

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Natural Rubber latex

Field latex from *Hevea Brasiliensis* tree is produced from its metabolism. The latex is obtained by tapping the latex exudes. NR latex consists of particles of hydrocarbon rubber and non-rubber substances dispersed in an aqueous serum phase. Almost 100% of the rubber hydrocarbon has *cis*-1,4-polyisoprene structure. Its content in latex may vary between 25-45% by weight depending on the clone and the time of year, but is usually about 30% [5]. The non-rubber substances consist of protein, amino acids, fatty acids, sterols, triglycerides and other neutral lipids, phospholipids, glycolipids, carbohydrates and inorganic salt. Latex fresh from the tree is stabilized by naturally occurring proteins and phospholipids. The rubber particles are surrounded by a continuous monolayer of negatively charged phospholipid-protein complex which provides colloidal stability.

Because field latex has high water content and susceptibility to bacterial attack, the latex is usually preserved and concentrated, so that the end product is stable and contains 60% rubber. A small amount of ammonia is added to prevent the coagulation of latex by bacterial process. Ammonia increases the colloidal stability of particle by adsorption of long chain fatty acids after phospholipids hydrolysis [6]. Centrifugation-spinning at high speed can separate a cream containing 60% rubber from a liquid part containing 5% rubber, from which dry skim rubber is made. The composition of typical latex is presented in Table 2.1.

**Table 2.1** Composition of typical latex

Composition	Field latex (100 gm)	Concentrated latex (50 gm)	Skim latex (50 gm)
DRC	32.5 gm	30 gm 60%	2.5 gm 5.0%
TSC	36.0 gm	30.75 gm 61.50%	5.25 gm 10.50%
TSC-DRC	3.5 gm	0.75 gm 1.5%	2.75 gm 5.50%
VFA N <sub>2</sub>	0.10	0.060	0.040
Mg <sup>++</sup>	200 ppm on latex	120 ppm	80 ppm
Serum	64 gm	19.25 gm 38.50%	44.75 gm 89.50%
total	100 gm	50 gm 100%	50 gm 100 %

Details of preservation system used in centrifuged concentrated latex are given in Table 2.2. The predominant latexes are the HA and LA-TZ types.

**Table 2.2** Type of preservation system used in centrifuged concentrate [5]

Preservation system	Abbreviation	Precent by weight
High ammonia	HA	0.7% ammonia
Low ammonia TZ	LA-TZ	0.2% ammonia, 0.025% zinc oxide, 0.025% tetramethylthiuram disulphide
Low ammonia pentachlorophenate	LA-SPP	0.2% ammonia, 0.2% sodium pentachlorophenate
Low ammonia boric acid	LA-BA	0.2% ammonia, 0.24% boric acid

The concentrated NR latex is very highly specified materials and a large measure of international agreement had been achieved regarding acceptable limits for their basic properties. Table 2.3 summarizes the requirements of the International Standard Organization (ISO) specifications for various types of natural rubber latex concentrate.

**Table 2.3** ISO 2004 requirement for the centrifuged and cream concentrate latex

Characteristic	Centrifuged concentrate latex		Cream concentrate latex	
	HA	LA	HA	LA
Total solid content (%) (min)	61.5	61.5	66.0	66.0
Dry rubber content (%) (min)	60.0	60.0	64.0	64.0
Non-rubber solids (%) (max)	2.00	2.00	2.00	2.00
Alkalinity (as NH <sub>3</sub> ) (on latex)	0.6(min)	0.29(max)	0.55(min)	0.35(max)
Mechanical stability (s) (min)	650	650	650	650
Coagulum content (%) (max)	0.05	0.05	0.05	0.05
Copper content (mg.kg <sup>-1</sup> of solids) (max)	8	8	8	8
Manganese content (mg.kg <sup>-1</sup> of solids) (max)	8	8	8	8
Sludge content (%) (max)	0.10	0.10	0.10	0.10
Volatile fatty acid number (max)	0.20	0.20	0.20	0.20
Potassium hydroxide number (max)	1.0	1.0	1.0	1.0
Color on visual inspection	No pronounced blue or grey			
Odor after neutralization with boric acid	No pronounced odor of putrefaction			

