THE POTENTIAL OF WOLLASTONITE AS A NEW FILLER FOR NATURAL RUBBER COMPOUNDS

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THE POTENTIAL OF WOLLASTONITE AS A NEW FILLER FOR NATURAL RUBBER COMPOUNDS

BY

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LIST OF ABBREVIATION

NR	Natural Rubber
SVR 3L	Standard Vietnamese Natural Rubber
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
DTG	Derivative Thermal Gravimetry
CB	Carbon Black
$CaCO_3$	Calcium Carbonate
CBS	N cyclohexyl-2-benzothiazole sulfonamide
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
APTES	3-Aminopropyltriethoxysilane
ZnO	Zinc oxide
ASTM	American Society for Testing and Materials
MDR	Monsanto Moving Die Rheometer
C_5H_8	Cis-1,4 polyisoprene
Phr	Part per hundred of rubber
M100	Stress at 100% elongation
M300	Stress at 300% elongation

LIST OF SYMBOLS

t_{90}	Cure time
t_{s2}	Scorch time
M_H	Maximum torque
E_b	Elongation at Break
Q_f/Q_g	Swelling index
dNm	Deci Newton Meter
$T_{50\%}$	Degradation temperature at 50 wt%
µm	Micrometer
min	Minute

POTENSI WOLLASTONITE SEBAGAI PENGISI BARU UNTUK SEBATIAN GETAH ASLI

ABSTRAK

Wollastonite atau kalsium silikat, ($CaSiO_3$) berpotensi sebagai pengisi baru di dalam sebatian getah asli (GA). Ciri-ciri, pematangan, sifat mekanik, kelakuan pembengkakan, kestabilan haba dan morfologi sebatian getah asli terisi wollastonite telah dikaji. Empat siri eksperimen telah dilakukan. Kesemua sebatian GA telah disediakan menggunakan mesin penggiling bergulung dua dengan pelbagai pembebanan pengisi daripada 0 hingga 40 bsg. Untuk siri pertama kesan pelbagai pembebanan wollastonite ke atas sifat-sifat sebatian GA telah dikaji. Keputusan menunjukkan masa pematangan (t_{90}), masa skorj (t_{s2}), kekuatan tensil dan pemanjangan pada takat putus (E_b) berkurang, manakala tork maksimum (M_H), modulus tensil, kekerasan, kestabilan haba dan kelakuan pembengkakah meningkat dengan penambahah pembebanan wollastonite. Untuk siri kedua, kesan rawatan fisikal wollastonite menggunakah 'ball mill' ke atas sifat-sifat sebatian GA telah dikaji. Wollastonite yang terawat telah meningkatkan sifat-sifat sebatian GA berbanding wollastonite tidak dirawat. Untuk siri ketiga, kesan 1 bsg 3-aminopropiltrietoksisilana (APTES) sebagai agen pengkupel telah dikaji. Kehadiran APTES telah meningkatkan sifat-sifat sebatian GA. Ini disebabkah kehadirah APTES telah meningkatkan interaksi getah-pengisi didalam sebatian GA. Untuk siri terakhir, kesan penggantian separa wollastonite dengan hitam karbon atau kalsium karbonat telah dikaji. Penggantian wollastonite dengan pengisi-pengisi komersial telah meningkatkan dan memperbaiki sifat-sifat sebatian GA.

THE POTENTIAL OF WOLLASTONITE AS A NEW FILLER FOR NATURAL RUBBER COMPOUNDS

ABSTRACT

Wollastonite or calcium silicate, ($CaSiO_3$) has potential as a new type of filler in natural rubber (NR) compounds. The curing characteristics, mechanical properties, swelling behavior, thermal stability and morphology of wollastonite filled NR compounds were investigated. Four series of experiments were performed. All NR compounds were prepared using a two roll mill with different filler loading from 0 to 40 phr. In the first series, the effects of different wollastonite loading on the properties of NR compounds were studied. Results indicated that the cure time (t_{90}), scorch time (t_{s2}), tensile strength and elongation at break (E_b) decreased, whereas, maximum torque (M_H), tensile modulus, hardness, thermal stability and swelling behavior increased with wollastonite loading. The second series, the effect of physical ball mill treated wollastonite on the properties of NR compounds was investigated. Treated wollastonite improved the properties of NR compounds as compared to untreated wollastonite. The third series, the effect of 1 phr of 3-aminopropyltriethoxysilane (APTES) as silane coupling agent was studied. The presence of APTES showed an improvement in the properties of NR compounds. This was due to the presence of APTES, which enhanced the rubber-filler interaction of NR compounds. In the last series, the influence of partial replacement of wollastonite by carbon black or calcium carbonate was investigated. The substitution of wollastonite by commercial fillers have improved the properties of NR compounds.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Natural rubber (NR) is one of the main elastomers and widely used in industrial and technology science, especially used for shock and vibration isolators owing to its high elasticity. However, reinforcing filler is still needed to improve properties of natural rubber compound products such as abrasion resistance, flex resistance, hardness, tensile strength, tensile modulus, which gum compounds are inadequate. NR is used in aero planes, buses and coaches, motor cars, bicycle, tyres, footwear, belts, hose, seals and gaskets, all expect trains are highly dependent on rubber (Simpson, 2002).

