EFFECT OF DIFFERENT ORIGIN OF NATURAL RUBBER, CARBON BLACK LOADING, AND VULCANIZATION SYSTEMS ON PROPERTIES OF NATURAL RUBBER COMPOUNDS

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by

YOS PHANNY

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List of Abbreviations

ASTM	American Standard for Testing and Materials
CB	Carbon black
CBS	N-cyclohexyl-2-benzothiazole sulfonamide
CRI	Cure Rate Index
CV	Conventional vulcanization
EV	Efficient vulcanization
IPPD	N-isopropyl-N’-phenyl-p-phenylenediamine
IRHD	International Rubber Hardness Degree
JIS	Japan Industrial Standard
NR	Natural rubber
phr	Part per hundred rubber
PRI	Plasticity retention index
SCR	Specified Cambodian Rubber
SEM	Scanning Electron Microscopy
SMR	Standard Malaysian Rubber
SVR	Standard Vietnamese Rubber
TSR	Technically Specified Rubber

List of Symbols

C	Compression set
d	Thickness
F	Force
M100	Tensile modulus at 100% elongation
M300	Tensile modulus at 300% elongation
M_c	Number average molecular weight of network chains
MH	Maximum torque
ML	Minimum torque
M_o	Original weight
M_t	Swelling weight
Po	Wallace plasticity
Q	Swelling ratio
t_{90}	Cure time
t_f	Final thickness
t_i	Original thickness
T_s	Tear strength
t_s	Thickness of the spacer bar
t_{s2}	Scorch time
V_l	Molar volume of the swelling liquid
V_r	The volume fraction of rubber in the swollen material
μ	A solvent-rubber interaction constant
ρ	Density of the network

KESAN PERBEZAAN TEMPAT ASAL, PEMBEBANAN HITAM KARBON (CB) DAN SISTEM PEMVULKANAN KE ATAS SIFAT SIFAT SEBATIAN GETAH ASLI

ABSTRAK

Dalam kajian ini, kelikatan Mooney bagi getah asli yang diperolehi daripada Malaysia (SMR CV60), Kemboja (SCR 10 dan SCR L) dan Vietnam (SVR 3L) telah diuji. Kesan tempat asal, pembebanan hitam karbon (CB) dan sistem pemvulkanan yang berbeza (sistem pemvulkanan cekap (EV) dan pemvulkanan lazim (CV)) telah dikaji. Getah asli yang diperolehi daripada tempat yang berbeza menunjukkan sifat-sifat vulkanizat yang berbeza disebabkan oleh berat molekul dan kandungan protein. Di dalam sistem EV, oleh sebab berat molekul dan kandungan protein yang tinggi yang terdapat di dalam SCR 10, kadar pemvulkanan bagi sebatian tanpa pengisi dan sebatian berpengisi adalah cepat. Bagi sistem CV pula, SCR L yang mempunyai berat molekul yang rendah tetapi mempunyai kandungan protein yang tinggi menunjukkan kadar pemvulkanan yang cepat. Kesan pembebanan CB dapat dilihat secara menyeluruh dengan peningkatan pembebanan CB dapat meningkatkan sifat-sifat fizikal and mekanikal sebatian getah asli tetapi pada masa yang sama, ia mengurangkan ketahanan terhadap kelesuan yang disebabkan oleh kestabilan sebatian. Sebatian yang menggunakan sistem CV menunjukkan sifat-sifat fizikal dan mekanikal yang lebih tinggi berbanding sistem EV, tetapi daya tahan terhadap haba yang lemah disebabkan oleh pemutusan sambung silang polisulfida.

EFFECT OF DIFFERENT ORIGIN OF NATURAL RUBBER, CARBON BLACK LOADING, AND VULCANIZATION SYSTEMS ON PROPERTIES OF NATURAL RUBBER COMPOUNDS

ABSTRACT

In this research, Mooney viscosity was tested for natural rubber (NR) from Malaysia (SMR CV60), Cambodia (SCR 10 and SCR L) and Vietnam (SVR 3L). The effect of different origins of NR, different loading of carbon black (CB) filled NR compounds, and different vulcanization systems (efficient vulcanization (EV) and conventional vulcanization (CV) systems) were studied. Origins of NR showed different cure characteristics due to molecular weight and protein content. In EV system, SCR10 possesses higher molecular weight and protein content hence give faster cure rate for both gum and filled compounds. For CV system SCR L possesses lower molecular chain but higher protein content exhibiting faster cure rate for gum compound. For effect of CB loading, higher CB loading significantly increased the physical and mechanical properties of NR compounds, but decreases fatigue life due to stability of the compound. Compounds with CV system show higher physical and mechanical properties compared to EV system, but CV system are vulnerable to heat ageing due to the breakage of polysulphidic crosslinks.

CHAPTER 1

INTRODUCTION

The rubber industry is a full-grown industry which really became known as a commercial enterprise after Charles Goodyear found out how to vulcanize rubber in 1839. From its early applications in shoe soles and bicycle tires, the industry has started a wide variety of products such as truck tires, farm tires, passenger tires, off-the-road tires, hose, conveyor belts, molded mechanical goods, matting and sheeting, tank lining, V-belts, shoe heel and soles, and sponge rubber.

1.1 Natural rubber composites

Rubbers are extensively used in many applications for their large reversible elastic deformation, excellent damping and energy absorption characteristic. Difference from other polymers, natural rubber (NR) is highly vulnerable to degradation, due to the presence of double bonds in the main chain. NR is easy to be attacked by solvents, deteriorated by oxygen, ozone, sun light, UV rays as well as humidity (Vinod et al., 2002). Therefore, reinforcing fillers are necessarily added into NR in most cases in order to gain appropriate properties for specific applications (Blow and Hepburn, 1982, Ismail and Poh, 2000, Choi et al., 2003). Rubber mount is widely used in vehicles powertrain (group of components that generate power and deliver it to the road surface, water or air) mounting system and plays an important role in noise, vibration and harshness (NVH) reduction. Also, it is used in vehicle cab mounting system, wheel suspension system, and other mobile or stationary machines' mounting systems (Blow and Hepburn, 1982, Mark, 2007).

