and Yilinaz's study. Conductivity in hydraulic, leachate analysis, unconfined compression, split tensile strength, one-dimensional condition, swell and freeze/thaw cycle tests were carried out to identify the properties of rubber samples and bentonite loaded fly ash. According to their study, overall results of bentonite and fly ash loaded rubber composite, were aligned with the required level of properties [18].

### **2.5.3 Fly ash filled Styrene-butadiene (SBR) based compounds**

Preparation and investigations were done for SBR based compounds with changing the fly ash content for the pneumatic tire was carried out by Xianjie. In his study, mechanical properties and adhesion of filled compounds were tested for a different kind of fly ash to study the influence of it. According to results, higher physical properties were shown in the smallest particle size used samples. Fly ash after ball mill treatment enhanced the rubber compound mechanical properties. Cure time was increased by adding fly ash to SBR based compound blend. The following were also observed in his study. Tensile strength was enhanced with partially replacing the silica by CB because of synergic effect and it was further improved by fly ash. The wet grip was improved in silica/fly ash/carbon black rubber compound blends. Bonding of brass coated steel and fly ash filled rubber compound was reduced compared to non-fly ash compound properties [19].

### **2.5.4 Development of fly ash filled rubber tiles**

Many types of research were done to check the possibility to use fly ash for rubber tile manufacturing, Nowadays rubber tile manufacturing added value especially for sidewalk pavements. Those tiles could reduce damage and replacement cost due to tree roots. Compare with cement concrete tiles, cost of fly ash filled rubber tiles were higher. Fly ash added pavement tiles were tested and confirmed the good properties.

Also, fly ash is used for many rubber applications like carpet manufacturing. Those studies have shown that some sired properties like improved wear resistance could be achieved in fly ash filled compounds at a cost of deterioration of some other properties of the composites [20].

Despite the above studies have shown the potential of the use of such fillers generated from various industrial applications, the solid tire industry still depends on the conventional fillers in their entire filler requirements. However, above studies found in literature suggests that fly ash too has a potential to use in solid tire applications. Therefore, it is worthwhile to study the potential of using fly ash in the

solid tire middle compound as a fully or partially replacement for the non-reinforcing fillers.

### **3. MATERIALS AND METHODOLOGY**

#### **3.1 Research plan**

The main objective of this study was to study the possibility of full or partial replacement of  $\text{CaCO}_3$  by fly ash in the solid tire middle compound. Two sets of experiments were carried out in this study. The first set of experiments was carried out using fly ash to identify the optimum  $\text{CaCO}_3$ /fly ash ratio that has the potential to use in solid tire middle compound. The second set of experiments was carried out using fly ash with reduced particle sizes and they were incorporated into a composite selected from the first set of experiments.

#### **3.2 Materials**

The main non rubber materials used were natural rubber, fly ash,  $\text{CaCO}_3$ , and other chemicals. As explained in the research plan, two experiment steps were carried out during this study. Therefore, the same raw material source was maintained to minimize the material property variations throughout all experiments. This action ensures the minimum influence of material quality variations on results. Different sets of experiments were carried out with raw materials of different batches from the same source. Ingredients used for this study comply with industrial grade and those used without further purification.

##### **3.2.1 Natural rubber (NR)**

Standard Thai Rubber (STR 20) was used as the base rubber material in the compound and it was imported from TI rubber Co. Ltd, Thailand. Technical specifications of STR 20 are listed in Appendix A.

##### **3.2.2 Fly ash**

Nearly 50kg of fly ash was collected from electrostatic precipitators from the Lakvijaya power station at Norochcholai, Sri Lanka.

### **3.2.3 Carbon black**

N 330 carbon black as the reinforcing filler and N 550 carbon black as a non-reinforcing filler was used in the preparation of the compound. Both carbon blacks were purchased from SKI Carbon Black (Pvt) Ltd, India.

### **3.2.4 Calcium carbonate**

CaCO<sub>3</sub> was used as a non-reinforcing filler in the compound. It was purchased from LANMIC Exports (Pvt) Ltd, Sri Lanka. The purity of the material 99%. Technical specifications of CaCO<sub>3</sub> are listed in Appendix B.

### **3.2.5 Activators**

Stearic acid was used as an organic activator and it was purchased from Pan century petrochemical Malaysia. Inorganic activator zinc oxide (99.5% purity) was supplied from Agromet Asia (Pvt) Ltd, Sri Lanka.

### **3.2.6 Protecting agent**

N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine(6PPD) and Polymerized 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ) antioxidants were used. Both materials were purchased from Shandong SunSine Chemical Co. Ltd, China.

### **3.2.7 Vulcanization agent**

Sulfur was supplied by Miwon Commercial Co., Ltd., Korea.

### **3.2.8 Pre vulcanization inhibitor**

N-(cyclohexyl-thio)phthalimide(CTP) was used as the pre vulcanization Inhibitor (PVI) to delay the initial stage vulcanization of rubber compounds. PVI was supplied from Flexsys, Malaysia.

### **3.2.9 Accelerator**

N- Tert-butyl-benzothiazole sulphonamide (TBBS) was the accelerator and it was purchased from Flexsys, Malaysia.

### **3.3 Characterization of Fly ash and CaCO<sub>3</sub>**

#### **3.3.1 The particle size distribution of fly ash and CaCO<sub>3</sub>**

The particle size distribution of fly ash and CaCO<sub>3</sub> samples were analyzed by using Beckman Coulter LS 13 320 particle size analyzer at Camso Loadstar, Sri Lanka according to ISO 13320. The aqueous liquid module was used to analyze the samples and particle size distribution are given as volume fraction against the particle size diameter.

#### **3.3.2 Morphology of fly ash and CaCO<sub>3</sub>**

Morphology of fly ash and CaCO<sub>3</sub> samples were studied using a Zeiss EVO 18 scanning electron microscope at the Department of Material science and Engineering at the University of Moratuwa.

#### **3.3.3 Thermogravimetric analysis (TGA) of fly ash and CaCO<sub>3</sub>**

Thermogravimetric analysis (TGA) was used to characterize fly ash and CaCO<sub>3</sub> according to ASTM D6370. TGA Q500 V20.13 build 39 analyzers at Camso Loadstar, Sri Lanka was used. Nitrogen gas was purged at 75 cm<sup>3</sup> per minute rate and the pan was heated to 50 °C and allowed the instrument to equilibrate for 2 minutes. The sample was heated from 50 to 560 °C. Then, the sample was cooled down to 300°C and allowed the temperature to equilibrate for 2 minutes. Purge gas was changed to oxygen at 75 cm<sup>3</sup> per minutes and the test was continued from 300 to 800 °C.

#### **3.3.4 Specific gravity (SG) of fly ash and CaCO<sub>3</sub>**

The bottle method was used to determine the specific gravity of fly ash by using the Specific Gravity Flask (Le Chatelier). According to ASTM C128. Kerosene was taken as the medium.

### 3.3.5 Sieve analysis of fly ash

Sieve analysis was carried for fly ash to narrow down the particle size and distribution at the Department of Material Science and Engineering at the University of Moratuwa, Sri Lanka by using 8 (53-700  $\mu\text{m}$ ) sieve sizes.

### 3.4 Rubber compounding

Atypical solid tire middle compound formulation was taken to study the cure characteristics, mechanical and thermal properties of the compound. Rubber compounding was carried out in two stages.

- 1<sup>st</sup> stage-Rubber mastication and adding fillers, antioxidants, activators.
- 2<sup>nd</sup> Stage - First stage compound mixed with curing agents, accelerators, retarders

#### 3.4.1 First stage mixing

Rubber mastication, incorporation of fillers and mixing of first stage compounding ingredients were carried out using a Farrel BR1600 Banbury® Mixer. Further mixing and compound sheeting were carried out on a two-roll mill at Camso Loadstar, Sri Lanka. The formulation used in this stage is given in Table 3-1.

Table 3-1: First stage mixing recipe

| Function                | Material                         | pphr  |
|-------------------------|----------------------------------|-------|
| Rubber                  | STR 20 (Thai Hua)                | 100.0 |
| Reinforcing filler      | N 330                            | 15.0  |
| Semi-reinforcing filler | N 550                            | 20.0  |
| Non-reinforcing filler  | CaCO <sub>3</sub> and/or fly ash | 60.0  |
| Organic activator       | Stearic acid                     | 2.0   |
| Inorganic activator     | Zinc Oxide 99.5 %                | 4.5   |
| Antioxidant-1           | 6-PPD                            | 1.5   |
| Antioxidant-2           | Vulkanox HS (TMQ)                | 1.0   |

Fly ash content was varied from 0 - 60 pphr to investigate the properties of compounds in the first set of experiments. The total loading of non-reinforcing fillers

was kept constant at 60 pphr. Compositions of inorganic filler system are given in Table 3-2. CaCO<sub>3</sub> 60 pphr sample was considered as Control.

Table 3-2: Content of non-reinforcing filler in recipe

| Material\ Sample         | Control | FA15 | FA30 | FA45 | FA60 |
|--------------------------|---------|------|------|------|------|
| CaCO <sub>3</sub> (pphr) | 60      | 45   | 30   | 15   | 00   |
| fly ash (pphr)           | 00      | 15   | 30   | 45   | 60   |

Selected inorganic filler composition was used in the second set of experiments to study the effect of reduced particle size and distribution on properties of the compounds. Reduced particle size ranges of the fly ash were (0-53) μm and (53-106) μm. Particle size was reduced to match with the CaCO<sub>3</sub> filler.

The maximum temperature was maintained below 140 ± 5 °C during the first stage mixing process. Rotor speed was maintained at 100-120.5 rpm throughout the mixing cycle in the Banbury mixer. The same mixing cycle shown in Table 3-3 was used, and the total mixing time was kept at 215 minutes for all batches.

Table 3-3: Mixing cycle of 1<sup>st</sup> stage compound

| Time (second) | Description  |
|---------------|--|
| 0             | TSR  |
| 30            | fly ash + CaCO <sub>3</sub> + N 330 + N 550 + Chemical |
| 50            | Ram Sweep-1  |
| 45            | Ram Sweep-2  |
| 90            | Dump @ 140 ± 5 °C                                      |

After completing the first mixing cycle compound lump was dumped on a two-roll mill to prepare a compound sheet to easy cooldown and eliminate the scorching. Compound sheets were kept for 24 hours for maturation before the second stage mixing.



### 3.4.2 Second stage mixing

The Banbury mixer and the two-roll mill used in the first stage were used for the second stage mixing. The compound ingredients listed in Table 3-4 were mixed with the compound sheets obtained in the first stage mixing at the ratios shown in the table.

Table 3-4: Second stage compound mixing the recipe

| Function                    | Material                       | PPHR   |
|-----------------------------|--------------------------------|--------|
| Rubber with chemicals       | 1 <sup>st</sup> stage compound | 204.00 |
| Vulcanizing agent           | Sulfur                         | 1.60   |
| Accelerator                 | TBBS                           | 2.00   |
| Pre vulcanization inhibitor | CTP                            | 0.08   |

Rubber compound lump was then dumped on a two-roll mill and was sheeted out. They were used to prepare the test specimen and vulcanizates for further studies.

### 3.5 Preparation of samples

Lab Tech lab press was used to vulcanize the test samples under the specific pressure at 4.5 bar following the according to ASTM D3182 standard. The test specimen was cured at  $150 \pm 2$  °C for respecting optimum cure time.

### 3.6 Sample testing

#### 3.6.1 Moving die rheometer (MDR)

MonTech MDR 3000 was used to measure the cure characteristics. Nearly 5mg of the test specimen was used for the test. Die oscillates at 0.5 degrees arc and 100 Revolutions per minute (rpm)for 30 minutes according to ASTM D 5289.

#### 3.6.2 Rebound resilience

FRANK Prufge rate GmbH rebound tester was used to test the rebound resilience of the vulcanizates which indirectly indicate the hysteric of the compound. It is a Schob type pendulum rebound device that evaluates impact resilience and

penetration of rubber by pendulum rebound. Direct measurements were taken under ASTM D7121 using a 70 mm diameter and 12.5 mm thickness samples.

### **3.6.3 Specific gravity**

Alfa Mirage MD 300S Electronic Densimeter was used to determine the specific gravity of the all vulcanizates during the experiment. Archimedes' principle is the measuring method under ASTM D 297, and it gives a direct measurement.

### **3.6.4 Physical properties**

The Geotech tensile machine (GT-7010-AE) was used to measure and calculate the physical properties of the samples. The thickness of the sheet was 2 mm and it was vulcanized using a curing press. dumb-bell shaped samples were cut by standard die cutters according to ASTM D412-A (Die C). 24 hours maturing time under room temperature was used and tests performed at room temperature.  $500 \pm 50$  mm/min strain rate was followed during the test. Tensile strength, 300% modulus, and Elongation at break % were calculated by using the following procedure and results obtained from tensile testing.

- Tensile strength =  $F/A$
- 300% modulus =  $F'/3A$
- Elongation at break % =  $(L-L_0)/L_0$

Where;

F -Breaking Force                      A - Initial Cross-sectional area

$L_0$  – Initial length                      L – Length at break

F' - Force at 300% elongation

### **3.6.5 Hardness**

Resistance to the indentation of rubber samples was measured by using the BAREISS (Germany) durometer hardness tester. ASTM D2240 test procedure was

followed to measure the hardness of test samples and Shore A was the unit of the measurement.

### 3.6.6 Dispersion

The dispersion of fillers in the compounds was studied using a DisperGRADER Alpha View available at Camso Loadstar, Sri Lanka following ASTM D7723.