Various types of fillers are used in the rubber industry prominently to reinforces, reduce material costs and improve processing (Rattanasom et al., 2007). The common reinforcements obtained through usage of inorganic particle fillers (mineral fillers) are effective method to enhance mechanical and physical properties of NR compounds. The mineral fillers are wollastonite, mica, talc, clay, silica and calcium carbonate can be used in amounts of 10% to 40% by weight (Hadal et al., 2004; Ding et al., 2012).

Wollastonite is one of the most extensive mineral filler used in β-isotactic polypropylene (iPP), which had begun to study by various scientists since 1980s. So many investigations indicated that wollastonite is an effective and low cost filler in thermoplastics, such as improved mechanical properties, as well as increased rate of crystallinity and nucleation (Ding et al., 2012; Wang et al., 2001; Hawley and Jaworski, 1998; Hanumantha Rao et al., 1998; Zhuang et al., 1997; Fu et al., 2002).

However, there are a little worked reported on the worth of wollastonite as a filler in rubber compounds (Guan et al., 2011; Xu et al., 2004). According to Xu et al. (2004), the resistance to wear, aging-resistant, fatigue-proof are enhanced after the rubbers are filled with such surface modified needle-like wollastonite powders. The chemical treated wollastonite use silanes or titanates to improve the interfacial bonding energy between the wollastonite and rubber matrix (Hanumantha Rao et al., 1998). The hydrophilic group of silane coupling agent chemically react with the hydroxyl group on the surface of wollastonite and the hydrophobic group has a certain degree of compatibility with the NR matrix.

The aims of this study is to investigate the potential of wollastonite on curing characteristics, mechanical properties (tensile strength, tensile modulus, hardness), swelling behaviour, morphology and thermal stability of wollastonite filled NR compounds.

1.2 Problem Statements

Natural rubber (NR) is widespread used as an effectively in industrial application. Fillers are incorporated into NR for reinforcement or cheaper rubber products. In recently, carbon black and silica were used popular in natural rubber compounds. Carbon black made from petroleum. It was added into NR compounds to give excellent resistance to UV light and antiozonants. However, the trouble of carbon black made black colour of rubber products, high cost and pollution. Silica is mineral natural filler, which gives significant mechanical properties of NR compounds and light colour of rubber products. But the disadvantages of silica are difficult to disperse in NR compounds due to its hydrophilic surface. This filler have to use silane coupling agent to improve the rubber-filler interaction, which expensive cost one.

Otherwise, wollastonite's source is the white mineral and very popular in the worlds. It was used as filler for rubber, which are low cost, light colour rubber products and high thermal stability of NR compounds.

By the way, one of the limitations of NR is its low temperature stability (Menon et al., 1996). In semi-crystalline polymeric materials, wollastonite, talc, calcium carbonate and clay are strongly influence the crystallization process, degree of cystallinity and nucleation of crystallites. Reinforcement with each of the above material increases crystallization temperature rate and lead to shorter processing time in injection moulding (Hadal et al., 2004).

Although, a little study has been done on wollastonite filled rubber compounds, there is no particular study focus on the filler loading and different methods for fillers treatment. For this study, we used different methods such as ball mill physical treated wollastonite, silane coupling agent (APTES) and hybrid composites by commercial fillers, which could give significant mechanical properties and thermal stability of NR compounds.

1.3 Research Objectives

This research was focused to study the potential of wollastonite as a new filler in NR compounds. Hence, the research objective is divided in three phases:

i. To study the effect of wollastonite loading on the properties of natural rubber compounds.
ii. To investigate the effect of ball mill physical and chemical (APTES) treatment on the properties of wollastonite filled NR compounds.
iii. To examine the effect of partial replacement of wollastonite by commercial fillers (carbon black, calcium carbonate) on the properties of NR compounds.