A composite material is a material brought about by combining materials differing in composition or form on a macroscale for the purpose of obtaining specific characteristics and properties. The constituents retain their identity such that they can be physically identified and they exhibit an interface between one another (Schwartz, 1992). Rubber composites are rubber vulcanizates with fillers. The properties of composites depend on interaction of fillers with elastomer including extensity, intensity and geometrical factors (Blow and Hepburn, 1982, Osman and Atallah, 2006, Fu et al., 2008). Fillers also have been used in rubber to cheapen the products and do not strongly affect the vulcanizate properties in rubber. The use of fillers in rubber is almost as old as the use of rubber itself (Blow and Hepburn, 1982). For a filler to provide significant reinforcement, it must possess high specific surface area. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Carbon black and silica are two types of fillers that are most effective for reinforcing rubber. They can be produced with a primary particle size as small as 100 Ǻ, corresponding to a surface area of a few hundred m^2 per gram of filler (Gent, 2001).

Origins of NR have been reported for their different in properties such molecular weight, gel content, protein content and nitrogen effect. Nitrogen groups from Hevea brasiliensis have been regarded as an important factor governing cured rubber properties (Sakdapipanich, 2007). Moreover, protein in NR have long been considered to be essential component that affect to the characteristic properties of NR, mainly cured rubber properties. Chenal et al. (2007) showed that decrease in average molecular weight leads to decrease in the crystallite growth at high crosslink density while crystallite volume is quasi-independent on average molecular weight at weak crosslink density. Bhowmick et al. (1986) showed that Hevea braziliensis is superior to synthetic Natsyn and guayule rubber in terms of mechanical and rheological properties for the same isoprene backbone chain.

1.2 Engine mount

The engine mounts are used to isolate engine vibration and prevent engine bounce from shock excitation. Engine mount improvement has been made for the requirement of vibration and noise level and for modern car designs having a trend for lighter car body with more power-intensive engines. Different types of engine mounting systems, from elastomeric to hydraulic and from passive to active, have been developed to improve the mount performance. Elastomeric mounts are rubber mounts designed for the necessary elastic stiffness rate characteristics in all directions for proper vibration isolation. Passive hydraulic mounts can provide a better performance than elastomeric mounts especially at low frequency. Semi-active techniques are usually used to further improve performance of hydraulic mounts by making them more tunable which meant one or more system parameters can be controlled to adjust the dynamic response of the system. The active engine mounting system can be very stiff at low frequency and be tuned to be very soft at the higher frequency range to isolate vibration (Kim and Singh, 1995, Yu et al., 2001, Hillis et al., 2005).

1.3 Problem statements

Cambodia still has limited knowledge of natural rubber composites and all natural rubber in form of dry rubber is exported to nearby countries. As more rubber trees are now planting in many parts of country, Cambodian natural rubber was used to study the properties in composites which are expected to be very useful in future work in Cambodia.

Different origins of rubber give different properties, hence very important to studies each property. Vulcanization systems also play important roles in determining rubber vulcanizates properties. Accelerated sulphur system is the most popular system for rubber compounding. Efficient vulcanization and conventional vulcanization systems are used to study the different properties of rubber composites for this research.

Addition of carbon black (CB) to certain loading has been found to offer substantial improvement in the mechanical properties of rubber because of its compatibility with rubber, but it will decreased to higher loading of CB. It was chosen in this study due to its significant reinforcement in rubber composites. Anti-vibration, damping, and noise; mounts are usually affected by fatigue action, compression, and loss of resilience. Mostly, engine mounts, being used as seal or lining, are faced with motor oil or other hydrocarbon such as petrol which caused swelling.

1.4 Objectives

This study was conducted to give better understanding on properties of natural rubber composites affected by different origin of natural rubber (Malaysian, Vietnamese and Cambodian natural rubber) with conventional vulcanization (CV) and efficient vulcanization (EV) systems. It also aimed to investigate the effect of carbon black loading on Cambodian natural rubber with EV system and the effect of different vulcanization systems, CV versus EV systems, on SCR 10 rubber. This work was carried out to achieve the following objectives:

i. To determine the properties of natural rubber composites with different origins of natural rubber

ii. To determine the effect of carbon black loading on physical and mechanical properties of the properties of Cambodian natural rubber composites.

iii. To investigate the effect of different cure systems, CV and EV systems, on SCR 10 rubber composites at 30 phr carbon black loading.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural rubber

2.1.1 Different origins of NR

Natural rubber (NR) can be extracted from different plant species which only a few are commercially important. There are a number of tree species for rubber which are native to many parts of Africa and the Far East. The outstanding source of natural rubber is the large forest tree Hevea brasiliensis, located in the southern equatorial region of America. It was brought to India in 1876 and sent to equatorial part such as Java, Borneo and Ceylon and more particularly in Malaya for the cultivation of rubber trees (Blow and Hepburn, 1982, Sethuraj and Mathew, 1992, Loadman, 2005). The Hevea Brasiliensis trees can grow up to 30 m high with a main trunk of about 50 cm diameter (Kothandaraman, 2008). Some historical interest rubber trees are listed below and Hevea braziliensis (Figure 2.1 (a)) produces almost all of the natural rubber products in the world (Loadman, 2005).