Dispersion is mainly discussed under two aspects considering different factors. Y value and Dispersion percentage.

Y-Value

The value obtained from results ranges from 1 to 10. 10 represents the total absence of agglomerates with a diameter of 23µm or large while 1 represent a large number of agglomerates corresponding to 19% of the test area [21].

$$Y = 10 - 9 \times \frac{N_w}{0.19 \times N_{tot}}$$

Equation 1: Calculation of Y-value in dispersion

$N_w$ – number of white pixels in the image of the test area due to nodules with an average diameter of 23µm or larger caused by underlying agglomerates

$N_{tot}$ –Total number of pixels in the image of the test area

Dispersion%

$$\text{Dispersion\%} = 100 - \frac{100}{\text{Sum of all image pixels}} \times \text{sum of all agglomerate pixels}$$

Equation 2: Calculation of dispersion %

That can be applicable for whole agglomerates size ranges from 2 to 62µm [21].

### **3.6.7 Tearing**

The Geotech tensile machine (GT-7010-AE) was used for the testing. ASTM D624 standard method was followed. 2 mm thick sheet was used to cut the crescent-shaped tear samples according to specimen type C. Width of the specimen was measured, and a specimen was loaded into the tensile grip. Testing was done by separating the tensile grips at a speed of  $500 \pm 50$  mm per minute. The maximum force at the break was recorded.

### **3.6.8 Dynamic properties**

The temperature of the sample is increased due to the cyclic load and due viscoelastic properties of rubber. The temperature difference of the sample is taken as heat build-up measurement. Time taken to blow the sample due to heat generation is taken as blow out time

#### **3.6.8.1 Heat build-up**

GABOMETER® 2000NE flexometer was used to measure the heat build-up of the vulcanizates with conditioned 30 minutes at 100°C. Samples were tested for 30 minutes at 100°C with giving sinusoidal compression load under ASTM D623. The test was conducted with 30 Hz and a 1 MPa static load, with using 4.45 mm dynamic stroke. The temperature rise of the vulcanizates was measured as heat build-up.

#### **3.6.8.2 Blow out**

BF Goodrich flexometer TECHPRO was used to test the blow out time of the vulcanizates. The static load is raised to 2 MPa and the same operating condition stated in Section 3.6.8.1 was maintained. The vulcanizate was blown due to heat generation and time taken to blow was the blow out time.

#### **3.6.8.3 Viscoelastic properties**

The dynamic mechanical analysis was carried out to study the viscoelastic behavior of vulcanizates using a DMA<sup>+</sup>100MetraVIBdynamic mechanical analyzer at Camso Loadstar, Sri Lanka under temperature sweep (from 30°C to 100 °C) at 1Hz.

Dynamic Mechanical Analysis (DMA) method is used to determine the compound viscoelastic properties. Sinusoidal strain or stress or is given as the input and stress or strain is measured as the output respectively. Because in strain for viscoelastic material phase delay could be observed due to damping [22].

Frequency sweep, Temperature sweep, and Strain sweep - Shear modes are used to conduct the testing and the following results can be obtained.

- $E'$  - storage modulus or elastic modulus
- $E''$  - loss modulus or viscous modulus
- $\tan \delta(E''/E')$  - the ratio of loss modulus to storage modulus

## 4. RESULTS AND DISCUSSION

In this section, characteristics of  $\text{CaCO}_3$  and fly ash are first presented. Secondly, the cure characteristics, physical, mechanical and dynamic properties of the first set of  $\text{CaCO}_3$ /fly ash filled rubber compounds are discussed. Finally, the properties of the rubber compounds filled with reduced fly ash particles are discussed.

### 4.1 Characterization of fly ash and $\text{CaCO}_3$ filler particles

#### 4.1.1 The particle size distribution of fly ash and $\text{CaCO}_3$

Particle size distributions of fly ash and  $\text{CaCO}_3$  particles are shown in Figure 4-1 and Figure 4-2, respectively. Particle diameters of fly ash were distributed in the range of 0.1– 300  $\mu\text{m}$  with a mean value of 51.89  $\mu\text{m}$ . Particle diameters of  $\text{CaCO}_3$  were distributed in the range of 0.1– 50  $\mu\text{m}$  with a mean value of 6.01  $\mu\text{m}$ .

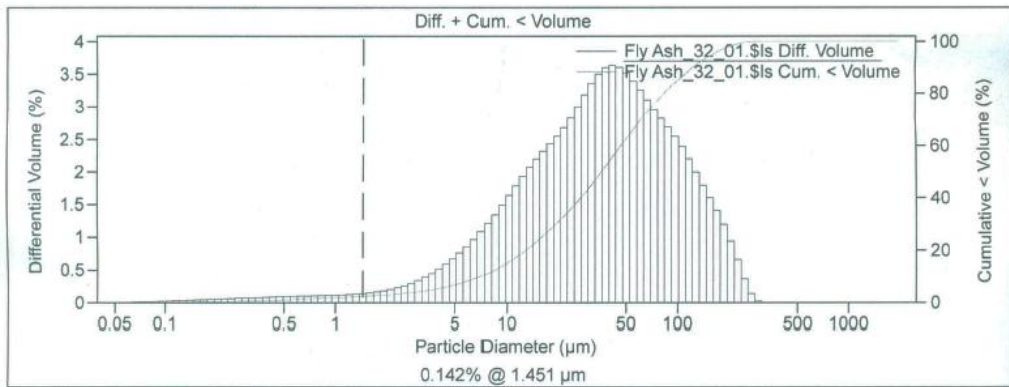


Figure 4-1: Particle size distribution of fly ash

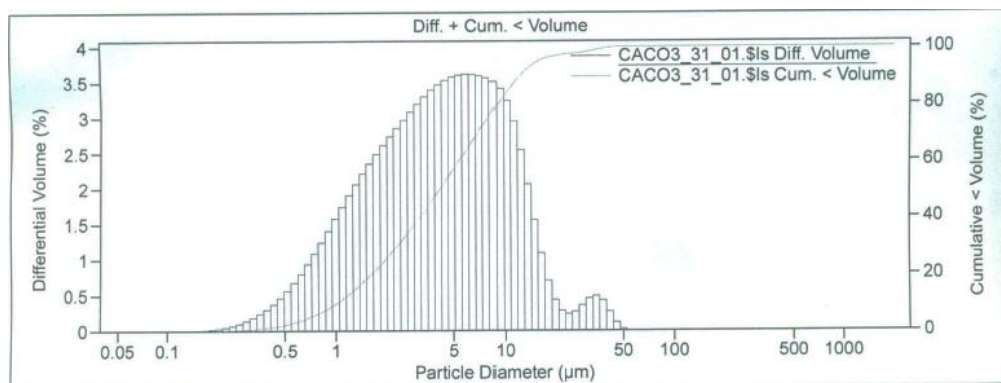


Figure 4-2: Particle size distribution of  $\text{CaCO}_3$

Fly ash shows a broader particle size distribution shifted towards the higher diameter side, whereas  $\text{CaCO}_3$  shows a narrower distribution shifted towards the lower diameter side.

Cumulative volume percentages of fly ash and  $\text{CaCO}_3$  particles at different diameter ranges are presented in Figure 4-3. It could be seen that fly ash particles are significantly larger compared to the  $\text{CaCO}_3$  particles. Therefore, it is expected that fly ash has a much lesser reinforcing effect than the  $\text{CaCO}_3$  in their rubber composites. There is a possibility to select the fly ash with reduced particle sizes in order to improve the performance. The particle size distributions of the selected two grades of fly ash with reduced particle size are shown in Figure 4-4 and Figure 4-5.