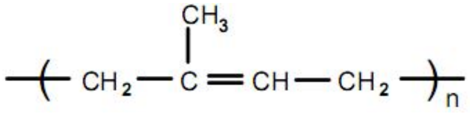
The characteristics of the wollastonite and NR compounds involved cure characteristics, mechanical tests, swelling test, hardness test, thermal stability test, and morphology. The cure characteristics parameter measured includes maximum torque (M_H), scorch time (t_{s2}) and cure time (t_{90}). The cure time is important to determine the time for rubber vulcanizate. The mechanical tests include tensile strength, elongation at break, tensile modulus at 100% and 300% elongations and hardness. Swelling test was conducted by measuring the swelling percentage of the NR compounds. Thermal test were focused on the thermogravimetric analysis (TGA) and morphological. All of the tests are important to be conducted so that the effect of the wollastonite filled natural rubber compounds can be understand.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber (NR) can be isolated from more than 200 different species of plant; including surprising examples such as dandelions. However, only one tree source Hevea Brasiliensis is one of the most commercial significant, which popular used in industrial application (Simpson, 2002). The chemical name of NR is polyisoprene $(C_5H_8)_n$, which is polymerized from mono-isoprene (C_5H_8). NR is cis-1,4-polyisoprene. In addition, the composition of NR also contains small amounts of non-rubber substances, protein, sugar, fatty acids and resinous materials that function as mild accelerator and activator for vulcanization. NR has excellent physical properties, but NR also has disadvantage that is poor resistance to oxygen, heat and ozone (Sirqueira and Soares, 2002). The chemical structure of natural rubber is shown in Figure 2.1 (Simpson, 2002).



$$-\left(CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right)_n-$$

Figure 2.1: Chemical structure of natural rubber (Simpson, 2002)

2.1.1 General properties of Natural Rubber

The chemical structure of natural rubber (NR) contains double bond. It is very important for chemically reacts of NR with other materials, especially which determines the chemical reactivity and its ability react of NR with sulphur or other ingredients in vulcanization rate (Treloar, 2005). NR has the ability to strain crystallize when stretched which enables NR gum compounds (without filler) to have good tensile strength. Moreover, NR has extremely high resilience, high tensile strength, good tear resistance, and high fatigue failure in cured state.

Rubber is a material that when stretched return quickly to its approximate original shape. This behaviour is called elasticity, and it can be explained by reference to the rubber molecules. The important thing about these molecules, they tend to be coiled up, not in any regular fashion, but unevenly twisted and twined, very much like a plate of spaghetti or a tangled skein of wool will consist of just one strand and in the tangled mass of many molecules (Huke, 1961).

2.1.2 Standard Vietnamese Natural Rubber

Vietnamese natural rubber is very popular in the world; in 2012 Vietnamese natural rubber reached 955000 tons increase 17 percent as compared 2011. Vietnamese natural rubber almost exports raw materials. Vietnam rubber group reported that in 2010 to 2011 got 811600 tons of natural rubber from the crops. Normally, Vietnamese natural rubber can export 816600, get $ 3.2 billion. This is the second part only after rice, which can export among the top agricultural of Vietnam agricultural. (http://www.globaltimes.cn/content/744010.shtml). Based on Table 2.1 showed the properties and specifications of SVR 3L (http://www.phuanrubber.com/tcvn3769-2004_en.pdf).

Table 2.1: SVR 3L properties and specifications
(http://www.phuanrubber.com/tcvn3769-2004_en.pdf)

Parameter	Value
Dirt (%wt, max)	0.03
Volatile matter (% wt, max)	0.8
Ash (%, max)	0.5
Nitrogen (% wt, max)	0.6
Initial plasticity (min)	35
Plasticity retention index (PRI) (min)	60
Lovibond colour index (max)	6

2.2 Vulcanizing Ingredients

2.2.1 Introduction

The curing or vulcanization is the process where the chains are chemically linked together to form a network, is also known as crosslinking. However, the term vulcanization covers not only the actual crosslinking process but also the method by which the crosslinking is produced (Hofmann, 1967). This process increases mechanical properties, abrasion resistance, decreases hysteresis and elongation.

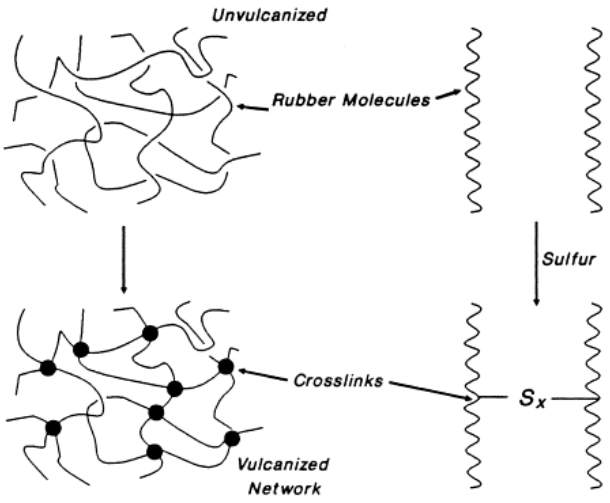


Figure 2.2: Vulcanization of the randomly oriented chains of natural rubber (Mark and Erman, 2005)

2.2.2 Sulphur

The most important vulcanizing agent for rubber is elementary sulphur, which is marketed in a ground form as sulphur for vulcanization. The solubility of sulphur varies from polymer to polymer. Sulphur dissolves relatively easily in natural rubber and styrene-butadiene rubber at room temperature (Hofmann, 1967). Sulphur with the raw gum rubber can react chemically together. It makes the long chains like the bridge, which gives more dimensionally stable and less heat sensitive product (Ciesielski, 1999). When rubber is vulcanized, sulfur molecules crosslink the polymer strands. That cross-linking helps hold rubber products together and allow them to resume their original shape after stretching (Freakley and Payne, 1978). Figure 2.3 shows the react chemically between polyisoprene and sulphur is formed crosslinked polyisoprene.