- Castilloa (elastica and ulei): The former is found in Central America and Mexico (Figure 2.1(b)), the latter in Peru and Brazil.
- Manihot glaziovii: From the Ceara region of Brazil.
- Ficus elastica: Found in Java and Malaysia (Figure 2.1 (c))
- Landolphia: Creepers found mainly in the Congo basin (Figure 2.1 (d))
- Funtumia elastica: Found in West Africa.

For many years there have been two mains types of rubber; crepe prepared by coagulating the latex, washing, rolling, and drying the coagulum; and smoked sheet prepared similar as creep rubber but drying the coagulum in the presence of smoke.

Within each grade, crepe and smoked sheet are categorised in a number of subgrades which resulted in more than 31 standard grades classified entirely on appearance without regard to the properties (Blow and Hepburn, 1982). The grades classification of standard Malaysian rubber is shown as in Table 2.1.

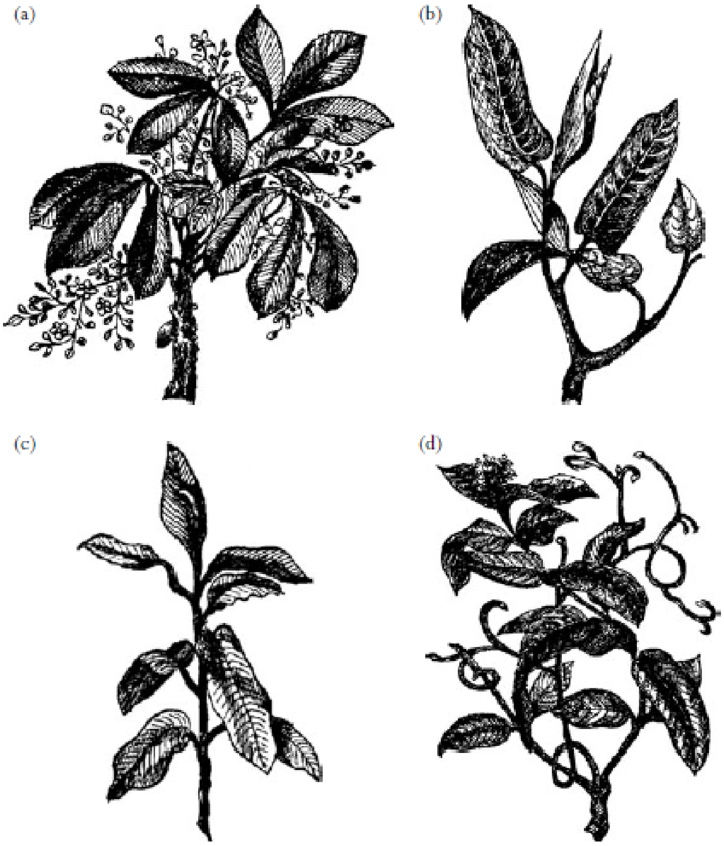


Figure 2. 1 (a) Hevea braziliensis, (b) Castilloa elastica, (c) Ficus elastica, and (d) Landolphia owariensis (Loadman, 2005)

Technically Specified Rubber (TSR) was adapted from Standard Malaysian Rubber (SMR) scheme which was introduce in 1965. TSR L is a color-specified rubber with a range limit of two Lovibond units within a production lot. The latex is preserved with a mixture of ammonia and boric acid and subsequently treated using 0.05% sodium metabisulphite to inhibit enzymic darkening. It is then coagulated by addition of formic acid and allowed to mature for up to 12 hours. The coagulum is processed into crumb form, followed by hot air drying at 100 °C and the dried crumbs are cooled to 60 °C and compressed into standard bales. For TSR CV, natural rubber undergoes an irreversible increase in viscosity that occurs during transport and storage.

For SMR CV60, the Mooney viscosity is in the range of 60 ± 5 MU. TSR 10, this grade consists predominantly of cuplump or field coagulum, where natural coagulation of the latex has been allowed to occur in the collecting cups. The raw materials are first soaked in water, blended, and then fed through a series of creper-hammermills, granulators and size reduction to produce clean crumbs that are dried and baled. SMR L and SMR CV60 possess similar properties, while the difference SMR CV 60 focus on Mooney viscosity and SMR L focus on Lovibond color scale shown in Table 2.1. SMR 10 shows higher range of dirt and ash content (Fulton and Thorpe, 1996). Natural rubbers used in this research, SVR and SCR, are similar to the SMR, which accordance with TSR.

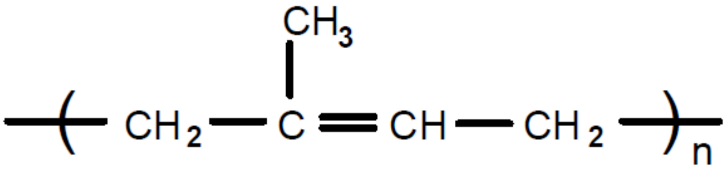
Table 2. 1 Grades classification of SMR CV60, SMR L and SMR 10 (Fulton and Thorpe, 1996)

Parameters	SMR CV60	SMR L	SMR 10
Dirt content (max, % wt)	0.02	0.02	0.08
Ash content (max, % wt)	0.50	0.50	0.75
Volatile matter content (max, % wt)	0.80	0.80	0.80
Nitrogen content (max, % wt)	0.60	0.60	0.60
Po (min)	-----	35.0	30.0
PRI (min, %)	60.0	60.0	50.0
Color Lovibond scale (max)	-----	6.00	-----
Mooney viscosity ML(1+4) 100	55–65	-----	-----

Cornish (2001) made a review on the investigation of rubber biochemistry factors that affecting rubber yield (biosynthetic rate, substrate availability and rubber particle size, number and ontogeny(growing)) and rubber quality (primarily rubber molecular weight) among plant species. She compared three different types of rubber, Hevea brasiliensis, Parthenium argentatum and Ficus elastica. The amount of protein associated with rubber particles varies tremendously between species and the number of different proteins is remarkably different. Hevea brasiliensis contains the most complicated particles. It is found that Hevea brasiliensis and Parthenium argentatum contain high molecular weight rubber while Ficus elastica contains low molecular weight rubber.