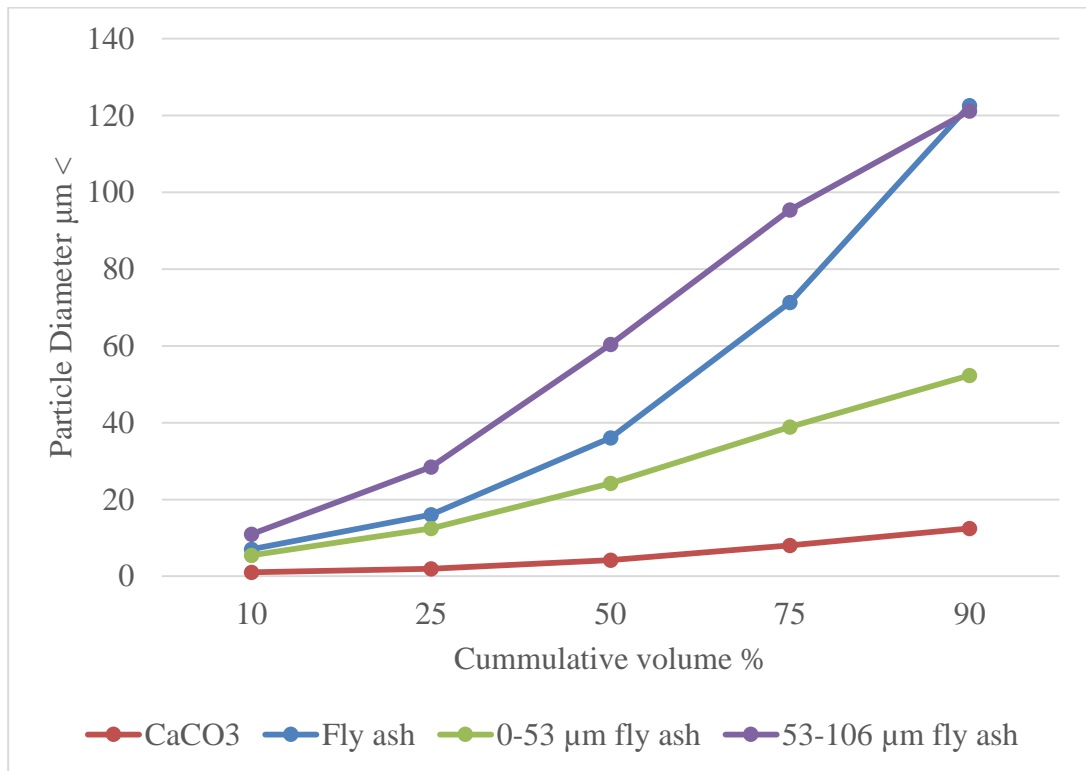


Figure 4-3: Volume % vs Particle Diameter

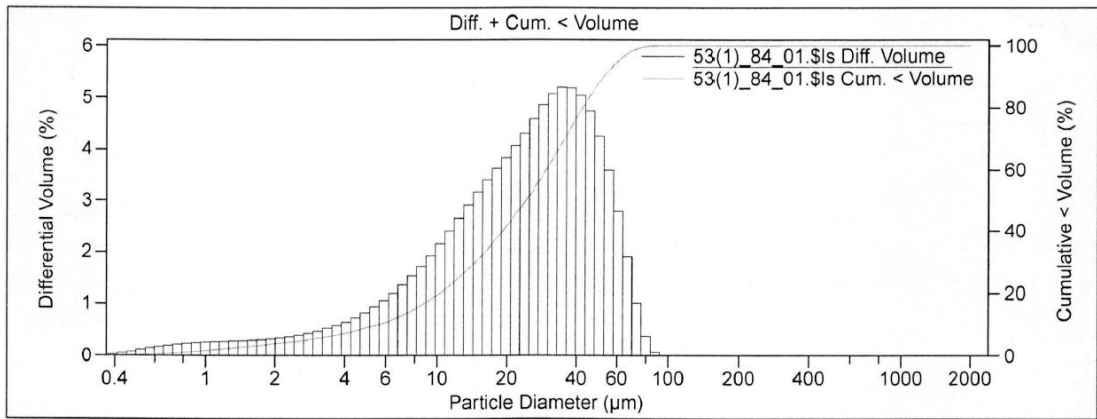


Figure 4-4: Particle size distribution of 0-53 μm fly ash

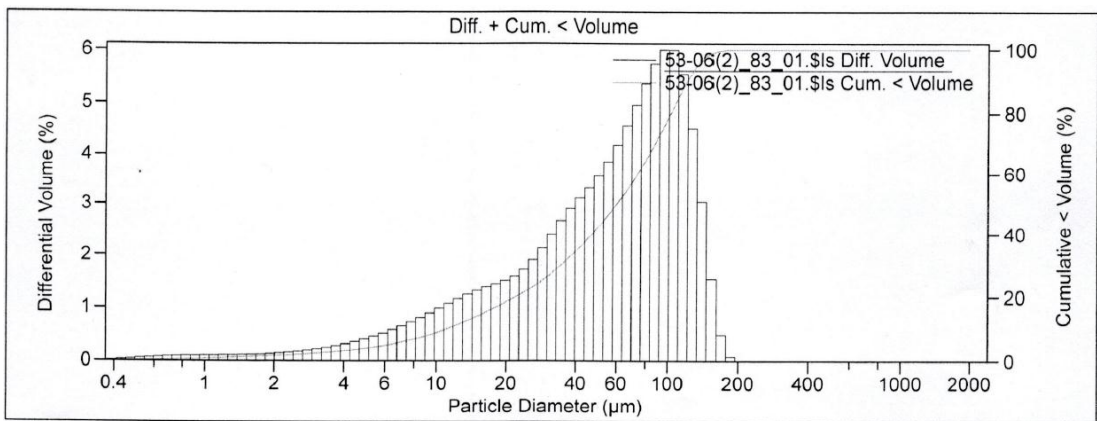


Figure 4-5: Particle size distribution of 53-106 μm fly ash



#### 4.1.2 Morphology of CaCO<sub>3</sub> and fly ash particles

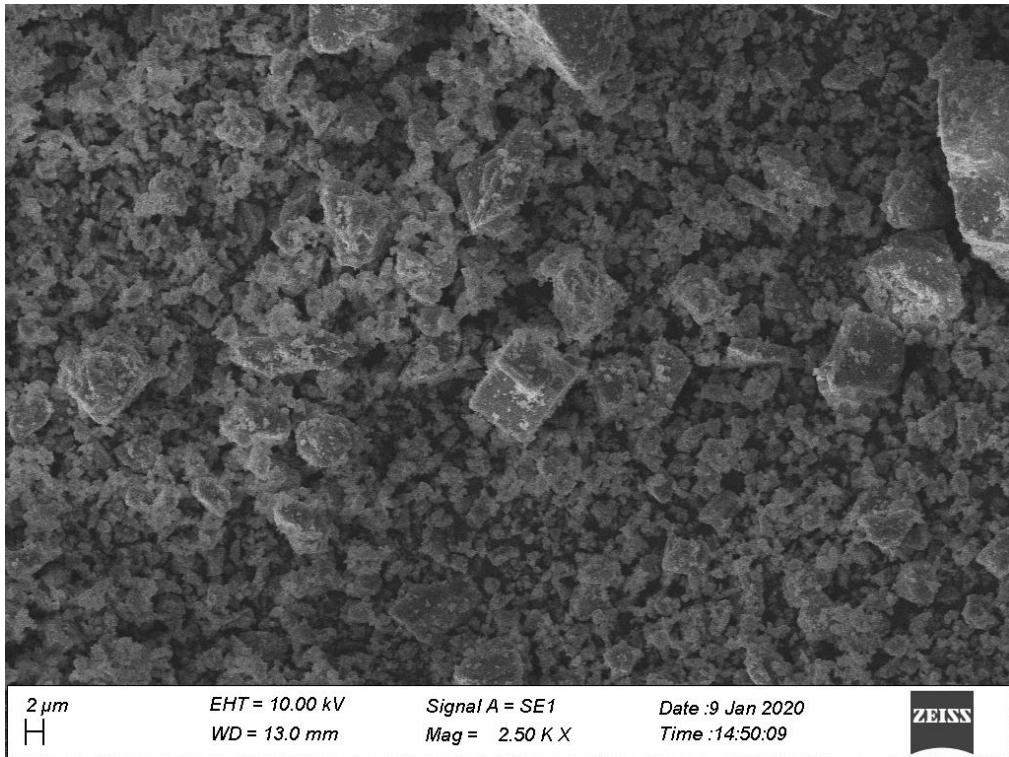


Figure 4-6: SEM image of calcium carbonate (magnification: 2.5 K)

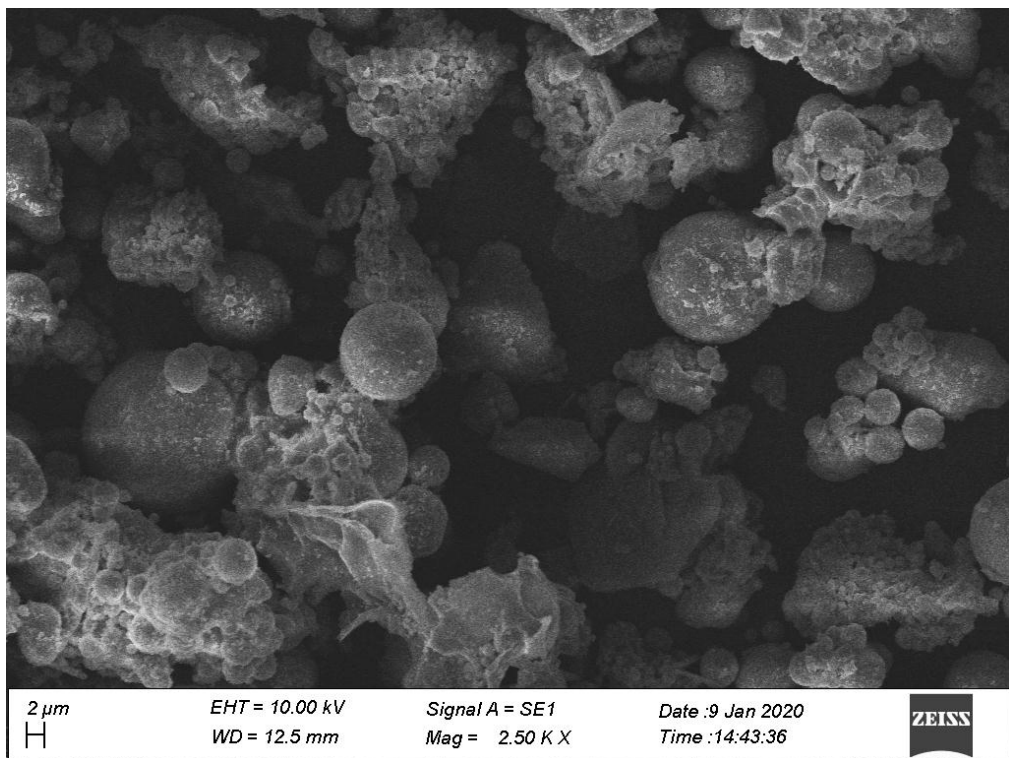


Figure 4-7: SEM image of fly ash (magnification: 2.5 K)

Scanning electron microscopic images of  $\text{CaCO}_3$  and fly ash particles are shown in Figure 4-6 and Figure 4-7 respectively. SEM images show that fly ash particles are spherical and have a wider particle size distribution as revealed by the particle size distribution analysis (Figure 4-1). Further, it could be seen that fly ash particles have a higher tendency to form agglomerates than the  $\text{CaCO}_3$  particles, which has an irregular shape and crystal type narrow particle size distribution.

#### 4.1.3 Thermogravimetric analysis (TGA)

The thermogram of fly ash is shown presented in Figure 4-9. Weight loss of 0.75% was registered at 100 °C probably due to the removal of reabsorbed moisture. There is another 1.3% weight loss at 600 °C indicating and evolution of remaining volatile constituent from the fly ash. As further heating it gives a horizontal line indicating that fly ash consists of 92.82% inert materials (such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc.) and removal of all volatile materials. Thermogravimetric analysis of fly ash reported in literature shows similar characteristics however with different quantities with volatile and inert materials [23, 24]. Therefore, TGA analysis of fly ash suggests that pre-drying of fly ash is essential when they are used as filler in preparation of rubber composites.

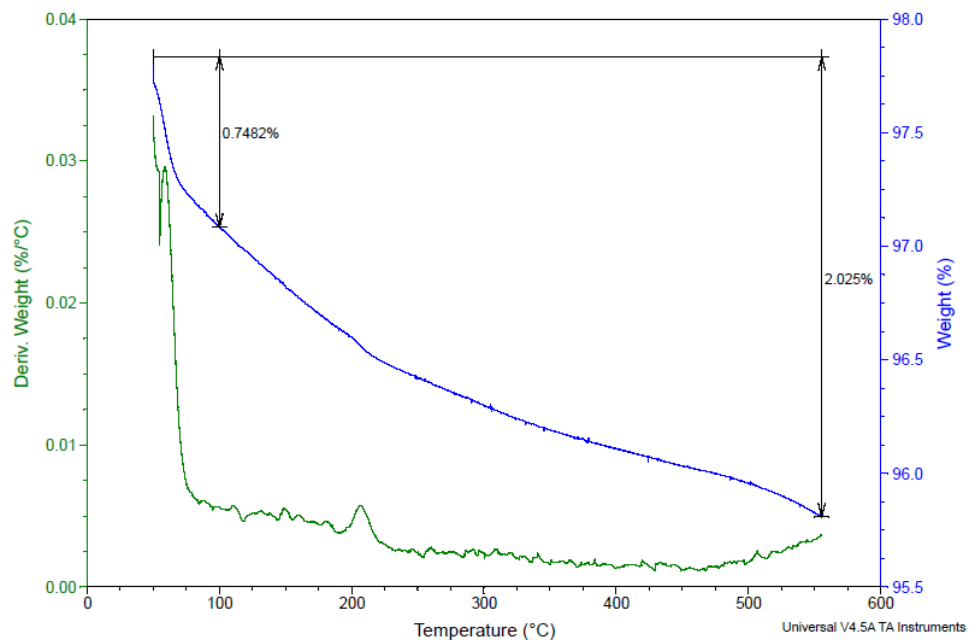


Figure 4-8: TGA graphs of fly ash in  $\text{N}_2$  medium

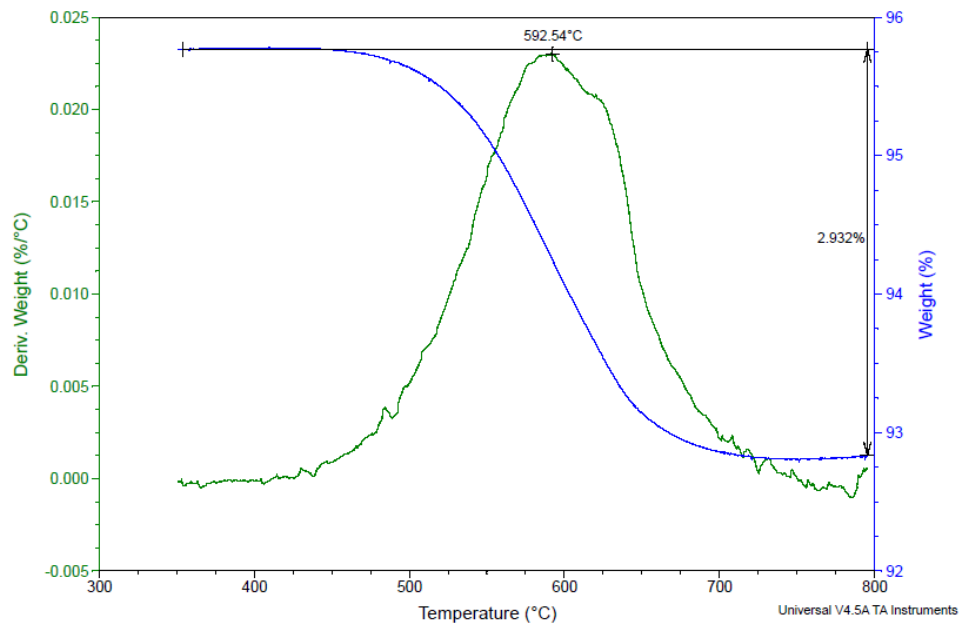


Figure 4-9: TGA graphs of fly ash in O<sub>2</sub> medium

Similar to the fly ash, CaCO<sub>3</sub> also contains predominantly inert materials as shown in the thermogram of CaCO<sub>3</sub> which is presented in Figure 4-10. However, unlike in fly ash, CaCO<sub>3</sub> does not contain volatile constituents and therefore, processing difficulties associated with moisture could not be occurred [25]. However, both fillers show their major decomposition temperature beyond 600 °C qualifying both materials as fillers for the manufacture of rubber products.

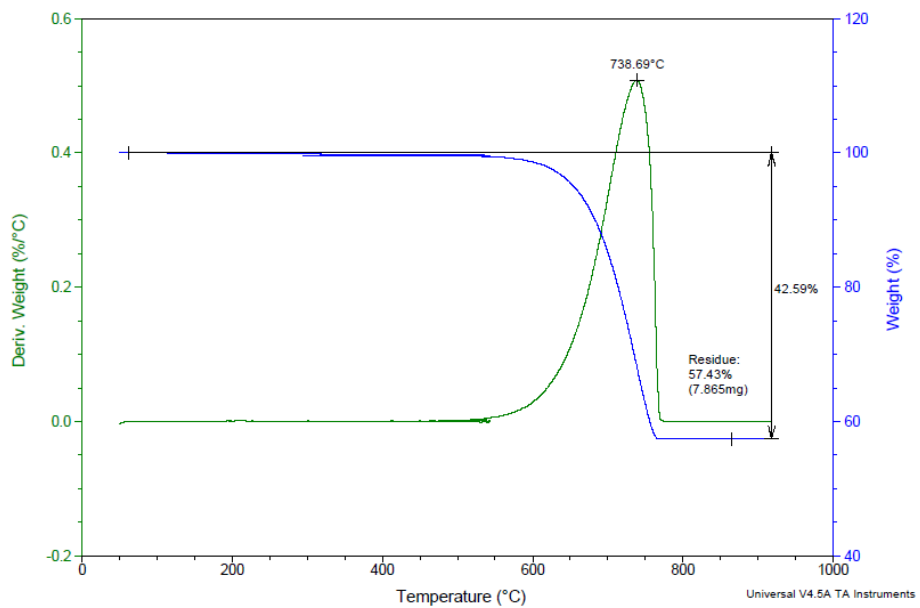


Figure 4-10: TGA graph of CaCO<sub>3</sub> in N<sub>2</sub> & O<sub>2</sub> medium

Final lower values registered for TGA analysis of the composites under oxygen environment inferred that both filler types have a portion of oxidisable materials.

#### 4.1.4 The specific gravity of CaCO<sub>3</sub> and fly ash

The specific gravity of fly ash and CaCO<sub>3</sub> were determined using the bottle method as explained in Section 3.3.4 was 1.99 and 2.71, respectively. Therefore, it could be inferred that rubber products made of fly ash filled natural rubber offers an economic advantage and product weight benefits due to reduction of required rubber weight to fill the tire volume.

## 4.2 Properties of fly ash filled rubber compounds/vulcanizates

### 4.2.1 Rheological properties

The rheological properties of fly ash filled compounds are shown in Table 4-1.