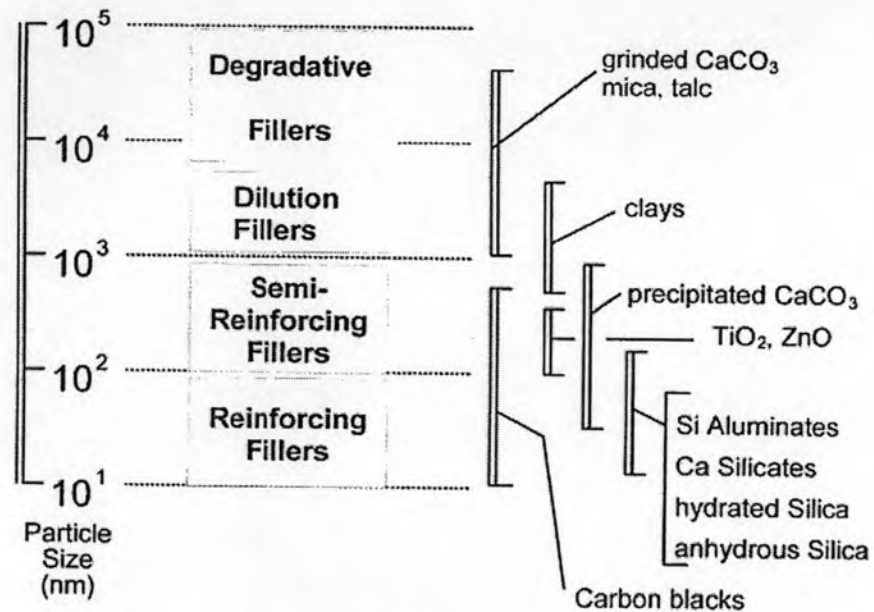
## 2.2 Fillers

Reinforcing fillers enhance the tensile properties of gum NR, and they improve, in particular, the abrasion and tear resistance [7]. The use of fillers especially carbon black together with accelerated sulfur vulcanization, has been the fundamental technique for achieving the incredible range of mechanical properties.

### 2.2.1 Reinforcement of filler

In rubber technology, reinforcement is often defined as the character of improvement in properties of rubber which generally means an increase in

modulus, hardness, tensile strength, abrasion resistance and tear resistance or other properties [8]. The efficiency of reinforcement depends on particle size and surface area of the filler [2]. In Figure 2.1, Carbon black (CB) is the most widely used in the reinforcement of NR. Due to its low polar surface, CB can be well mixed with non-polar rubber, including NR.



**Figure 2.1** Classification of filler according to average particle size [2]

## 2.3 Carbon black

### 2.3.1 CB characteristics

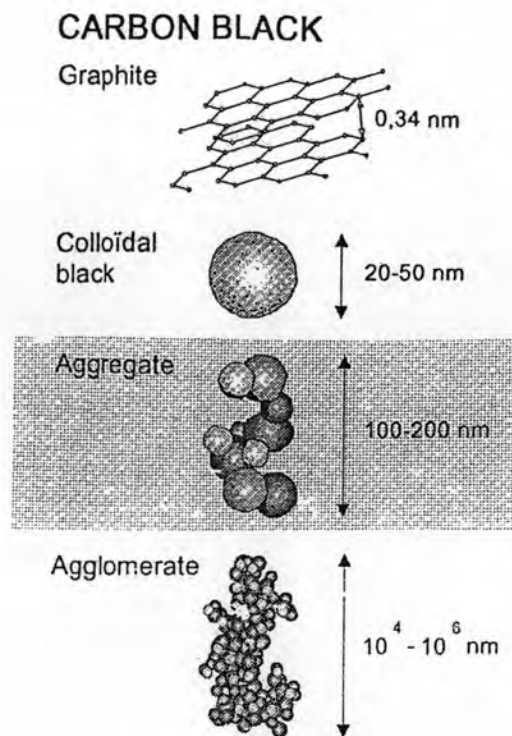
CB used in rubber products is fabricated using 3 basic processes, i.e. channel, thermal or furnace process. The channel black is produced by using gas as a source of carbon. Natural gas is combusted and deposited on channel iron of burner tip by impinging with flame. In this process, CB with acidic in nature with the size of 10-30 nm is obtained. The thermal process is subsequently developed to produce larger size of CB, such as semi-reinforcing black (10-80 nm) by decomposition of natural gas at  $1,300^\circ\text{C}$  in the absence of air. It is found that both the channel and thermal processes are not very efficient and polluted. The oil-furnace process rapidly displaces the former process for economic and