2.1.2 General properties of NR

NR is a polymer composed of long chains of isoprene which are randomly agglomerated and entangled with the empirical formula of C_5H_8. NR is *cis*-1,4-polyisoprene, of molecular weight 200,000-500,000, with small level of highly important non-rubber constituents which include proteins, sugars and fatty acids (Blow and Hepburn, 1982, Billmere, 1984, Sethuraj and Mathew, 1992, Kothandaraman, 2008). The trace elements present include potassium, manganese, phosphorus, copper and iron which can act as catalysts for oxidation (Simpson, 2002). NR is produced from the coagulation of natural rubber latex containing 25-40% of rubber hydrocarbon (Billmere, 1984, Dick, 1987). NR possesses superior building tack over other synthetics with sticky quality that is needed to build different rubber products from uncured rubber. NR has the ability to strain crystallize when stretched which enables NR gum compounds (compounds without fillers) to have good tensile strength. NR has extremely high resilience, high tensile strength, good tear resistance, and high fatigue to failure in cured state. The carbon–carbon double bonds in its chains possesses poor ageing properties weather heat ageing, weathering or ozone attack and poor resistance to oil (Dick, 1987, Zhou et al., 2000, Nakason et al., 2005). Figure 2.2 shows general repeat unit of isoprene of natural rubber. For this structure, two carbon atoms are joined together by a double bond and locked in a rigid structure. Because of the presence of an asymmetric carbon atom, *cis* (two same groups attached to each carbon are in the same sides) and *trans* (two same groups attached to each carbon are in the opposite sides) forms are possible.



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

Figure 2. 2 Repeat unit of NR (polyisoprene) (Simpson, 2002)

2.1.3 Mooney viscosity and gel content

Mooney viscosity is a measure of the viscosity of a raw rubber or rubber compound determined in a Mooney shearing disk viscometer. Mooney viscosity was first used in technically classified rubber for grading standard rubber (Simpson, 2002). For raw rubber, the measured viscosity is done at temperature of 100 ^{o}C with one minute preheating and four minutes running test which is written in short $ML(1+4)_{100}$ (Ehabé et al., 2005). Mooney viscosity of rubber sample relates roughly to the rubber's average molecular weight. It also reflects the molecular weight distribution and the amount of network structure that is exhibited in rubber (Blow and Hepburn, 1982, IRI, 1998).

Bhowmick et al. (1986) investigated the effect of gel and molecular weight on properties of natural rubber. Samples with different gel contents but similar molecular weights and samples with the same gel content with varying molecular weights prepared from the extraction of natural rubber. The gel content was varied from 1.5 to 29% and molecular weight from 1 x 10^5 to 9.9 x 10^5 g mol^{-1}. Samples with higher molecular weight and higher gel content showed better stress-strain properties. Chenal et al. (2007) investigated the strain-induce crystallization (SIC) of natural rubber compounds which focus on molecular weight between physical entanglements. It showed that natural rubber is essentially constituted of cis-1,4 polyisoprene which stereoregularity allows rapid crystallization when it is stretched more than 300% of its original length. This strain-induced crystallization (SIC), gives NR a self-reinforcement characteristics, and increase in crosslink density which reduced the NR matrix mobility and delays the orientation of the crystallites during the stretching process.

2.1.4 Wallace rapid plasticity (Po) and plasticity retention index (PRI)

Plasticity can be described as ease of deformation of rubber so that highly plastic rubber is determined by one that deforms or flow easily (Brown, 1986). The PRI reflects the vulnerability of the product to thermo-oxidation, whereas Po provides the viscosity of an average for the range of shear rates throughout the rubber of the raw material. Plasticity is determined by the Wallace plastimeter which used as quality control for most natural rubber product (Bonfils et al., 1999).

2.2 Fillers

2.2.1 Definition and classifications

The concept of cost reduction by use of filled materials has been known throughout the ages (Blow and Hepburn, 1982, Lutz and Grossman, 2001). In general, fillers are defined as materials (can be in the form of solid, liquid, or gas) that are added to the formulation to lower the compound cost. The appropriate selection and optimization of such materials, not only lower the price but improved other properties such as processing and mechanical behaviour (Lutz and Grossman, 2001).

For effective utilization of fillers, a complete understanding of individual characteristics is essential. Each class of fillers appears to exhibit specific characteristics which suited for the given application. For example, aluminium powder is used to improve the resistance of the compounds toward heat, ozone and gamma irradiation (Vinod et al., 2002), calcined clays for electrical properties (González et al., 2000). Although these fillers retain their inherent characteristics, very significant differences are often observed, depending on the molecular weight, compounding technique, and the presence of other additives in the formulation. Therefore, once the basic property requirements are established, the optimum filler type and loading for cost/performance balance can be determined (Wypych, 2000, Lutz and Grossman, 2001).

Fillers can be classified in many different ways, ranging from their shapes (sphere, rods, ribbons, flakes) to specific characteristics (conductivity, fire retardancy)(Wypych, 2000). For simplicity, fillers can be classified in two categories: extenders (primarily occupies space and is mainly used to lower the formulation cost) and functional/reinforcement materials (has a definite and required function in the formulation apart from cost) (Lutz and Grossman, 2001). In general, an ideal extender should:

- be spherical to permit retention of anisotropic properties
- have an appropriate particle size distribution for particle packing
- no chemical reactivity with the polymer or additives
- have a low specific gravity
- have a desirable refractive index and color
- low in cost.