Table 4-1: Effect of the fly ash loading on rheological properties

| Property \ Sample (fly ash pphr)        | Control | FA15  | FA30  | FA45  | FA60  |
|---|---------|-------|-------|-------|-------|
| Maximum Torque (M <sub>H</sub> ) (dN m) | 27.6    | 26.06 | 24.51 | 24.11 | 22.82 |
| Minimum Torque (M <sub>L</sub> ) (dN m) | 1.5     | 1.49  | 1.68  | 1.86  | 2.14  |
| Scorch Time (t <sub>s2</sub> ) (m:s)    | 4.28    | 4.3   | 4.33  | 4.34  | 4.29  |
| Cure Time (t <sub>90</sub> ) (m:s)      | 9.32    | 9.25  | 9.38  | 9.34  | 9.28  |

Maximum Torque (M<sub>H</sub>) has exhibited a decrease with an increase in the fly ash loading in the compounds. As discussed earlier, the particle size distribution of CaCO<sub>3</sub> is in the narrower range than that of the fly ash particles. Despite both materials are inactive at the processing temperature, larger particle size i.e. lower surface area leads to a reduced Van der Waals forces between filler particles and the rubber matrix. Consequently, a decrease in filler-rubber interactions could be expected as the fly ash percentage increase in the filler system. This justifies the reduction in M<sub>H</sub> with the fly ash loading. The same behavior has been observed by

Mohd Nor and Othman in their study on the effect of filler loading on curing characteristics of natural rubber nanocomposites [26].

Minimum torque ( $M_L$ ) values are same for the Control and FA15 compound beyond which it increased with the increase of fly ash loading. This may be due to the resistance exerted by the increased level of larger size fly ash particles available in the uncross-linked rubber matrix at low temperatures [17]. However, this increment is not significant and maintains within the recommended range (1.5-3.5 dN m) for all compounds.

Cure time and scorch time of the compounds show similar values as shown in Table 4-1. This might be due to the neutral role played by the fly ash in the curing process as similar to  $\text{CaCO}_3$  filled rubber compounds. In general, silica-based fillers contain hydroxy groups which lead to retardation of curing reactions. Therefore, according to curing characteristic results, it suggests the unavailability of such active groups in fly ash used in this study. The unavailability of reactive groups in the fly ash is already confirmed by the TGA studies. Besides, this observation it is inferred that the difference in particle size of the fillers has no impact on the cure time, despite fillers having low surface area could accelerate the curing process (Ishak et al) [6]. In other words, fly ash particles cannot adsorb accelerators leading to a reduction in cure rate. Further, the above observations confirm that both  $\text{CaCO}_3$  and fly ash has no impact on the vulcanization process and therefore, use of fly ash no negative impact on the production rate of fly ash-based rubber products.

## **4.2.2 Mechanical properties**

### **4.2.2.1 Tensile strength**

The effect of the tensile strength of the vulcanizates as a function of total filler loading is graphically presented in Figure 4-11.

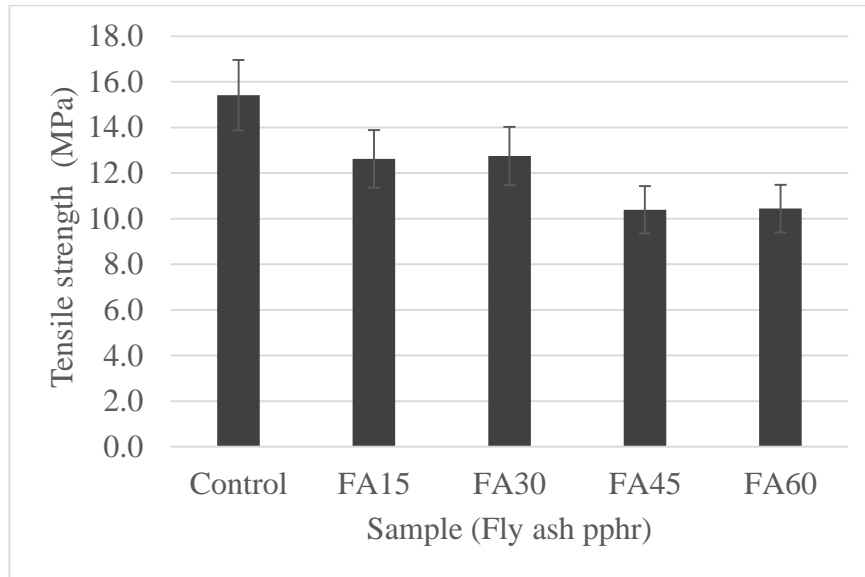


Figure 4-11: The effect of fly ash loading on the tensile strength

Tensile strength is significantly reduced with the replacement of 15 pphr  $\text{CaCO}_3$  from fly ash. Bidkar et al have reported that the incorporation of fly ash and  $\text{CaCO}_3$  at low filler loading (up to 40 pphr) increases the tensile strength until an optimum loading registered, beyond which tensile strength is decreased in their studies on fly ash and  $\text{CaCO}_3$  filled chloroprene rubber [27]. Therefore, it could be inferred that the filler loading used for this study has exceeded that optimum limit for the system or the filler surface characteristics are different depending on the source. It has also been shown that  $\text{CaCO}_3$  filled vulcanizates registered the higher tensile strength than the fly ash filled once at the same filler loading (control and FA60). This reduction corresponding to fly ash filled vulcanizates has been explained by the surface silanol content, adsorbed water level and higher surface area of the filler particles. Therefore, the observed significant decrease in the tensile strength with 15 pphr replacement of  $\text{CaCO}_3$  could be attributed to the above-mentioned factors. Further replacement of  $\text{CaCO}_3$  with fly ash has also shown a gradual decrease in tensile strength. This may be due to the agglomeration of fly ash filler particles with increasing particle loading forming stress concentrating centers. However, tensile strengths of vulcanizates filled with fly ash loading up to 30 pphr loadings are still higher than the minimum specifications required for a solid tire middle compound. Tensile strength reduction may be due to the larger size of the fly ash loading in the

rubber compound. Beside this, poor interaction between filler particles and rubber due to incompatibility between fly ash and polymer matrix may also be caused to this reduction as suggested by the work carried out by, Kahlid et al and Saban Bulbul et al in their studies [28, 29].

#### 4.2.2.2 Modulus<sub>300%</sub>

According to the results presented with accepting 10% error variation in Figure 4-12, it could be seen that modulus of the vulcanizates show a slight increment up to 30 pphr fly ash loading beyond which a reduction of the modulus value is registered. Natural rubber is a material that could undergo a strain-induced elongation. Strain-induced elongation is also one of the factors which positively affect the modulus (at comparative strain). Particle size distribution and uniform filler particle dispersion are the filler related factors that affect the modulus. Filler distribution studies (will be discussed later) have shown that beyond 30 pphr of fly ash loading, filler agglomeration could be observed. When the filler related factors are considered, at high filler loading, all the above factors weaken the filler-matrix adhesion causing a reduction in the modulus of the vulcanizates. The same behaviour has been observed by Richard et al who studied the use of fly ash filler in rubber vulcanizates [17].

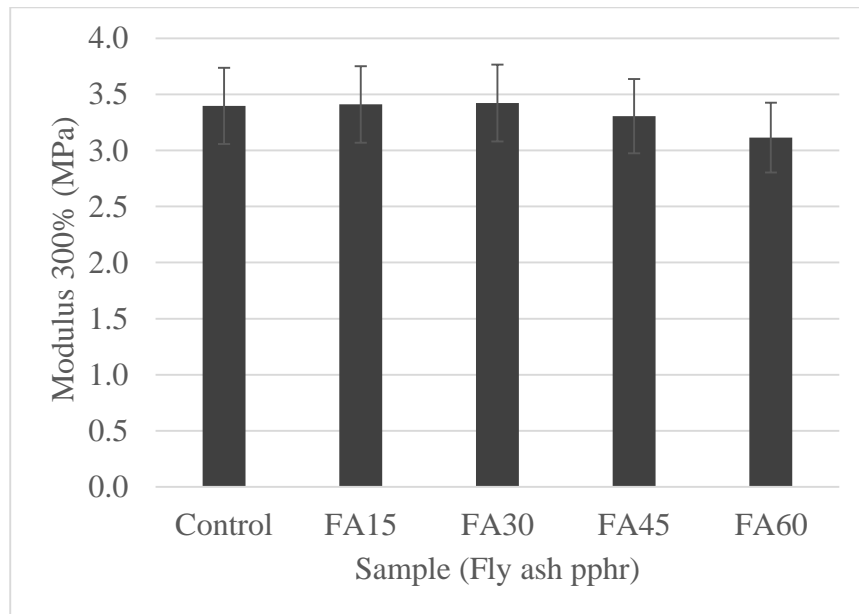


Figure 4-12: The effect of fly ash loading on the modulus

### 4.2.2.3 Elongation at break

As shown in Figure 4-13, elongation at break decreases with an increase in the fly ash loading similar to the trend observed for tensile strength.

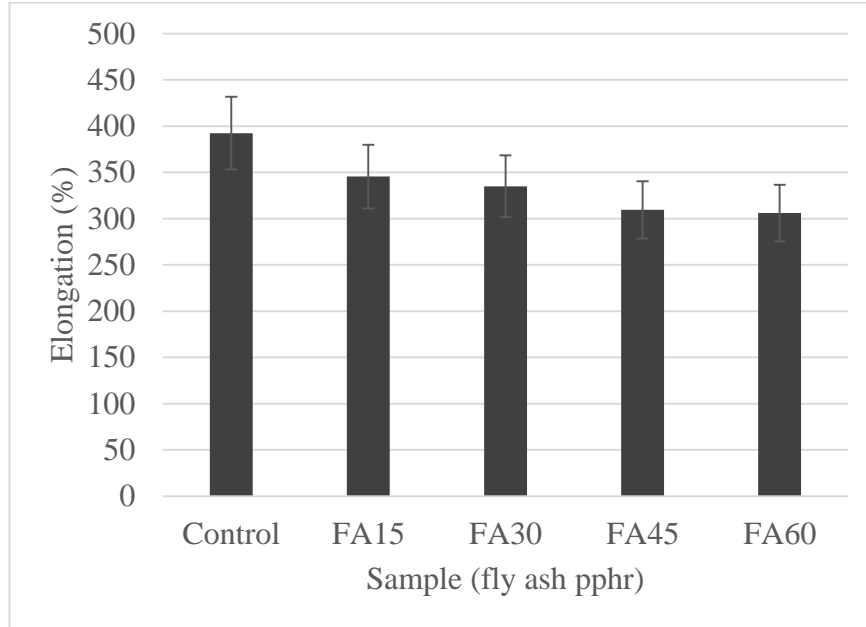


Figure 4-13: The effect of fly ash loading on the Elongation at break

It is known that when the filler is added and increased the filler loading in a composite, interaction between filler and rubber matrix become poorer, if the filler and the macromolecular matrix do not form interactions. Fly ash which has a higher particle size and its distribution than that of  $\text{CaCO}_3$  also has a higher tendency for agglomeration. Therefore, as the fly ash percentage in the hybrid filler system of fly ash and  $\text{CaCO}_3$  increases, filler-matrix interactions become lesser yielding lower elongation at break. Besides, a decrease of the extensible material (rubber) percentage in the vulcanizate may also contribute to this trend which is supported by the previous studies carried out by Saban Bulbul et al on the effect of wood ash on the mechanical properties of rubber compound [29].

However, elongation at break values fulfils the required minimum level up to 30 pphr fly ash added vulcanizates, according to in house specification given in Appendix C.



#### 4.2.2.4 Tear strength

Similar to the tensile strength, tear strength also reduces with an increase in the fly ash loading to rubber compounds, as it could be seen in Figure 4-14.

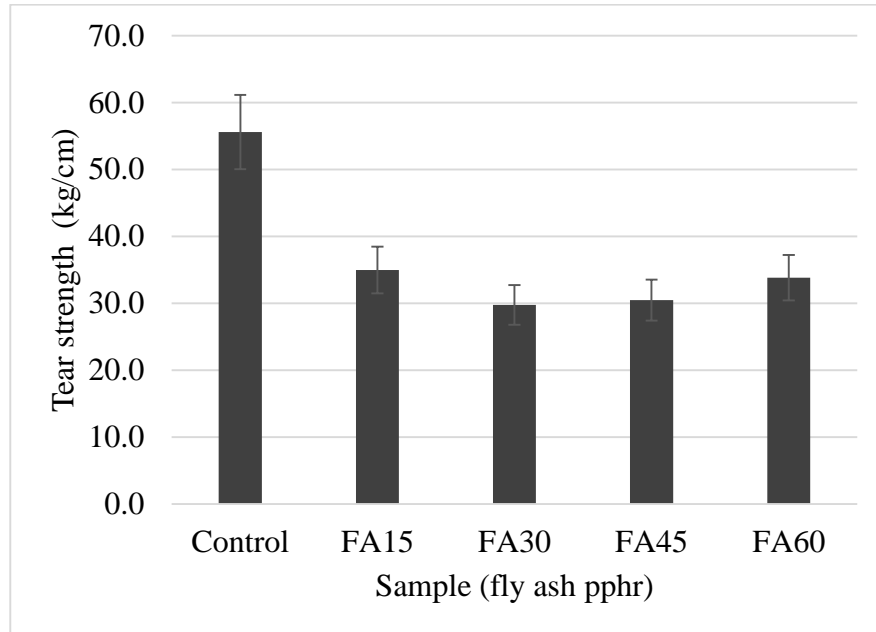


Figure 4-14: The effect of fly ash loading on the tear strength

It is known that the tearing strength of the compounds will vary according to the filler amount and the filler type. FA60 sample shows a slightly improved tear strength compared to FA45 samples. Tear strength reduction might be due to increment of stress concentration at the crack tips in the presence of fly ash, particularly those with large particles compared to  $\text{CaCO}_3$ . Even though, when increasing the fly ash loading up to a critical level, crack propagation might block and give better restrictions to crack propagation. Fly ash filler particles reduce the tear strength of NR although at higher loading goes a long way to restoring the tear strength. This could be confirmed with the support of previous studies done by Richard et al, where similar behavior has been reported in their research [17, 29].