environmental reason. This process concerns the incomplete combustion of petroleum feed stock. By varying the oxygen content, temperature, oil rate, amount of additives, burner type and furnace geometry, various sizes and structure of CB in a number of grades from N110 to N770 series can be provided. The furnace black is alkaline and often forms strong aggregation compared with the channel one.

In commercial, CB in variety of grades are available. In general, the selection of CB to be used in rubber product is relied on four basic properties such as size, surface area, structure, and chemical nature of surface which are known to have the greatest influence on its reinforcing character.

#### Particle Size

Size of CB is very important for elastomer reinforcement. The small CB size can be used to produce high modulus rubber. The size of CB can be determined by electron microscopy [7]. Results from high resolution electron microscopy show that CB is made up of clusters of spherical colloidal black (20-50 nm in diameter) which consist of rotational graphitic layer. CB can be easily aggregated (100-200 nm), agglomerated ( $10^4$ - $10^6$  nm) and eventually in pellet form as in Figure 2.2. The aggregate is the smallest form of CB well dispersed in an elastomer that will still keep all the reinforcing capabilities of the filler. In the aggregated form, the large surface allows topological interaction with segments of polymer matrix [2, 9]



**Figure 2.2** Relevant carbon black dimensions [1]

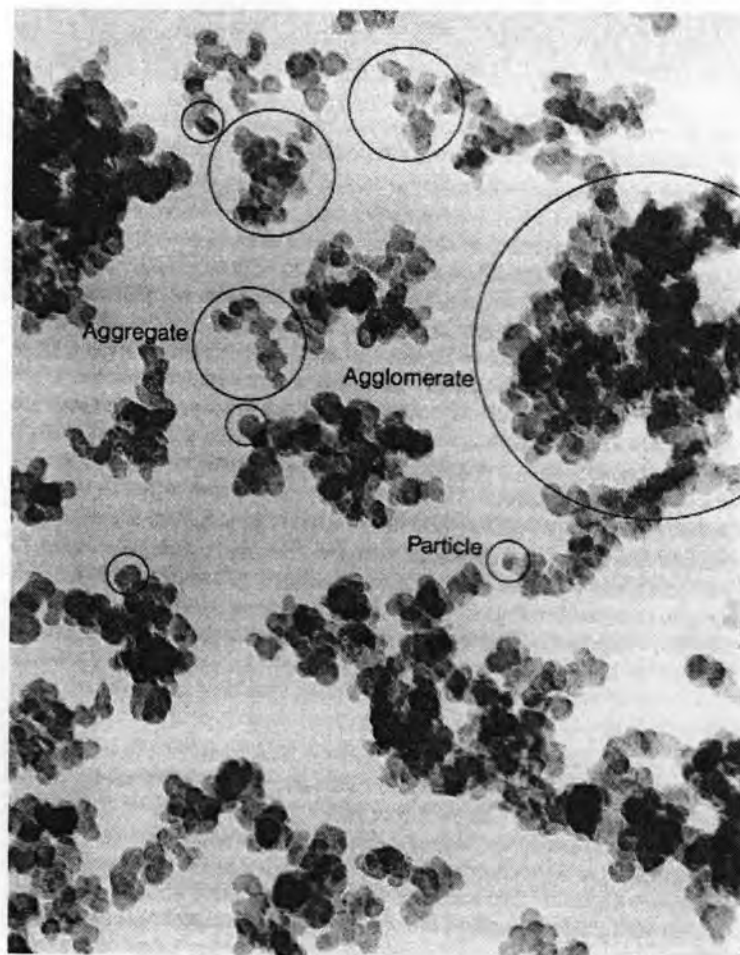
### Surface area

CB with high surface area generally causes high interaction with rubber and other materials presented in a rubber compound and greatly reinforces final product [2]. The surface area is characterized by different adsorption methods of specified molecule. The most widely used adsorption methods are [4]:

- Iodine number, which reflects a 'not true' surface area because it is affected by porosity, surface impurities and surface oxidation.
- Cetyltrimethyl ammonium bromide (CTAB) method which analyzes the external surface area which corresponds to the accessible surface area of CB for an elastomer.
- Brunaver Emmett Teller (BET) method which provides the 'total' surface area including porosity by nitrogen adsorption surface area.
- Statistical thickness surface area (STSA) which is an alternative technique for the determination of the external surface area.

### Structure

The primary particles formed during the initial carbon black formation stage fuse together building up three dimensional branched clusters called aggregates. High structure blacks exhibit a high number of primary particles per aggregate which is called a strong aggregation, low structure blacks show only a weak aggregation. These aggregates may form loose agglomerate linked by Van der Waals interactions [10]. The void volume between the aggregates and agglomerates expressed as the volume of dibutylphthalate (DBP) absorption which is described by the term of CB 'structure'. CB has the ability to form chains from single particles which are not destroyed by mechanical influences. These are called *primary filler structure*. Because of adsorption forces, more or less large *secondary structures* can be formed by agglomeration which can be destroyed by mechanical forces [7].



**Figure 2.3** TEM of carbon black in many forms [36]

**Table 2.4** Carbon black Grades [9]

Grades	ASTM Designation	Iodine Adsorption (g/kg)	DBP No. (cm <sup>3</sup> /100g)
SAF	N110	145	113
SAF-HS	N121	121	132
ISAF-HM	N220	121	114
ISAF-LM	N231	121	92
ISAF-HS	N242	121	121
HAF-LS	N326	82	72
HAF	N330	82	102
HAF-HS	N347	90	124
FEF-LS	N539	43	111
FEF	N550	43	121
GPF-LS	N642	36	64
GPF	N660	36	90
GPF-HS	N650	36	122
SRF-LM	N762	27	65
SRF-HM	N774	29	72
MT	N990	9	36

#### Chemical nature of particle surface

CB is essentially elemental carbon (90-99%) which is partly graphitic in structure. The other main constituents are hydrogen and oxygen. In addition, it may contain very small amounts of nitrogen and sulphur depending upon the nature of the hydrocarbon used in the manufacture. These atoms are set into several organic functional groups such as hydroxyl group or carboxylic group on its surface. The general chemical character of CB surface is presented in Figure 2.4 [2]. The principle groups presented on CB surface are divided into two main types such as acidic group e.g. carboxyl, phenolic, quinonoid, lactone, and anhydride. The other is basic group e.g. chromene and pyrone [9]. These groups have been formed which can react chemically with rubber molecules.