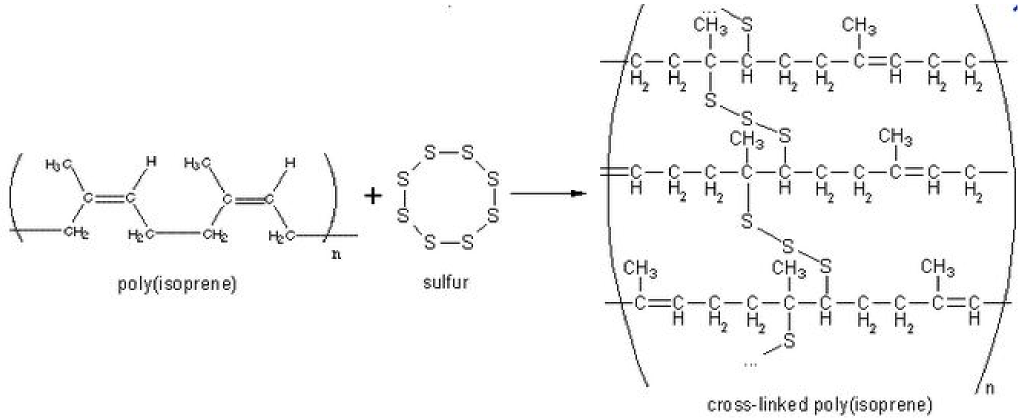


Figure 2.3: Sulphur vulcanization (Ciullo and Hewitt, 1999)

2.2.3 Activator

Activator is used to enhance the accelerators efficiency. One of the vulcanizing ingredients responsible for most of the conflicting theories existing is the activator. This compound is experimentally proved to improve the processing and final vulcanizate properties. In natural formulations, the activator most commonly used is the zinc oxide. Not only use zinc oxide but also use stearic acid each other to proceed more rapidly vulcanization as compared with vulcanization by sulphur alone (Barlow, 1993).

2.2.4 Accelerator

The rate of vulcanization of a rubber compound is controllable by the choice of accelerator. There are different types of accelerators used which vary to the vulcanization systems, methods and temperature of curing. The accelerator is used to reduce cure time by increasing cure rate of the rubber compounds (Simpson, 2002; Barlow, 1993). Table 2.2 shows commonly accelerator use in rubbers (Rodgers, 2004).

Table 2.2: Accelerator Classes (Rodgers, 2004)

Class	Response speed	Acronyms
Aldehyde-amine	Slow	_
Guanidines	Medium	DPG, DOTG
Thiazoles	Semi-fast	MBT, MBTS
Sulfenamides	Fast, delayed action	CBS, TBBS, MBS, DCBS
Dithiophosphates	Fast	ZBPD
Thiurams	Very fast	TMTD, TMTM, TETD
Dithiocarbamates	Very fast	ZDMC, ZDBC

The accelerator used for:

- Considerable scorch delay
- Better cure rate
- Cost effective
- Improve appearance and avoid blooming on the products
- Enhanced the resistance of degradation
- Allow vulcanization process to occur at high or low temperature

2.2.5 Antioxidant

Antioxidants are used to protect rubbers from the effects of thermal oxidation. Peroxide vulcanisates are usually protected with dihydroquinolines. Other antioxidants react adversely with the peroxide inhibiting the crosslinking reaction (Simpson, 2002). Different types of antioxidants possess different degree of chemical reactivity with oxygen and ozone, different degrees of solubility, and different diffusion rates in the rubber compounds. It determine how much protection a given antioxidants will impart to the rubber vulcanizates and whether it will be long-term or short-term proction p-phenylenediamine (PPD). It is used in rubber products such as tires and mechanical goods, as an antiozonant, antioxidant, and antiflex agents (Gent, 2001; Dick, 2003). Some common antioxidants or antiozonants derived from PPD, N-isopropyl-N’-phenyl-p-phenylenediamine (IPPD) is one of the most popular antioxidant being used in NR compounds (Malshe et al., 2006). Figure 2.4 shows the chemical structure of IPPD.