### 4.2.3 Hardness

The hardness values of the vulcanizates have shown a slight increase with an increase in the fly ash percentage in the total filler loading (Figure 4-15).

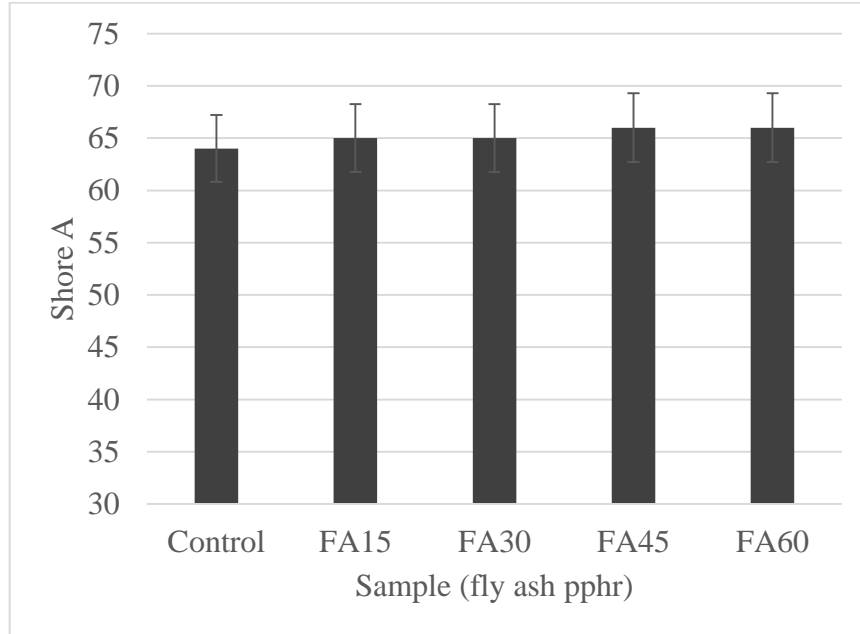


Figure 4-15: The effect of fly ash loading on the hardness values

In general, maximum cure torque of the compounds can interpret the hardens behavior of the vulcanizate, ie. hardness should be decreased with a decrease in the  $M_H$  value, vice versa. However, in this case, hardness increases with increasing filler loading, despite a reduction in  $M_H$  value with filler loading has been shown in earlier studies. Hardness is depending on chemical and physical factors in compounds.  $M_H$  gives information on both the number of cross-links available in a unit volume affected by chemical reactions and rigidity of filler and its reinforcement. Being a silica-rich material fly ash has a high hardness value and therefore, a trend observed was an expected trend. The slight increase suggests that fillers, fly ash and  $CaCO_3$  have similar characteristics in terms of hardness of the material and the reinforcement ability except for the practical size. The same behaviour has been observed and discussed in previous studies by Richard et al and White & Case who studied on use

of fly ash filler in rubber and characterization of fly ash from coal-fired power plants respectively [17, 23].

#### 4.2.4 Specific Gravity

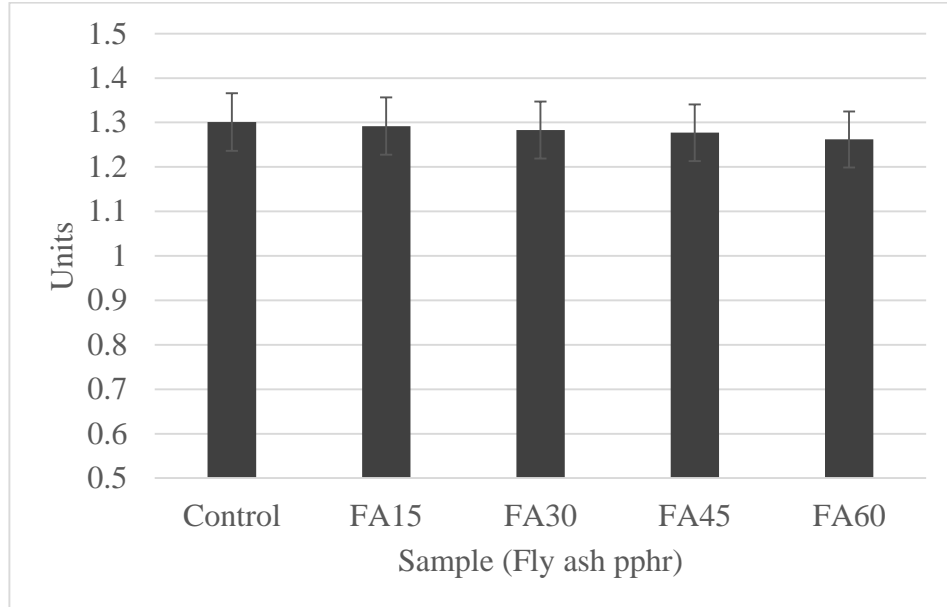


Figure 4-16: The effect of fly ash loading on the specific gravity

The specific gravity of the compound reduced with an increase in the fly ash percentage as shown in Figure 4-16 with considering 5% error acceptance. This is a well-expected trend when the specific gravities of fillers presented earlier are discussed in Section 4.1.4. Fly ash specific gravity is lesser than the specific gravity of  $\text{CaCO}_3$ . Therefore, compound-specific gravity should be reduced with an increase in fly ash percentage in total filler loading.

##### 4.2.4.1 Dispersion level and Dispergrader $\alpha$ view

Overall Y values gradually decrease with an increase in the fly ash loading (Figure 4-17). Y values are mainly considered agglomerates. It may be increased with an increase in fly ash loading due to particle size increment. In this analysis, diameter above 23  $\mu\text{m}$  particles are considered as agglomerates [21]. The large particles of the non-reinforcement filler are increased with the increase of fly ash percentage. It is

also evident from the results that percentage of particles/agglomerate that have diameter more than 23  $\mu\text{m}$  are higher in fly ash compared to  $\text{CaCO}_3$ .

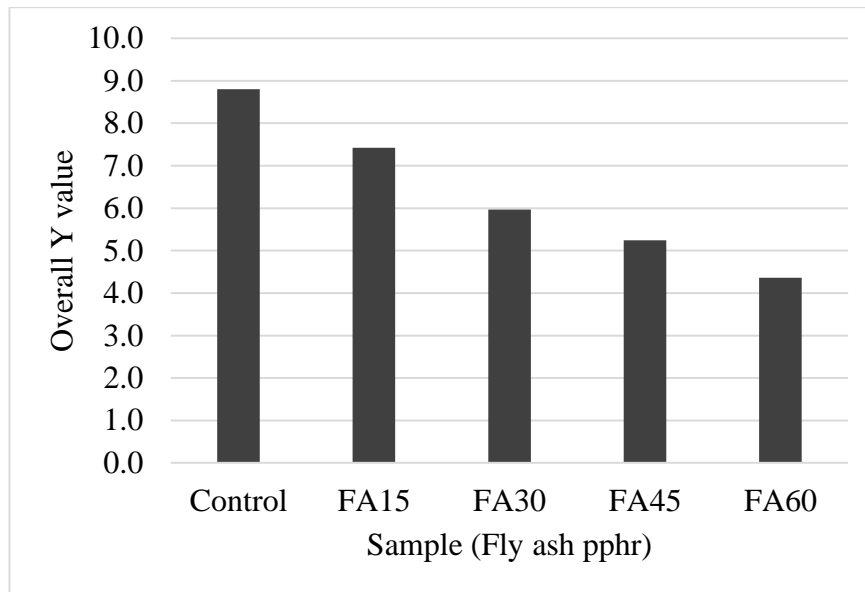


Figure 4-17: The effect of fly ash loading on the overall Y value

Overall dispersion percentage also decreases with an increase in the fly ash percentage, as given in Figure 4-18. This may be also due to higher particle size of fly ash compared to  $\text{CaCO}_3$  particles as described previously in Section 4.1.1 [5]. Further, the dispersion behaviour observed here may be due to poor filler interaction with an increase in the fly ash percentage. However, filler dispersion is acceptable up to 30 pphr of fly ash loading according to the specification given in Appendix C. Further, filler distribution is a satisfactory level up to 30 pphr, no particle agglomerations could be seen according to filler dispersion shown in Figure 4-19. Dispersion level is, however, acceptable up to 30 pphr fly ash loading according to the specification given in Appendix C.

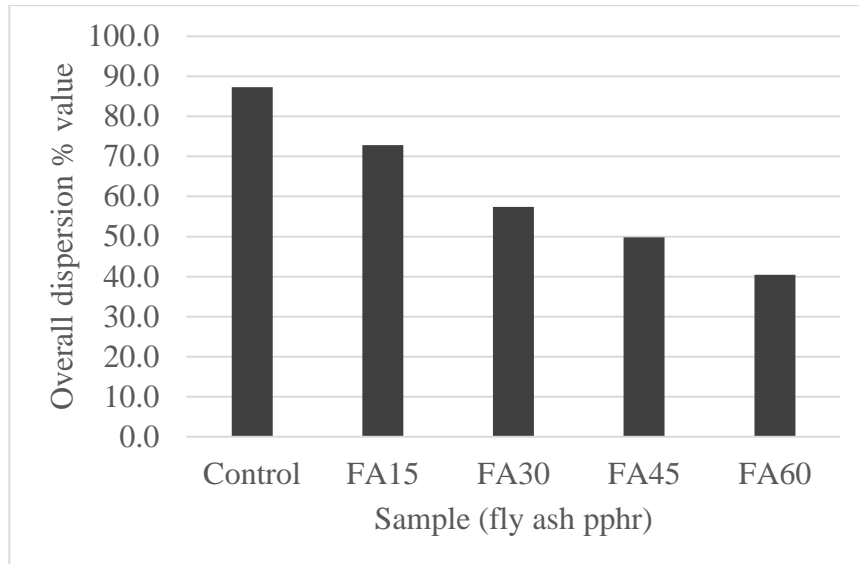
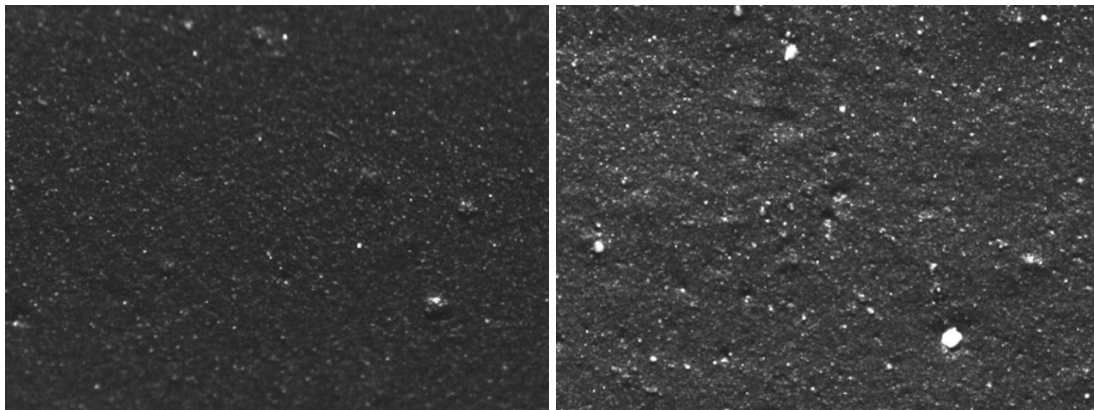


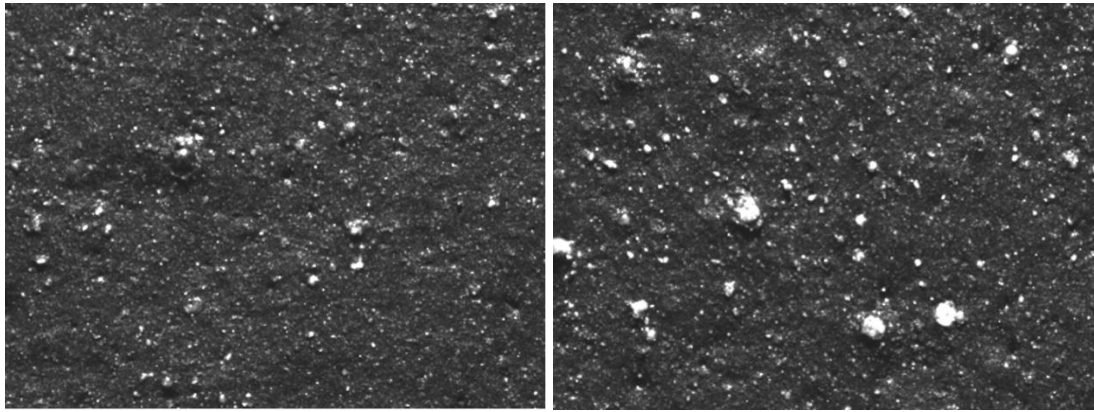
Figure 4-18: The effect of fly ash loading on the dispersion %

Dispergrader  $\alpha$ view shows filler dispersion in the samples. They are shown in Figure 4-19. Presences of agglomeration in samples increase with an increase in the fly ash percentage. It is well reported in the literature that larger agglomerates, lower the surface area and hence reduces filler-rubber interactions particularly these types of non-reinforcing fillers. This observation supports and explains dispersion value, tensile strength, and tear strength trends discussed earlier [19].