Common extenders are limestone, kaolin clay and talc. For functional group, precipitated silica and carbon black are commonly used among commercial fillers and these are extensively used when high strength is essential.

2.2.2. Fillers characteristics

Fillers are added to the matrix to improve the properties (tensile strength, tear resistance, abrasion resistance) of composites (Blow and Hepburn, 1982, Dick, 1987). Fillers can constitute either a major or a minor part of a composite. Modulus of rubbers is increased by the incorporation of reinforcing fillers such as carbon black or silica. The key elements of rubber reinforcement with fillers are particle size, surface area, structure, dispersion and interaction between the surface of the reinforcing material and the rubber (IRI, 1998). The structure of filler particles ranges from precise geometrical forms, such as spheres, hexagonal plates, or short fibers, to irregular masses. Extensive usage of particulate fillers in many polymers is for the enhancement in stiffness, strength, dimensional stability, toughness, heat distortion temperature, damping, impermeability, and cost reduction (Herman, 2003).

2.2.2.1 Particle size

Average filler's particle size is one of the most important characteristics in predicting the function for a given filler to impart the properties of rubber. In general, the smaller the average particle size of a filler, the higher the degree of reinforcement imparted to the vulcanizate. Improvement in reinforcement means the tensile, modulus, abrasion resistance, and tear resistance showed very large increase in properties. Large particles of fillers caused severe cracking. Fillers with average particle sizes range (1 to 5 microns) are dilution fillers which do not significantly improve or have a negative effect on the physical properties of the vulcanizate provided the loadings are not too high (Dick, 1987). However, due to increases in both surface area and volume ratio with a reduction in filler particle size, finer particles are prone to agglomerate for the conservation of internal energy and are more difficult to be dispersed (Herman, 2003).

2.2.2.2 Particle shape and structure

The structure and particle shape of a filler are also important. Structure relates to the aggregation of particles. Carbon blacks tend to have much higher structure than inorganic fillers. The structure of most inorganic fillers is lower than carbon black and tends to break up easily during mixing. Carbon blacks with the same particle size but with different structures will give different physical properties in rubber. A higher structure carbon black (Figure 2.5(b)) in a rubber compound will impart less extrudate shrinkage, swell less on extrusion and impart a higher modulus than a lower structure carbon black (Dick, 1987). Figure 2.3 shows the basic particle shapes and typical aspect ratios which is the ratio of the longest length of a particle to it thickness. In general, a high aspect ratio material is more difficult to process and yields higher anisotropy in composites, but it tends to provide better mechanical properties, than a low aspect ratio one (Sekutowski, 1996).

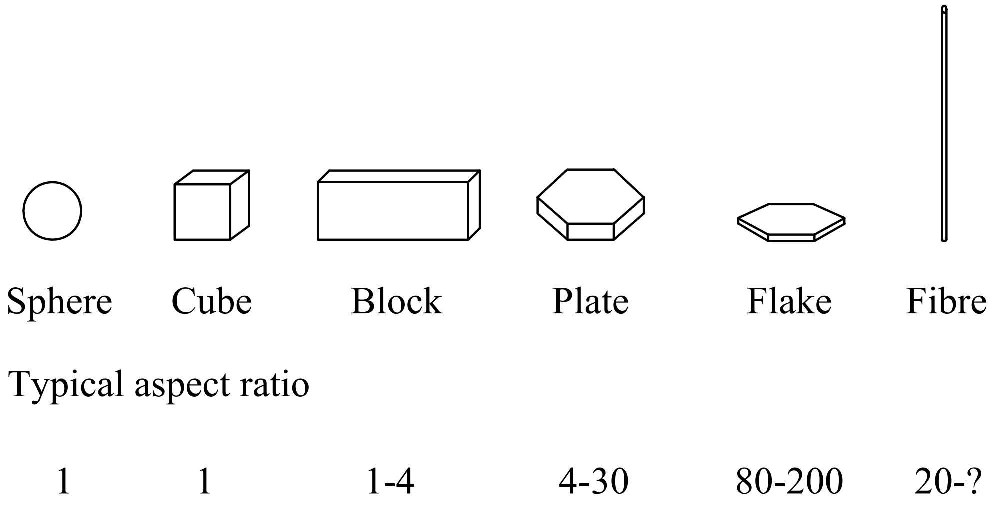


Figure 2. 3 The fillers various morphology with aspect ratio (Sekutowski, 1996)

2.2.2.3 Surface activity

The nature of the solid surface may vary in a chemical sense, with different chemical groups: hydroxyl or metaloxide in white fillers, organic carboxyl, quitone, or lactone groups in carbon black and other organic fillers. In physical sense they may be different in adsorptive capacity and in energy of adsorption. Chemical surface groups play an important role in their effect on the rate of cure with many vulcanizing systems. However, the physical adsorption activity of the filler surface is much greater importance than its chemical nature for the mechanical properties of the general purpose rubbers (Blow and Hepburn, 1982, Dick, 1987). Rattanasom and Prasertsri (2009) studied the properties of partial replacement of clay with different types of carbon black filled natural rubber composites at similar hardness level. It showed with SEM micrographs, in Figure 2.4, for various NR vulcanizates revealing that the dispersion of fillers in the N330 is better than N550, N774 and the control (calcined clay). The arrows in this figure point out the large agglomeration of the fillers that can be observed in N550, N774 and the control.