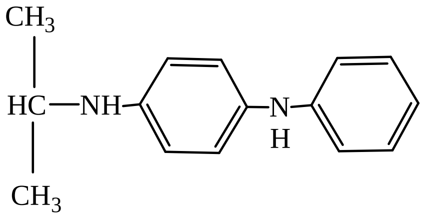


Figure 2.4: N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) (Roff et al., 1971)

2.3 Rubber Compounding

The rubber compound is found by Goodyear and Hancock. Nowadays, the natural rubber compounds are developed very large as materials for industrial application (Ciesielski, 1999). Compounding is a process of combining raw rubber and all compounding ingredients to ensure efficient manufacture of a promising product with desired properties and performance. The compounding process consists of the selection of the type and amount of various compounding ingredients used in a mix, the manner of mixing and processing of the finished mixing (Dick and Annicelli, 2009). The specific formulation is shown in Table 2.3.

Table 2.3: The specific formulation (Ciesielski, 1999)

Material	Part per hundred of rubber
Raw gum elastomer	100
Sulfur	from 0 to 4
Zinc oxide	5
Stearic acid	2
Accelerators	from 0.5 to 3
Antioxidant	from 1 to 3
Filler	from 0 to 150
Plasticizer	from 0 to 150

Each of ingredients has a specific function, either processing, vulcanization or end use of the product. The various ingredients may be classified according to their specific function in the following groups:

- Fillers (carbon blacks and non-black fillers)
- Plasticizers or softeners (extenders, processing aids, special plasticizers)
- Age resistors or antidegradants (antioxidants, antiozonants, special age resistors, protective waxes)
- Vulcanizing ingredients (vulcanizing agents, accelerators, activators)
- Special-purpose ingredients (coloring pigments, blowing agents, flame retardants, odorants, antistatic agents, retarders, peptizers).

2.3.1 Compounding process

The polymers, fillers, processing aids, vulcanizing ingredients, and other additives, which compounder has decided on, have to be mixed together. The two basic machines for this process are the two-roll mill and the internal mixer. The compounding of the ingredients into rubber often involves compromise. High viscosity promotes high shear, which is required to break up filler aggregates; low viscosity assists wetting of the particles, which is essential to achieve uniform modulus and other properties. It has been said that the quality of the final product is made in the mill room or compounding department because it is a uniform and high level of dispersion and consistent rheological properties must be produced in the batches of mixed compounds (Blow, 1971).

2.3.2 Forming process

After mixing, the green stock generally requires forming (shaping) into blanks of suitable dimensions. At this stage the stock will retain the shape imposed on it because it is predominantly plastic. Combined shaping and vulcanization operation known as moulding produce the majority of products. Three distinct types of moulding are used compression, transfer and injection (Nagdi, 1993).

For this research used compression moulding only. In the compression moulding, a compression type mould, the rubber blank is placed directly into the cavity mould where it is heated by conduction and caused to flow by application of pressure. The mould is held between the heated platens of the hydraulic press. The prepared quantity of moulding compound is placed in the mould and the moulding placed in the press. The press closes with sufficient pressure to minimize flash at mould parts line. The compound softens and flows to shape, chemical cure then occurs as the internal mould temperature becomes enough high. The press is opened and the mould removed. The vulcanization time is highly dependent on these three factors i.e. temperature, size of product and their heat transfer (Blow and Hepburn, 1982).

2.3.3 Vulcanization process

The green stock (unvulcanize) need to be converted to an elastic material after it has been formed to the desired shape. This can be achieved by the vulcanization process, which usually takes place under pressure at elevated temperature, using different techniques, such as: press vulcanization, open vulcanization, continuous vulcanization and cool vulcanization. Chemically, the process involves insertion of cross-links between polymer macromolecules through the action of vulcanization ingredients. Without these chemical bonds, no improved in the physical properties of the rubber mix can occur.

It is quite probable that the crosslink of the macromolecules together in such a way that the whole mass becomes a single molecule. The cross-linking of rubber is also referred to as curing, because it is a process whereby a raw material is converted into a useful product (Nagdi, 1993). When rubber is vulcanized, sulfur molecules crosslink the polymer strands. That cross-linking helps hold rubber products together and allow them to resume their original shape after stretching (Freakley and Payne, 1978).

2.4 Fillers

2.4.1 Introduction

Filler incorporated into rubber compound for many purpose such as improve processability, modify the physical properties and reduce cost of the rubber product (Sae-oui et al., 2009). Some fillers are added in natural rubber with large amount of fillers to improve mechanical properties of natural rubber compounds. Carbon black and natural mineral such as silica, talc, and clay are common used filler in rubber compounds. Some of these fillers have an influence on the rate of crosslink generation due to their acidity or alkalinity. Silica and silicates are anomalous in their effects on cure systems for one would expect them to behave as alkaline in nature and thus accelerate sulphur vulcanization, in fact they contain substantial amounts of combined oxygen, which represses or retards the reaction (Simpson, 2002).