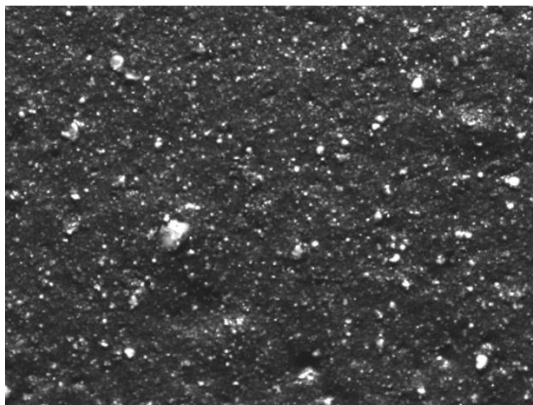
(a)

(b)



(c)

(d)



(e)

Figure 4-19: Dispergrader  $\alpha$ view of the fly ash /  $\text{CaCO}_3$  added compounds: (a) Control, (b) FA15 (c) FA30, (d) FA45, (e) FA60

#### 4.2.5 Heat build-up

The heat build-up increases with an increase in fly ash percentage as shown in Figure 4.19. It is known that heat generation depends on polymer, filler and other components of a compound. An increase in filler loading results in the agglomeration of filler particles and creates more voids (free spaces) in the vulcanizates as described in Section 3.6.6. This facilitates increase in the internal mobility of polymer chains that could be taken place as discussed by Eberhard and Wagner in their work on “Heat generation and rubber-filler coupling bonds and effect of CB loading and crosslink density on the heat build-up in elastomers” [30, 31]. Consequently, heat

generation increases, and the final temperature rises compared to low particle size composites due to molecular vibrations.

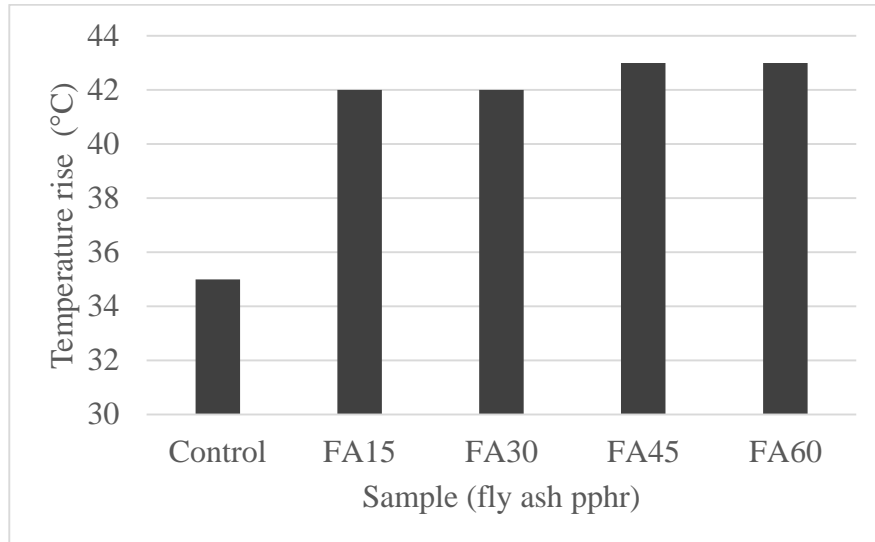


Figure 4-20: The effect of fly ash loading on the heat build-up

#### 4.2.6 Blow Out time

The time required to blowout the sample was measured.

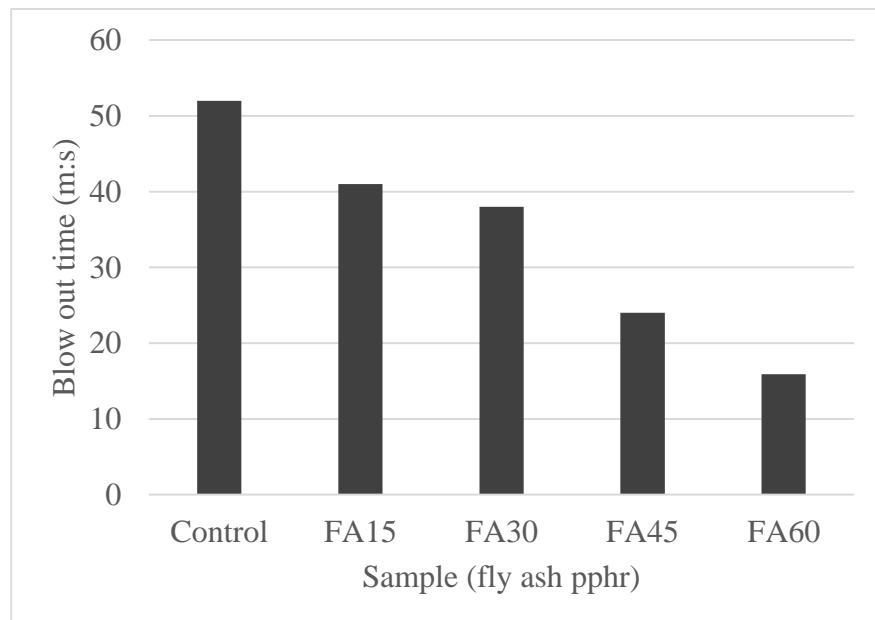


Figure 4-21: The effect of fly ash loading on the blowout time

This is also related to free space availability in the vulcanized sample due to the agglomeration of particles as discussed in Section 4.2.5. Then obviously, blow out time should be reduced gradually with an increase in the fly ash percentage. This observation is confirmed by the results presented in Figure 4-21.

#### 4.2.7 Rebound resilience

Rebound resilience values are reduced with an increase in the fly ash loading, but no significant change could be observed according to given Figure 4-22. When applying an impact, energy waste is higher in large agglomerate containing particles as discussed in Section 4.2.5. This may be the reason for the reduced rebound resilience value with an increase in the fly ash loading.

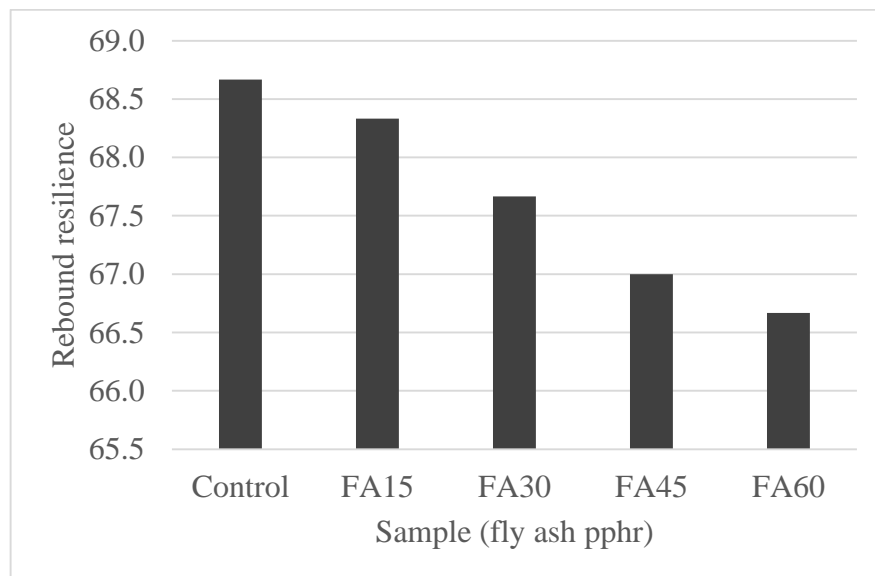


Figure 4-22: The effect of fly ash loading on the rebound resilience



### 4.3 Selection of optimum fly ash content to achieve required test results

Considering the industrial application in question, tensile strength, elongation at break, dispersion and blow out time were selected to choose the optimum composite for further development. The values of the above-selected properties of the composites studied are reproduced in Table 4.3 along with the properties of other samples and specifications of the application in question (solid tire middle compound). Based on the performance, the composite loaded with 30 pphr fly ash was selected as the optimum sample for further improvements.

Table 4-2: Summary of problematic results of unmodified fly ash added samples

| Property/sample (fly ash pphr) | Control | FA15 | FA30  | FA45 | FA60 | Specification |
|--------------------------------|---------|------|-------|------|------|---------------|
| Tensile Strength (MPa)         | 15.4    | 12.6 | 12.1  | 10.4 | 11.0 | 12.0-17.0     |
| Elongation at break (%)        | 392     | 345  | 335   | 310  | 306  | 330-440       |
| Overall Dispersion %           | 87.3    | 72.8 | 57.42 | 49.8 | 40.5 | Above 50      |
| Blow out time (m:s)            | 52      | 41   | 38    | 24   | 15.9 | Above 40      |

### 4.4 Results of particle size reduced fly ash filled sample testing

In this study, the properties of the four systems were investigated. These composites were

- (i). Control composite: – 60 pphr CaCO<sub>3</sub> filled composites
- (ii). Unmodified optimum sample: – 30 pphr un-sieved fly ash filled composite
- (iii). Sieved S sample: - 30 pphr fly ash containing smaller particle size range (0-53) μm
- (iv). Sieved L sample: - 30 pphr fly ash containing large particle size range (53-106) μm

#### 4.4.1 Rheological properties

Table 4-3: Rheological properties of CaCO<sub>3</sub> / fly ash loaded composites

| Property \Sample<br>(fly ash pphr)   | Control<br>(0) | Unmodified<br>(30) | Sieved S<br>(30) | Sieved L<br>(30) |
|--------------------------------------|----------------|--------------------|------------------|------------------|
| Maximum Torque (dN m)                | 28.08          | 24.94              | 25.42            | 26.45            |
| Minimum Torque (dN m)                | 1.97           | 2.21               | 2.14             | 1.81             |
| Scorch Time (t <sub>S2</sub> ) (m:s) | 3.47           | 3.51               | 3.52             | 3.47             |
| Cure Time (t <sub>90</sub> ) (m:s)   | 8.78           | 8.84               | 8.86             | 8.78             |

Table 4-3 presents the rheological properties of composites mentioned above. It shows the rheological properties of 60 pphr CaCO<sub>3</sub> filled (control) and selected composite (30 pphr CaCO<sub>3</sub> and 30 pphr fly ash) for comparison. The maximum torque (M<sub>H</sub>) reduces with the replacement of CaCO<sub>3</sub> with fly ash. Fly ash-filled composite and sieve analyzed fly ash with particle size reduced in 53-106 μm range show almost similar M<sub>H</sub> values. Fly ash loaded with the smallest particle size incorporated sample shows the closest characteristics to the control sample. As described in section 4.2.1, this is expected that smaller size particles filled composites possess higher M<sub>H</sub> values. Larger particle size fly ash loaded composites show lower value in M<sub>H</sub>, due to the same reasons explained for fly ash incorporated composites.

The M<sub>L</sub> values of the composites also show similar observations. The control sample and fly ash with smallest particle size loaded composites exhibit almost similar, but lowest M<sub>L</sub> values while unmodified and larger particle size fly ash loaded composites exhibit slightly higher M<sub>L</sub> values. As described in section 4.2.1, when adding smaller size particles, it reduces the stiffness of the rubber compound. This might be due to low restriction by small non-reinforcement filler particles. It may act as a slipping agent and reduce the blockage in unvulcanized samples as explained by Alnad el al in their study [5].

According to curing characteristics given in Table 4-3, It is evidenced from the results, that there is no significant difference in t<sub>S2</sub> and t<sub>90</sub> in these samples. As

previously discussed, both types of fillers and the size reduction of filler particle size do not influence the curing reactions.

#### 4.4.2 Physical properties

According to the results presented in Table 4-4, there is no considerable difference could be observed in the hardness of the composites studied. However, Unmodified fly ash added sample and large particle loaded sample show the higher values than that of the control and smaller particle size fly ash loaded composites. These results are in line with the generally observed results for hardness when the composites filled with non-reinforcing fillers with larger particle sizes (Sieved-S) are considered. However, it should note that the control sample and the fly ash particle size incorporated composites (Sieved- S) sample exhibit similar hardness values.

Table 4-4: Physical properties of CaCO<sub>3</sub> / fly ash filled compound

| Property \ Sample<br>(fly ash pphr) | Control<br>(0) | Unmodified<br>(30) | Sieved S<br>(30) | Sieved L<br>(30) |
|-------------------------------------|----------------|--------------------|------------------|------------------|
| Hardness (Shore A)                  | 64             | 65                 | 66               | 64               |
| Tensile (MPa)                       | 14.8           | 12.1               | 12.5             | 13.7             |
| Elongation (%)                      | 348            | 297                | 319              | 352              |
| Modulus 300 % (MPa)                 | 3.9            | 3.9                | 3.6              | 3.8              |
| Tear strength (kg/cm)               | 52             | 36                 | 43               | 51               |

It could be seen a significant improvement tensile, elongation at break and tear strength in small particle size fly ash loaded composites (Sieved-S) than the other two fly ash loaded vulcanizates. This observation suggests that particle size reduction to the lowest level used in this study (0-53)  $\mu\text{m}$  improves filler-matrix interface adhesion to a certain extent yielding an improvement in these properties of the smallest size fly ash filled vulcanizates.