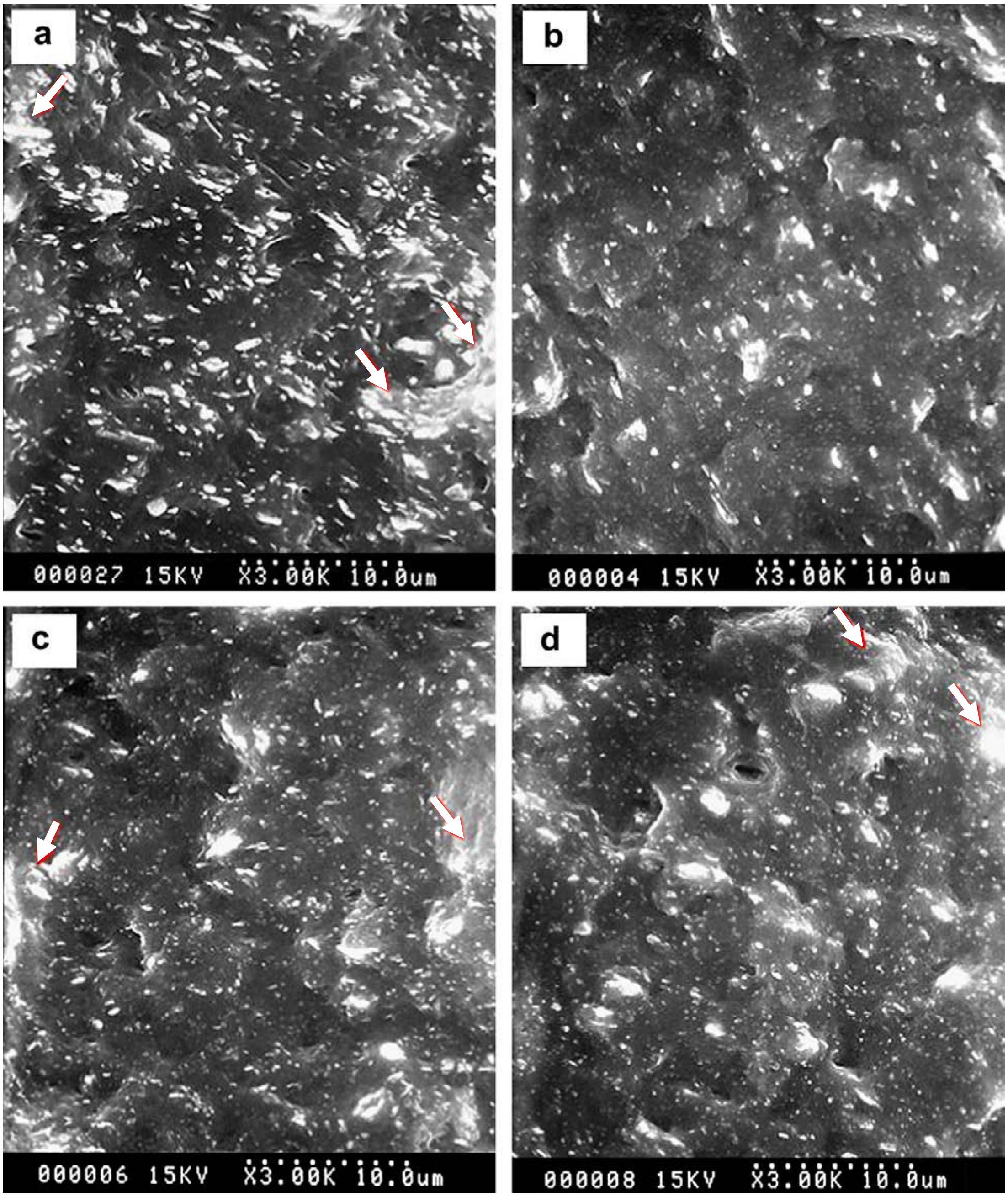


Figure 2. 4 SEM micrographs of fracture surfaces of various NR vulcanizates: (a) Control, (b) N330, (c) N550 and (d) N774 (Rattanasom and Prasertsri, 2009)

2.2.2.4 Matrix-filler interaction

The interaction between rubber and filler give significant effect on reinforcement of filled rubber composites. The rubber–filler interactions strongly depend on their characteristic and their amount. Matrix-filler interaction showed the compatibility between rubber and filler while filler-filler interaction occur due to the bonding between the fillers and their ability to form networks which are aggregates (agglomerates) (Kohls and Beaucage, 2002). The interaction in the rubber composites occurs by chemical and physical combination interactions (Mark et al., 2005).

In general, reinforcement can obtained through applied stress transferred from polymer to fillers. Through more uniform distribution of stress from a large number of extremely small flaws, weak points or cracks that tend to open up at points of high local stress concentration. The unique reinforcing capacity of carbon black may be due to its surface adsorption characteristics. These relatively strong bonds limit further slippage and contribute to the strength of vulcanisate (Blow and Hepburn, 1982). Carbon black has been found to offer substantial improvement in the mechanical properties of rubber due to its good compatibility with rubber. Practically, the crosslink density in rubber vulcanizates increases significantly with increasing carbon black content. These crosslinks control extensibility of the rubber chains caused by swelling and make it more difficult for oil to diffusion into the gaps between rubber molecules and decrease the swelling percentage (Mostafa et al., 2009) which showed the increase in filler-rubber matrix interaction. Leblanc (2002) reviewed the rubber-filler interactions and rheological properties of rubber filled carbon black and silica composites. It showed filler particle size and structure as primary parameters, and surface characteristics as secondary particle parameters. Figure 2.5 shows the functional groups of carbon black on surface chemistry which results in high interaction to rubber matrix. A review of characterization dispersion state of filler and polymer-filler interactions in rubber-carbon composites was done by Karásek and Sumita (1996). The uniform dispersion of carbon black throughout the rubber matrix is very important for rubber compounding to achieve optimum vulcanizate properties and the degree of dispersion is a factor which ultimately controls the physical properties of the composite.