The disadvantage of carbon black is black colour in the products. Hence, the non black fillers are used for the purpose colour of the products. However, depending on the purpose which we can decide the filler for the material ingredients of rubber compounds. The non black fillers such as clays, calcium carbonate, talc, silica usually use in natural rubber compounds, which improve the colour of rubber product, flex resistance and abrasion resistance (Ciullo and Hewitt, 1999; Rodgers, 2004).

2.4.2 Wollastonite

Wollastonite is mineral filler. It has white colour, acicular crystal and alkaline. The wollastonite composition is almost calcium oxide (CaO), silicon dioxide (SiO_2) and others a little metal oxide. The reaction to form wollastonite is:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2\uparrow$$

Wollastonite has the chemical composition $CaSiO_3$. The molecular structure of wollastonite is shown in Figure 2.5 (Ciullo and Robinson, 2002).

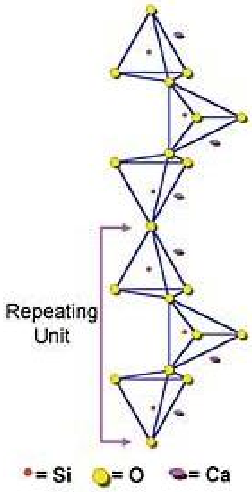


Figure 2.5: Wollastonite structure (Ciullo and Robinson, 2002)

Most of the world's production comes from the United States, although production comes from Finland, Mexico, and India is steadily increasing. Wollastonite is the naturally occuring white mineral which is wholly acicular. The length to diameter ratio typically varies from 3:1 to 20:1 but higher aspect ratios are also available.

Furthermore, wollastonite has 9.8 pH value, low coefficient of thermal expansion (6.5×10^{-6}/°C), and a low moisture content (less than 0.5%). Wollastonite is becoming an increasingly important filler as an asbestos replacement but its most important applications are due to its high brightness, low oil absorption, and reinforcing effect. In latex coatings, its high pH helps in stabilizing pH of the latex which improves the stability and shelf-life of the paint. In plastics applications, wollastonite reinforces tensile strength, flexural strength, impact strength, scratch resistance, improves thermal stability, increases welding strength, and decreases warpage or shrinkage (Wypych, 2000; Robinson, 2003).

Wollastonite is very special in the reinforcing mineral area. This mineral is the non-metallic, white mineral that is needle-like in particle shape. Wollastonite reinforced in thermoset and thermoplastic resin-based compounds (Robinson et al., 2002). Chemical treatment or silane coupling agent improve filler-rubber adhesion. The stronger bonding between filler and natural rubber matrix improve mechanical properties, weather resistance, and reduces shrinkage (Karian, 1999). The Table 2.4 and Table 2.5 showed chemical composition and physical properties of wollastonite.

Table 2.4: Typical Chemical Composition of Commercial Wollastonite Products (Karian, 1999)

Component (wt%)	Minerals (New York)	Minera (Mexico)	Finland	India	China	Africa	Synthetic grade
CaO	47.5	46.1	44.5	47.0	45.3	44.6	45.7
SiO_2	51.0	51.4	51.8	49.5	50.6	50.5	52.6
Fe_2O_3	0.40	0.25	0.22	0.43	0.34	0.42	0.26
Al_2O_3	0.20	0.66	0.44	0.60	0.68	0.80	0.47
MnO	0.10	0.05	0.01	0.29	0.06		0.04
MgO	0.10	0.50	0.56	0.20	0.70	0.50	0.55
TiO_2	0.02	0.02	0.05	0.01	0.02	0.09	0.13
K_2O	0.05	0.32	0.01	0.11	0.12	0.13	0.38
Loss on ignition	0.68	0.65	2.20	1.79	1.60	2.32	0.36

Table 2.5: Physical Properties of Wollastonite (Karian, 1999)

Property	Values
Morphology	Acicular
Nominal aspect ratio	20:1 to 3:1
Particle size	Products vary from -10 mesh to -1250 mesh
Loose bulk density, kg/m^3 (lb/ft^3)	Products vary from 220 to 1360 (14 to 85)
Tapped bulk density, kg/m^3 (lb/ft^3)	Products vary from 420 to 1440 (26 to 90)
Specific gravity of solids	2.87-3.09
pH (10 wt% slurry)	8-10
Molecular formula	$CaSiO_3$ or alternatively $CaO.SiO_2$
Color	Brilliant white to cream
Melting point (°C)	1540
Water solubility (g/100 cm^3)	0.0095

2.4.3 Carbon black

Carbon black is 90-99% elemental carbon with combined hydrogen and oxygen. Typical functional groups which are located on the surface of blacks are phenol, carboxy, lactol, quinine, ketone, pyrone and lactone. There also may be traces of chemically combined sulphur present associated with the source of some feedstocks. There is no evidence that this combined sulphur has any influence on rubber crosslinking (Simpson, 2002). Carbon black plays quite important a role in rubber compounding technology and in determining rheological and processing behaviour. Carbon black has very good compatibility with rubbers (Yan et al., 2005). Rattanasom et al., (2007) found that the mechanical properties and abrasion resistance are increased, when CB was added in rubbers.