The specific gravity of the composites shows similar behaviours to the unmodified fly ash loaded samples already described in section 4.2.2.

Physical and mechanical properties performance comparison is given in Figure 4-23. After using particle size reduced fly ash, small particle size fly ash shows almost similar properties to the control sample in all properties studied except tensile strength.

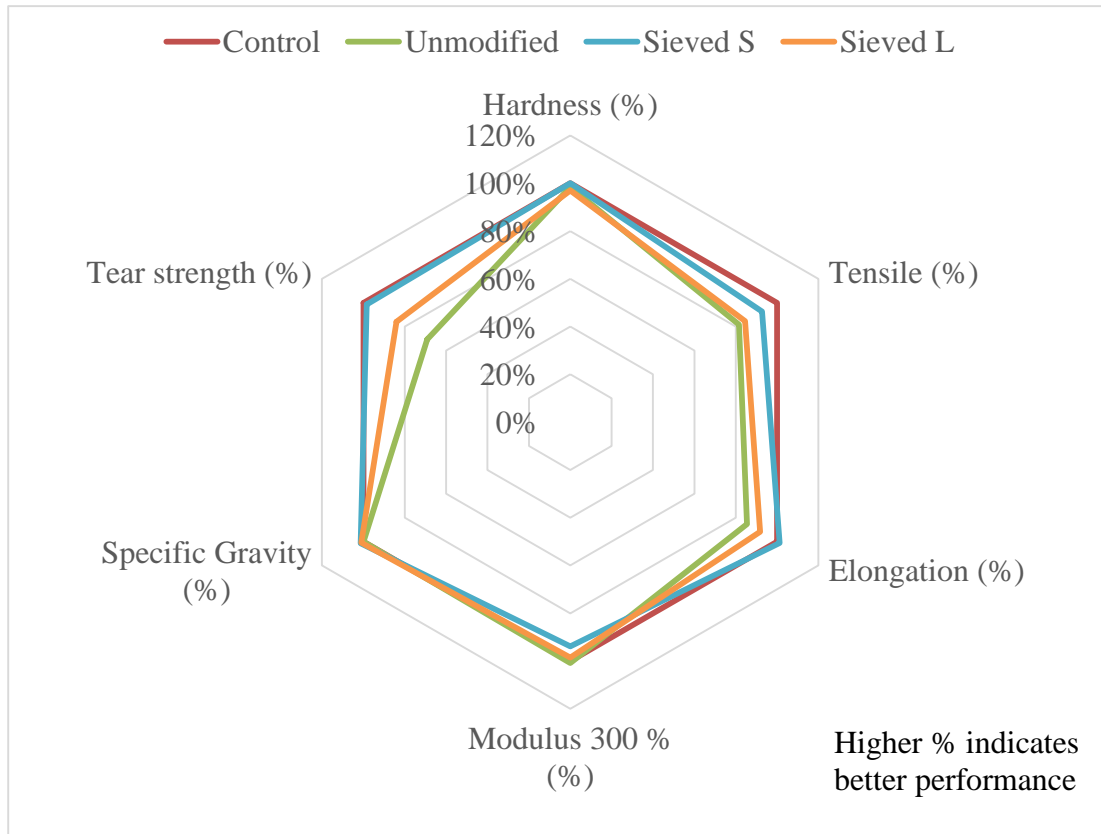
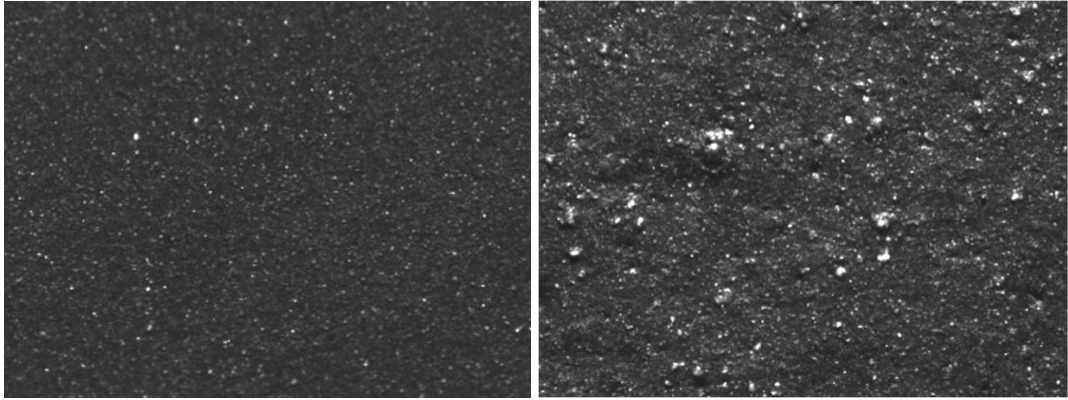


Figure 4-23: Physical properties comparison

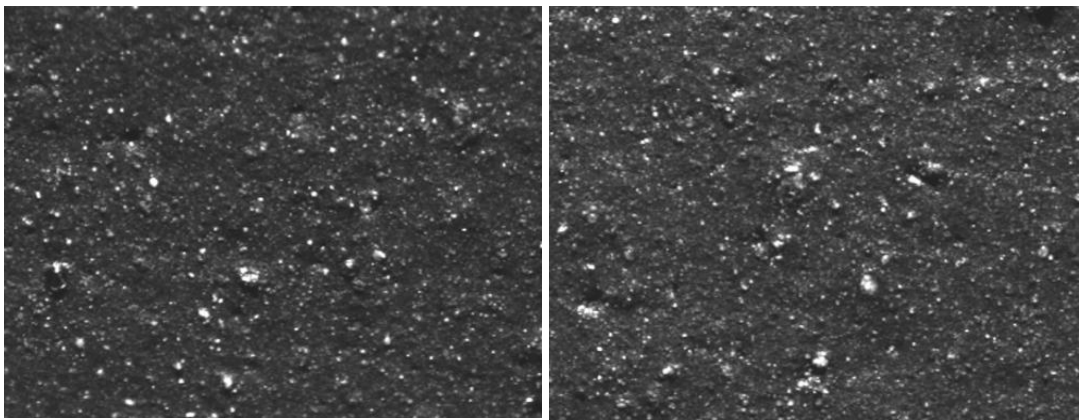
#### 4.4.3 Dispersion level

According to dispersion  $\alpha$ view (Figure 4-24) and overall dispersion percentage results (Figure 4-25), dispersion percentage was decreased with fly ash loading, even with adding particle size distribution reduced fly ash. However, better dispersion results were obtained in the particle size distribution reduced fly ash added samples compared to normal fly ash added samples. It may be due to the larger size of fly ash particles than  $\text{CaCO}_3$ . This observation supports the physical and mechanical properties yielded by the vulcanizates studied in this work.



(a)

(b)



(c)

(d)

Figure 4-24: Dispergrader  $\alpha$ view of the fly ash /  $\text{CaCO}_3$  added compounds: (a) Control, (b) Unmodified, (c) Sieved S, (d) Sieved L

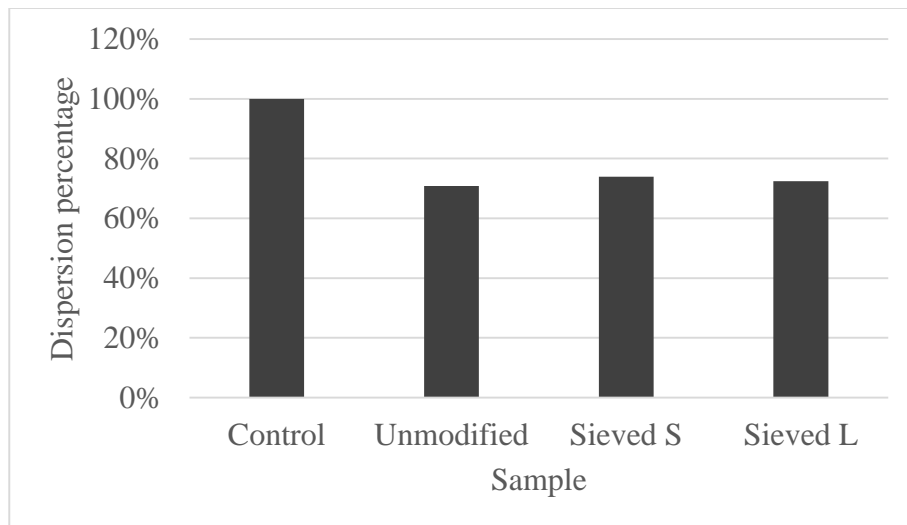
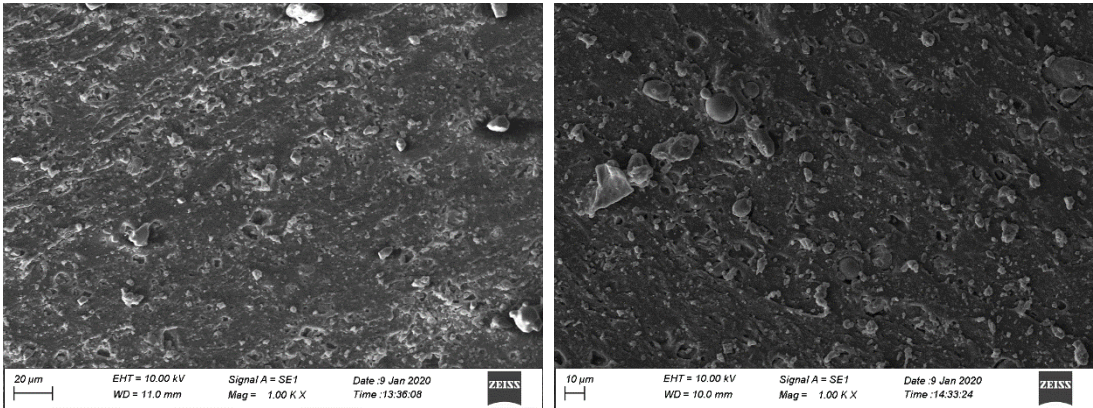


Figure 4-25: Overall dispersion % value

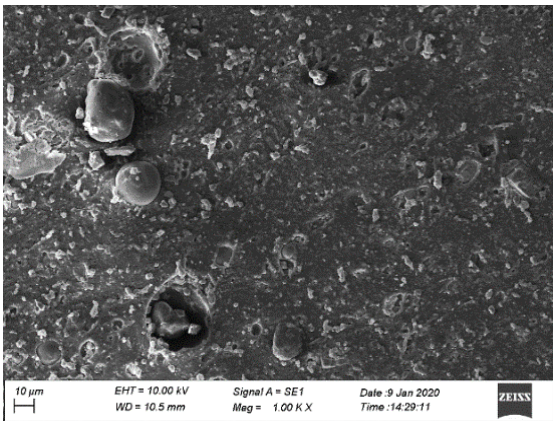
In addition to the above observation, scanning electron microscope images of Control to Sieved S and Sieved L samples were compared. These images are given in Figure 4-26.

According to these images, it confirms the previously described most of the hypothesis and trends. Spherical shape fly ash particles reduce the rubber incorporation and degraded properties.



(a)

(b)



(c)

Figure 4-26:SEM image of vulcanized samples: (a) Control, (b) Sieved S, (c) Sieved L

#### 4.4.4 Dynamic Properties

Figure 4.25 presents the performance of blowout time and heat build-up of fly ash filled vulcanizates compared to the control sample (60 pphr CaCO<sub>3</sub> filled

vulcanizates). It shows that fly ash (small particle size) filled vulcanizates reached 80% the performance of the control vulcanizate while the other two vulcanizates reached rather lower performance. Concerning the heat build-up too, the same composites have shown the closest performance to the control. This observation also confirms that heat build-up and blow out time performance could be improved by incorporating the smaller size non-reinforcing fillers into the rubber matrix. This could be elucidated by the particle size differences of the filler materials and the interactions between the rubber matrix and the filler particles as discussed in section 4.2.5 and section 4.2.6.

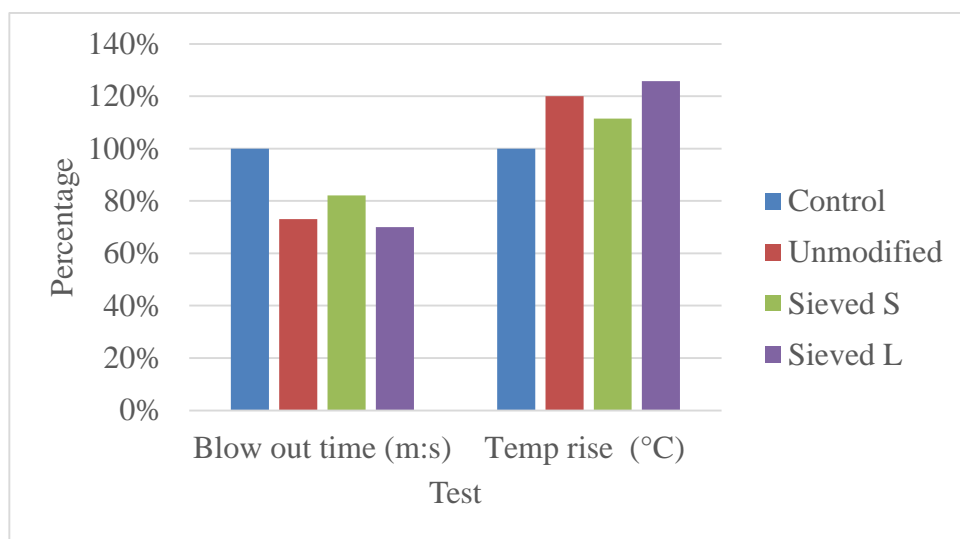


Figure 4-27: Dynamic properties

#### 4.4.5 Viscoelastic Properties

According to Figure 4-28,  $E'$  increases with the incorporation of fly ash and their particle size. Elastic modulus ( $E'$ ) represents the elastic portion of the rubber compound and this may be due to reducing interaction with the addition of large non-reinforcement practicals to the rubber matrix. Interactions with polymer filler interaction and filler aggregate-aggregate interaction poor in fly ash filled composites as reported by Dutta and Tripathy [32].