2.2.3 Carbon black

Carbon black is an amorphous carbon of quasi-graphitic structure. The particles range from 10 nm to 500 nm in diameter. A common value used for the density of carbon black in rubber is 1.80 and carbon blacks consist of 90 to 99 percent elemental carbon. The other major constituents are hydrogen and oxygen. Carbon blacks are produced by converting either liquid or gaseous hydrocarbons to elemental carbon and hydrogen by partial combustion or thermal decomposition. Carbon black particle surfaces have quinine, lactone, carboxyl, and other organic functional groups, shown in Figure 2.6, which improve the interaction between the carbon black and rubber (Blow and Hepburn, 1982, Dick, 1987, Barlow, 1993, Kohls and Beaucage, 2002, Leblanc, 2002, Simpson, 2002, Mark et al., 2005). Figure 2.6 showed the TEM micrograph of carbon black N326 in (a) low structure and (b) high structure. A higher structure carbon black in a rubber compound will impart less extrudate shrinkage, swell less on extrusion and impart a higher modulus than a lower structure carbon black.

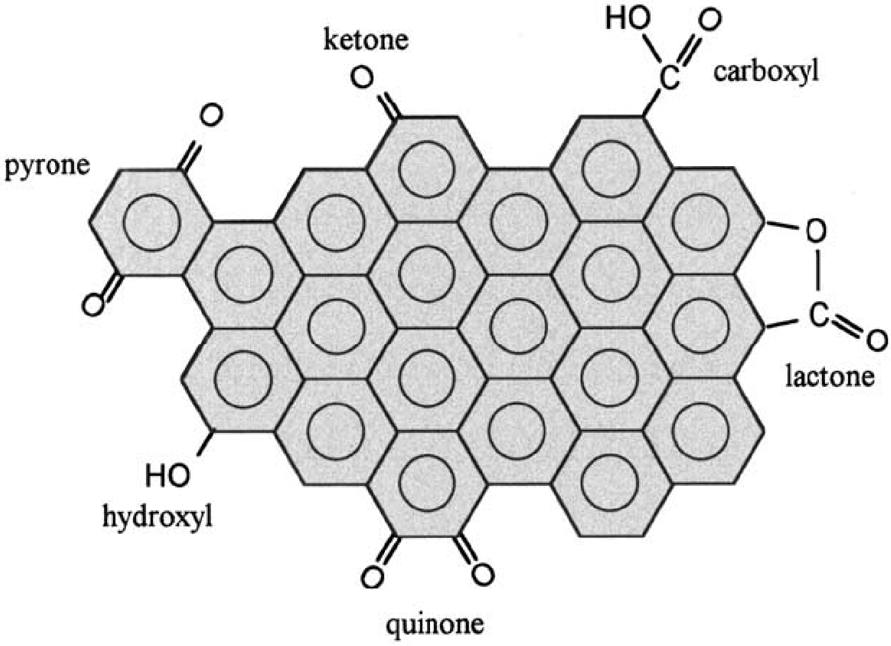


Figure 2. 5 Surface chemistry of carbon black (Leblanc, 2002)

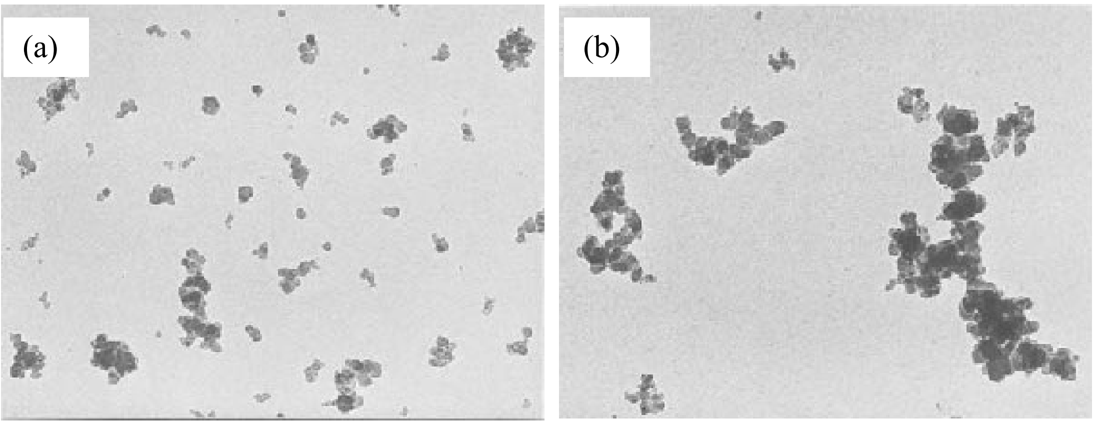


Figure 2. 6 TEM micrograph of carbon black N326: (a) low structure and (b) high structure (Wypych, 2000)

2.2.3.1 Classifications of carbon black

Carbon blacks are produced different processes, by converting hydrocarbons from petroleum to elemental carbon and hydrogen. From American Society of Testing Materials (ASTM) has chosen the particle size of carbon black as parameter for its classification shown in Table 2.2 (Dick, 1987, Simpson, 2002, Mark et al., 2005). Furnace black are carbon black produced by the thermal decomposition of heavy aromatic petroleum oil feedstock in horizontal furnaces in the range of N100 to N 700. Thermal black are the pyrolysis of natural gas in larger vertical furnaces within the range of N 800 to N 900. Table 2.3 shows the physical characteristic of carbon black (N330) including average particle size, surface area and density (Dick, 1987, Barlow, 1993, Lutz and Grossman, 2001).