Strongly adsorbed rubber at the surfaces of the carbon black reduces the rubber’s mobility and becomes bound rubber (Simpson, 2002). The incorporation of carbon black with high surface area in an elastomer results in a high level of reinforcement and higher tensile strength, tear strength, and abrasion resistance, but also results in a compound with high hysteresis, high cost, and one which is more difficult to mix and process (Evans, 1981). The improvement in properties such as tensile strength, modulus, tear strength, and abrasion resistance when carbon black was added to elastomers has motivated much research into the mechanisms of such reinforcement. There are likely both chemical and physical interactions between carbon back and the rubber matrix, resulting in property improvement, but the understanding of the nature of carbon black reinforcement is still growing (Barlow, 1993). The structure of carbon black is shown in Figure 2.6 (Wang et al., 2003).

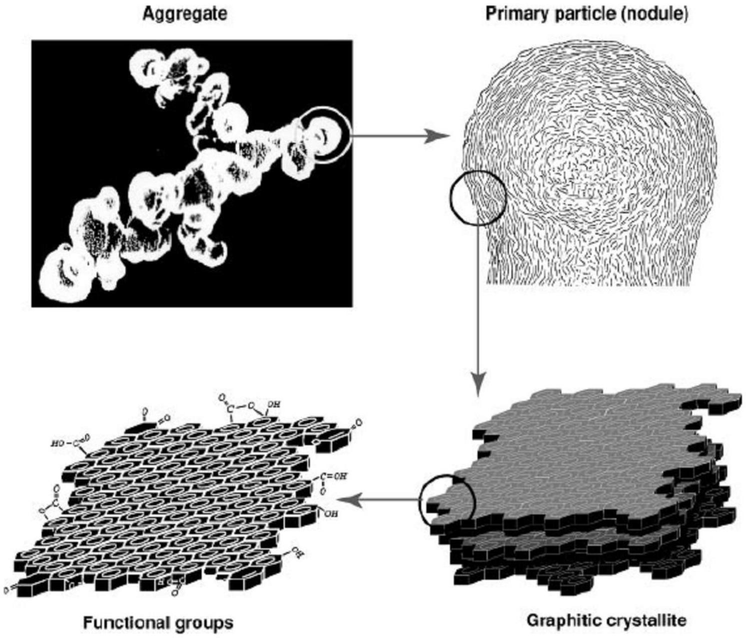


Figure 2.6: Structure of carbon black (Wang et al., 2003)

Table 2.6: Effect of Carbon Black on Rubber Properties (Rodgers, 2004)

	Effect of increase in carbon black properties		
Rubber Property	Surface	Structure	Loading
Uncured properties			
Mixing temperature	Increases	Increases	Increases
Die swell	Decreases	Decreases	Decreases
Mooney viscosity	Increases	Increases	Increases
Dispersion	Decreases	Increases	Decreases
Loading capacity	Decreases	Decreases	_
Cured properties			
300% Modulus	Insignificant	Increases	Increases
Tensile strength	Increases	Insignificant	Increases[a]
Elongation	Insignificant	Decreases	Decreases
Hardness	Increases	Increases	Increases
Tear resistance	Increases	Decreases	Increases[a]
Hysteresis	Increases	Insignificant	Increases
Abrasion resistance	Increases	Insignificant	Increases[a]
Low strain dynamic modulus	Increases	Insignificant	Increases
High strain dynamic modulus	Insignificant	Increases	Increases

[a] Increases to an optimum, then decreases.

2.4.4 Calcium carbonate

Calcium carbonate (CaCO3) is one of the common mineral filler used in polymer composites that can improve thermal resistance properties, could control viscosity, reduce shrinkage, have light colour and easy to be compounded (Etelaaho et al., 2011). Calcium carbonate is non-reinforcing filler, which increase impact properties of polymer composites, inexpensive and used to provide colour and minimize the price of the products (Deodhar et al., 2011).

There are two main types of calcium carbonate available that is ground natural limestone and precipitated calcium carbonate. The ground lime is prepared by grinding mineral limestone, whilst the precipitated calcium carbonate is obtained by chemical precipitation from salt solution (Mittal et al., 2011). The ground limestone has less than 100 meshes and used as an inert diluents and cheapening filler for rubber compounds (Simpson, 2002).

There are so many application of calcium carbonate, the major polymer applications such as PVC, PE, PS, silicone, acrylic, rubber, polyester and many more (Wypych, 2000). Calcium carbonate can show high brightness and high gloss in the products. It also imparts some disadvantages to the products include lowered tensile strength and elongation, and low resistance to organic acids (Maier and Calafut, 1998). The common properties of calcium carbonate are listed in Table 2.7 (Wypych, 2000).