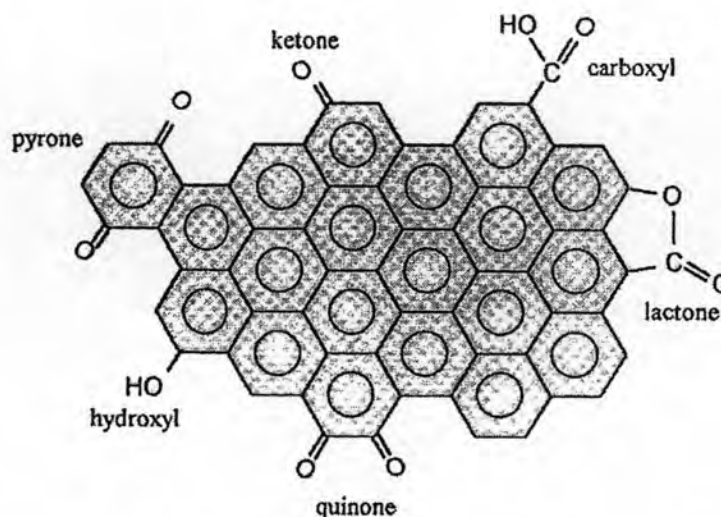
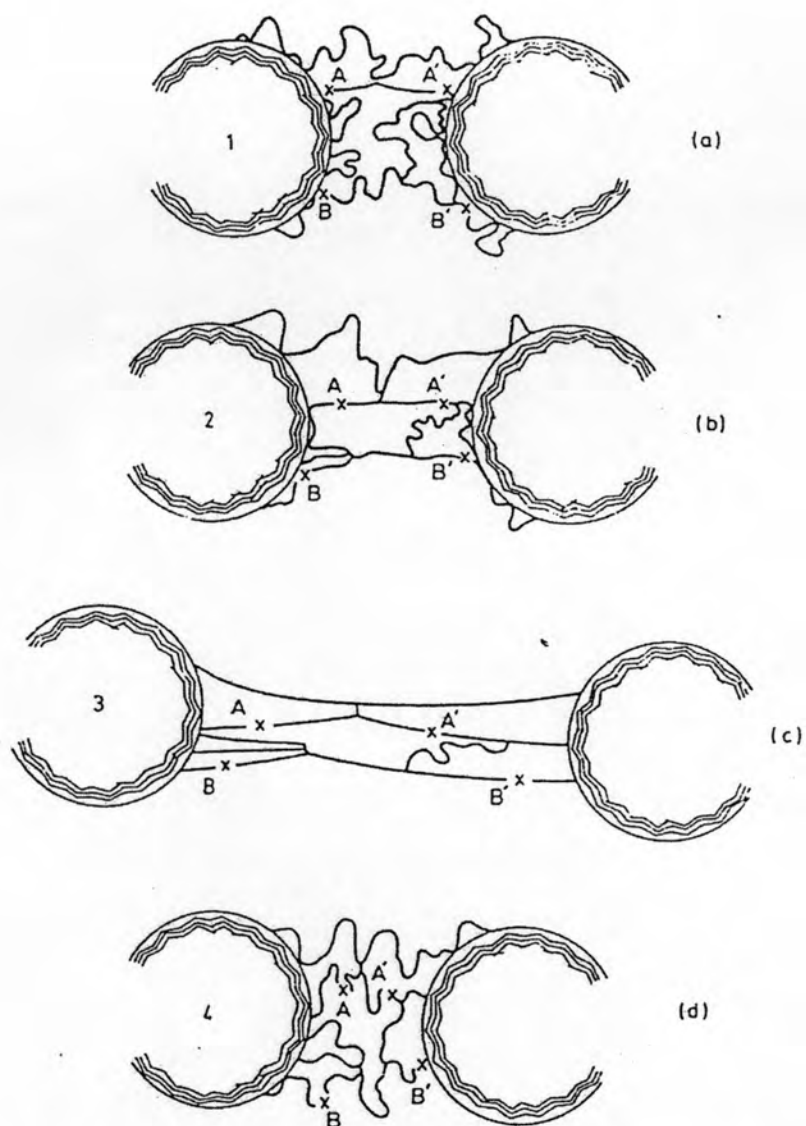


Figure 2.4 Surface chemistry of CB

#### 2.4 Rubber to filler linkage mechanism

Chemical bond between elastomer and CB functions as crosslinking and, therefore, causes an increase in modulus of rubber. The number and intensity of the linkage depend on surface activity of CB. Mullins proposed the principle of molecular basic called the “Mullins” effect as schematically shown in Figure 2.5.

It is demonstrated that two CB particles are linked by a series of elastomer chain [13, 14, 15]. When stress is applied to a polymer reinforce with carbon black, three chains of different lengths between the two CB particles in the direction of stress are displayed. As the stretching process proceeds from stage 1, the first chain slip at the point of connection A and A' until the second chain B and B' is taut in stage 2. Elongation continues until finally a stage 3 is reached in which all three chains are stretched to their maximum and equally shared the imposed load. The homogenous stress distribution causes a high improvement in strength. In stage 4 the tension is relieved and the test piece has retracted. There is now still a difference from the original situation (stage1) due to the slippage does not have to be furnished as was the case originally.