Table 2. 2 Carbon black classification (Dick, 1987, Simpson, 2002, Mark et al., 2005)

ASTM number	Average particle size (nm)	Old classification
900 – 999	201 – 500	MT (Medium Thermal)
800 – 899	101 – 200	FT (Fine Thermal)
700 – 799	61 – 100	SRF (Semireinforcing Furnace)
600 – 699	49 – 60	GPF (General Purpose Furnace)
500 – 599	40 – 48	FEF (Fast Extruding Furnace)
400 – 499	31 – 39	FF (Fine Furnace)
300 – 399	26 – 30	HAF (High Abrasion Furnace)
200 – 299	20 – 25	ISAF (Intermediate Super Abrasion)
100 – 199	11 – 19	SAF (Super Abrasion Furnace)
000 – 099	1 – 10	___

Table 2. 3 Physical characteristics of carbon black (N330) (Dick, 1987, Barlow, 1993, Lutz and Grossman, 2001)

Parameter	Carbon black (N330)
Average particle size (μm)	0.026 – 0.03
Surface area (m^2/g)	98.9
Density (g/cm^3)	1.8

2.2.3.2 Effects of carbon black on rubber composites properties

The primary purpose for using carbon black with rubber for reinforcement which included the enhancement of tensile strength (TS), modulus, abrasion, and tear resistance. Carbon blacks affect both rubber processing and vulcanizate properties due to physical properties (particle size, surface area and character, and structure) and chemical interaction. Probably the most important property of a carbon black is the surface that is accessible for reaction with rubber molecules per unit of weight. Carbon black aggregate particles can be tightly clustered together like a bunch of grapes, or the same number of particles can be arranged in more open fashion, giving greater bulk, in a manifestation called high structure (Gent, 2001, Arroyo et al., 2003, Choi et al., 2003). Fan et al. (2001) studied the effect of curing temperature on properties of gum and N330-filled natural rubber vulcanizate with conventional (CV), semi-efficient (SEV), and efficient (EV) cure systems. The presence of carbon black in natural rubber vulcanizates increased their tensile strength, 300% modulus, and hardness as shown in Figure 2.7.

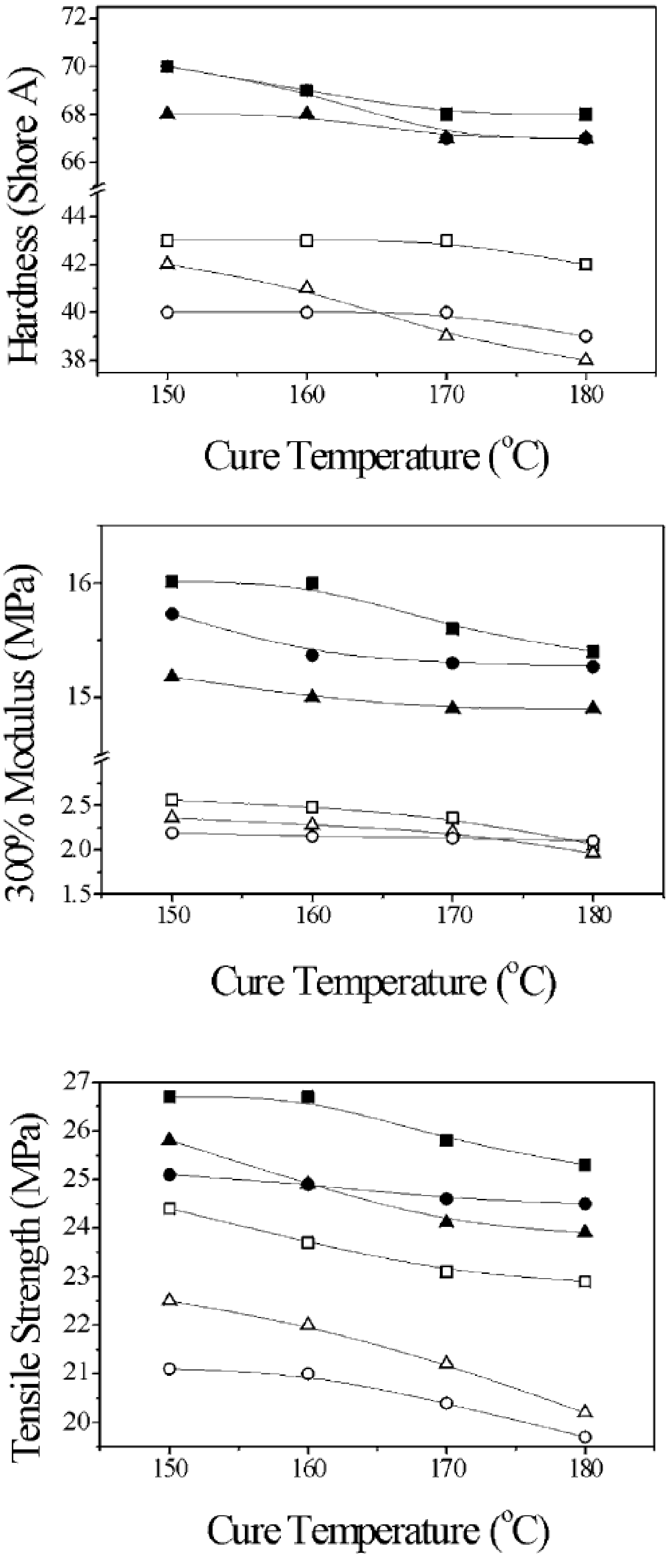


Figure 2. 7 Effect of curing temperature on the mechanical properties of NR vulcanizates: □, Δ and ○ represent gum CV, SEV and EV; ■, ▲ and ● represent N330-filled CV, SEV and EV vulcanizates (Fan et al., 2001)