Table 2.7: The properties of calcium carbonate (Wypych, 2000)

Property	Value
Density (g/cm^3)	2.7-2.9
Decomposition temp (°C)	1150
Hardness (Mohs scale)	3-4
Melting point (°C)	1339
Moisture content (%)	0.01-0.5
Chemical resistance	Reacts with acids
pH of water suspension	9-9.5
Brightness	82-94
Particle shape	Irregular
Oil absorption (g/100g)	13-21
Specific surface area (m^2/g)	5-24

2.5 Planetary Ball Mill

The purpose of the ball mill physical treated is reduction particle size using Planetary Ball Mill (model Retsch PM 100). The particle size is one of a factor to enhance the mechanical properties such as tensile strength, tensile modulus of the polymer composites (Kauly et al., 1996). Consequently, Planetary Ball Mill is finer one of the methods to reduce particle size. This is one of the most popular mills used for synthesizing almost all materials. In this type of mill, the milling has considerably high energy.

The working principle of the Retsch PM 100 is based on the relative rotational movement between the grinding jar and the sun wheel diameter and speed of rotation this speed ratio is decisive for the energy input and therefore for the results of the size reduction process. There are two speed ratio settings in this machine. For example, a ratio of 1:-1 means that each time that the sun wheel rotates the grinding jar also rotates exactly once in the opposite direction. With a speed ratio of 1:-2 the grinding jar rotates twice for each sun wheel rotation. In order to follow the rotational movement of the grinding jar you have to imagine that you are standing at the center of the sun wheel. During the sun wheel rotation you will see the red reference point exactly twice, i.e. the grinding jar has rotated twice (see Figure 2.7) (http://www.retsch.com/products/milling/planetary-ball-mills/pm-100/).

Figure 2.7: Speed ratios and grinding jar of Planetary Ball Mill

2.6 Interface

The function of silane coupling agent are chemically link between organic and inorganic materials. The study of mechanism of the silane coupling agents was begun in 1960s. The main applications of silanes were the bonding between glass fibres and thermoplastic resins, which result improve the reinforcement (Rodgers, 2004). The mineral fillers such as clay, silica, and silicates, which have surface silica groups can hydrolyzed to silanols (-SiOH). These silanol groups behave as acids (-SiO^-H^+) are active. If the fillers have higher surface area, they have more silanol and give more active, which show increases mechanical properties and improve abrasion resistance. The methoxy or ethoxy groups react during mixing with silanol groups on the surface of silica (SiO_2) particles to give better bonding between filler and NR matrix (Ciullo and Hewitt, 1999). The chemically reaction of wollastonite and silane coupling agent facilitates improvement the properties of NR compounds is shown in Figure 2.8 (Ma et al., 2011). Meng and Dou, (2008) found that the pimelic acid (PA) treated wollastonite filled polypropylene composites improve the interfacial interaction of the filler into matrix.

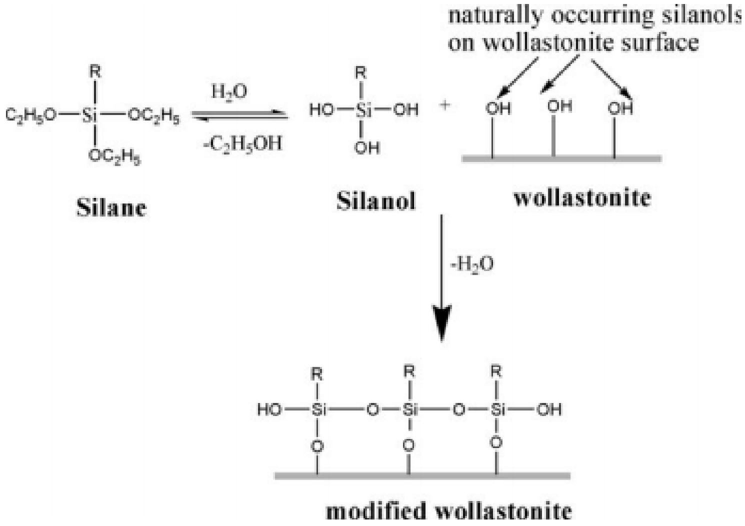


Figure 2.8: Schematic of silane mineral reaction to produce the modified wollastonite filler surface (Ma et al., 2011)

2.6.1 Silane Coupling Agent

Silane coupling agents improve properties of compounds containing silica and silicate fillers by forming chemical bond across the filler and the rubber interface. They can also give improved properties with other materials, such as carbon blacks. They can be used with clays, which do not form strong chemical bonds with the polymer, thus bringing them into the general category of useful processing additives. The improved compound properties result from a better compatibility and linkage of the rubber and filler. The coupling agent can be added direct to the mixer with the filler (Ren et al., 2006; Poh and Ng, 1998; Simpson, 2002).