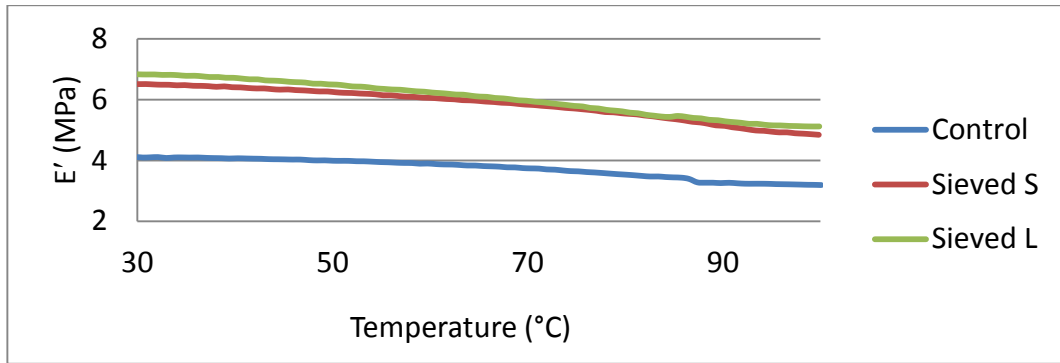


Figure 4-28: E' Storage Modulus vulcanizates

E'' represents the viscous part of the vulcanizate similar to E', E'' also increases with fly ash loading and increasing fly ash particle size ( see Figure 4-28).

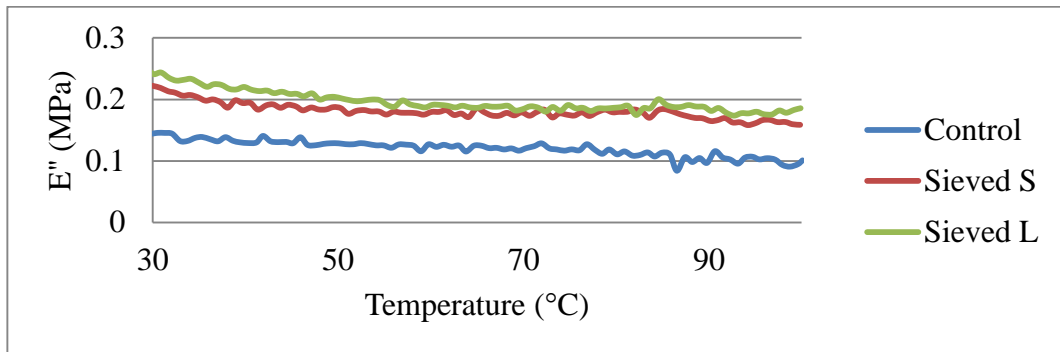


Figure 4-29: E'' Loss Modulus of vulcanizates

As discussed above, both storage modulus and loss modulus increased with the incorporation of fly ash to the compound. Therefore, Tan  $\delta$  which is shown in Figure 4-30, shows similar behaviour in all vulcanizates since Tan  $\delta$  is the ratio of loss modulus to storage modulus. Tan  $\delta$  at 60 °C tells about the rolling resistance of the solid tires. Therefore, addition of fly ash is not significantly affected to the rolling resistance of the solid tires.

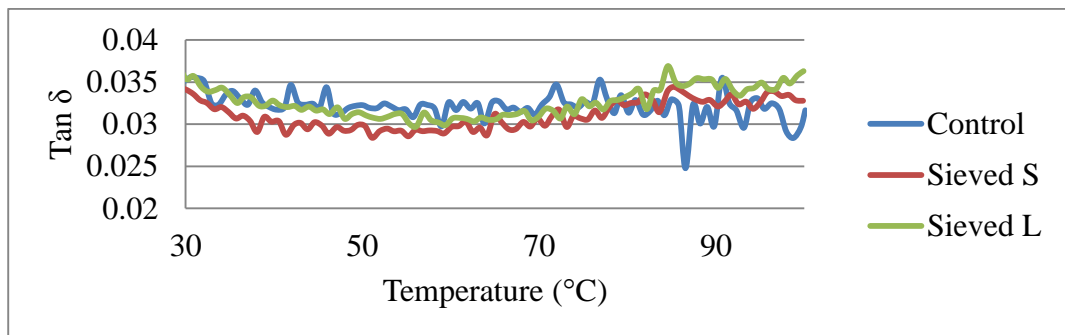


Figure 4-30: Tan  $\delta$  of vulcanizates



## 5. CONCLUSIONS AND RECOMMENDATIONS

This research focuses on the replacement of fly ash with  $\text{CaCO}_3$  in a solid tire middle compound formulation and the effect of particle size reduction of fly ash fillers on the performance of the vulcanizates. The following conclusions could be made from the study.

- (i). Fly ash filled rubber vulcanizates has lower specific gravity than the commercial  $\text{CaCO}_3$  filled vulcanizates at the same filler loading. Consequently, fly ash filled rubber compound possesses lower qualifying the potential of fly ash in reduction of composite weight.
- (ii). Replacement of fly ash from  $\text{CaCO}_3$  in the solid tire middle compound recipe used here has no adverse effect on the curing characteristics of the composites. In other words, there are no significant processability difficulties due to the replacement of  $\text{CaCO}_3$  from fly ash fillers or their particle size distribution. Curing characteristics such as  $t_{S2}$  and  $t_{90}$  are independent of fly ash loading and their particle size distribution.
- (iii). Incorporation of fly ash improves the hardness of the vulcanizate and reduces the mechanical and dynamic mechanical properties of the vulcanizates. However, 30 pphr fly ash with smaller particle size loaded vulcanizates exhibit the closest properties to the 60 %  $\text{CaCO}_3$  filled vulcanizates.
- (iv). The reduction of particle size of the fly ash has improved the mechanical properties while no influence was made on curing characteristics.
- (v). Blow out time is decreased with increasing fly ash loading and shows improved or increased in blowout time when the small particle size of fly ash is loaded to the hybrid filler system. Incorporation of fly ash increases heat build-up and fly ash particle reduction reduces the heat build-up of the vulcanizates.
- (vi). Incorporation of fly ash does not influence the visco-elasticity of fly ash filled natural rubber vulcanizates in comparison to the  $\text{CaCO}_3$  filled once.

(vii). As per the overall experimental results, 30 pphr fly ash incorporated composite with smaller particle size could be suggested as the most promising recipe for solid tire middle compound to replace  $\text{CaCO}_3$  partially from fly ash.

Based on the finding of the present study, it is recommended the following further studies.

- (i). The potential use of nano scale fly ash to replace  $\text{CaCO}_3$  in the solid tyre middle compounds.
- (ii). The effect of various chemically treated fly ash on the corresponding vulcanizate performance.
- (iii). Further studies can be recommended to assess the possibility of using other non-reinforcement fillers in similar size range for solid tire middle compound

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# APPENDIX - A: TECHNICAL SPECIFICATIONS OF STR 20

**TI RUBBER CO LTD**  
**91 MOO 4 TAMBON KRASAEBON**  
**AMPUR KLAENG RAYONG THAILAND 21110**

COPY

## TEST CERTIFICATE

MESSRS TO WHOM IT MAY CONCERN

DESCRIPTION OF GOODS: NATURAL RUBBER STR 20

Date tested : 22/10/2019

| Property                                     | Mean test results of Lot No. |           |           |           |           | STR20 Limit |
|--|------------------------------|-----------|-----------|-----------|-----------|-------------|
|  | C051                         | C052      | C053      | C054      | C055      |             |
| Dirt (retained on 44 $\mu$ aperture) %wt     | 0.026                        | 0.028     | 0.025     | 0.034     | 0.034     | 0.16 max    |
| Ash %wt                                      | 0.28                         | 0.27      | 0.27      | 0.26      | 0.28      | 0.80 max    |
| Volatile matter %wt                          | 0.21                         | 0.18      | 0.21      | 0.18      | 0.15      | 0.80 max    |
| Nitrogen %wt                                 | 0.33                         | 0.33      | 0.34      | 0.34      | 0.23      | 0.60 max    |
| Initial Wallace Plasticity (P <sub>0</sub> ) | 31.3                         | 31.4      | 31.4      | 30.9      | 31.4      | 30.0 min    |
| range  | 30.0-33.5                    | 30.0-33.5 | 30.0-32.5 | 30.0-32.5 | 30.0-32.5 |             |
| Plasticity Retention Index (PRI)             | 74.7                         | 75.0      | 74.9      | 74.6      | 74.5      | 40.0 min    |
| Mooney Viscosity ML (1+4) 100°C              | 65.9                         | 66.0      | 65.3      | 66.0      | 64.4      |             |

Date tested :22/10/2019

| Property                                     | Mean test results of Lot No. |  |  |  |  | STR20 Limit |
|--|------------------------------|--|--|--|--|-------------|
|  | C056/1-3                     |  |  |  |  |             |
| Dirt (retained on 44 $\mu$ aperture) %wt     | 0.034                        |  |  |  |  | 0.16 max    |
| Ash %wt                                      | 0.28                         |  |  |  |  | 0.80 max    |
| Volatile matter %wt                          | 0.11                         |  |  |  |  | 0.80 max    |
| Nitrogen %wt                                 | 0.21                         |  |  |  |  | 0.60 max    |
| Initial Wallace Plasticity (P <sub>0</sub> ) | 30.9                         |  |  |  |  | 30.0 min    |
| range  | 30.0-32.5                    |  |  |  |  |             |
| Plasticity Retention Index (PRI)             | 74.1                         |  |  |  |  | 40.0 min    |
| Mooney Viscosity ML (1+4) 100°C              | 64.8                         |  |  |  |  |             |

23/10/2019

Date of issue

มจรุจก

Officer - in - charge

SHIPPING MARKS AND NOS

# APPENDIX – B: TECHNICAL SPECIFICATIONS OF CaCO<sub>3</sub>

## LANMIC EXPORTS (PVT) LTD

Head Office:  
No 64, 2nd Lane, Ratmalana,  
Sri Lanka.  
Tel: +94 11 2625761, 2622453  
Fax: +94 11 4215368  
E mail: lanmic@slnet.lk

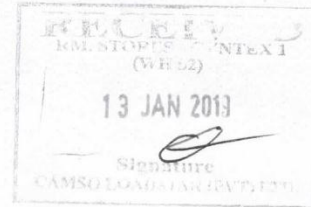
Head Office:  
No 64, 2nd Lane, Ratmalana,  
Sri Lanka.  
Tel: +94 11 2625761, 2622453  
Fax: +94 11 4215368  
E mail: lanmic@slnet.lk



No: 4839

### Certificate of Analysis

Customer : Camso Loadstar (PVT) Ltd  
Product : Lakcarb 08  
Batch No : 3L08L18361  
Quantity : 20 MT  
Date Tested : 27/12/18  
Date of Production : 27/12/18  
Dispatch Date : 13/01/19  
Invoice No : LE 5532  
P.O. No : 4400030228 – 87,88  
A.O.D No : D 6850, D 6851  
Lot No : 000075



#### Quality Control Information

|                                     |                               |
|-------------------------------------|-------------------------------|
| <b>PACKING VERIFICATION</b>         |                               |
| <input type="checkbox"/>            | Not Acceptable                |
| <input checked="" type="checkbox"/> | As Per Camso SPEC, Marks & No |
| <input type="checkbox"/>            | Standard SPEC & Packing       |

#### Sieve Analysis:

|          |          |     |
|----------|----------|-----|
| + 5# %   | + 30# %  |     |
| + 18# %  | + 100# % |     |
| + 25# %  | + 325# % |     |
| + 120# % | + 500# % | Nil |

Raw Material Specific gravity (g/ml) : 2.69  
Particle Size D<sub>97</sub> : 13.20  
Particle Size D<sub>50</sub> : 2.85  
Moisture Content % : 0.08  
Colour : White

#### Chemical Testing

HCl Insolubility % :

Purity : 99%

|                  |             |
|------------------|-------------|
| Batch            | 0000156764  |
| G.R.N            | 5008803526  |
| WH 52<br>Cyntex1 | 14 JAN 2019 |

27/12/2018  
26/12/2020

We certify that this product meets the above mentioned specifications.

Jan.13.2019  
Date

Prepared By

For Chemist



**REVIEWED**



## APPENDIX – C:IN-HOUSE PROPERTIES SPECIFICATION

| Property                             | Range      |
|--------------------------------------|------------|
| Maximum Torque (dN m)                | 20-28      |
| Minimum Torque (dN m)                | 1.5-3.5    |
| Scorch Time (T <sub>S2</sub> ) (m:s) | 2.50-4.30  |
| Cure Time (T <sub>90</sub> ) (m:s)   | 6.00-10.00 |
| Hardness (Shore A)                   | 64-70      |
| Tensile (MPa)                        | 12.0-17.0  |
| Elongation (%)                       | 330-440    |
| Modulus 300 % (MPa)                  | 2.67-3.83  |