**Figure 2.5** Molecular slippage model of reinforced mechanism based on rubber to filler linkage [13, 14, 15]

## 2.5 Mixing technology

The mixing of compounds on open mills proceeds as follows: The rubber is first worked on mill until a coherent band is formed on the mill rolls. Subsequently, chemicals are added which are difficult to mix, and which are used in small quantities only, namely protective agents and accelerators, so that they will be well dispersed during the mixing cycle. Next, part of the filler is added, together with stearic acid, if required. On adding softeners, the band will generally

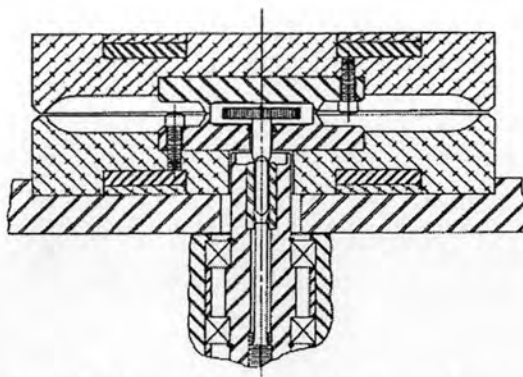
split, and it has to heal before additional fillers are added to the compound. Finally, the sulphur is mixed in, if no ultra-fast accelerators are present. Otherwise the sulphur is added on the warm up mill before processing. During the mixing process, the band must not be cut, and only after all ingredients have been incorporated in the compound, the band is cut and folded, that is, the compound is homogenized. When the mixing cycle is completed, the compound is cut from the mill as slabs, and cooled in a water bath and stored, or it is cut into slabs on batch-off equipment. Because of the fact, that mixing on mills is very time extensive, mixing on internal mixers is mostly preferred [7].

NR is very tough, and requires mastication prior to compounding in order to reduce the viscosity of rubber and permit a faster absorption and dispersion of fillers and chemicals. During mastication, the NR molecules are mechanically broken down by means of high shear forces. The mastication can be carried out on mills at low temperatures, or at elevated temperatures in the presence of peptizing agents. High degrees of mastication are only required if the NR is to be used in very soft compounds. Low degrees of mastication make it already possible to incorporate chemicals and fillers readily in NR which then necessitates very little mastication only. This results in extrudates which have a high green strength and do not deform easily. In the other hand, it also results in reduced extrusion rates. If NR has been masticated only a small degree, it can accept higher filler loadings, and the vulcanizates also give better mechanical, elastic, and dynamic properties than those from NR which has been severely masticated. For economic reasons, it is desirable to keep mastication and mixing cycles as short as possible [7].

## **2.6 Testing of unvulcanized samples**

### **2.6.1 Mooney viscosity**

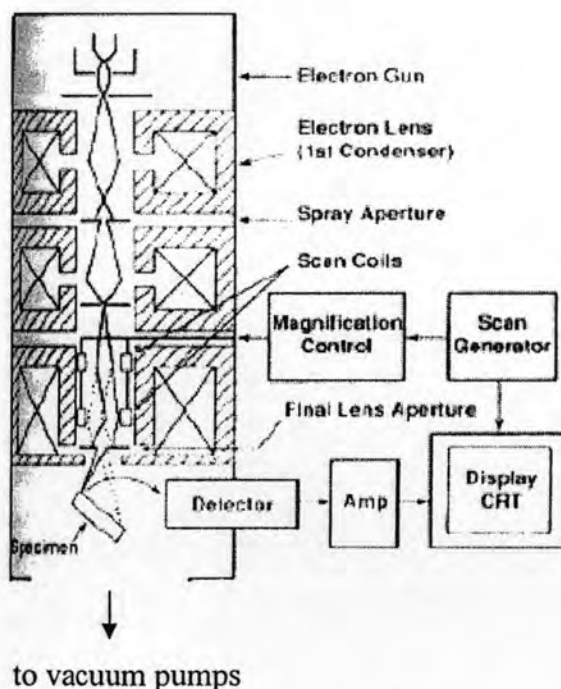
The determination of Mooney viscosity values permits the differentiation between different batches of the same compound and also the prediction about the processibility of rubber compounds at low shear rates. However, because of the low shear rate and the absence of slippage at the wall during the determination of the Mooney viscosity, it is not possible to predict correctly behavior during process at high shear rates or with slippage at the wall [7].



**Figure 2.6** Die and rotor of Mooney viscometer

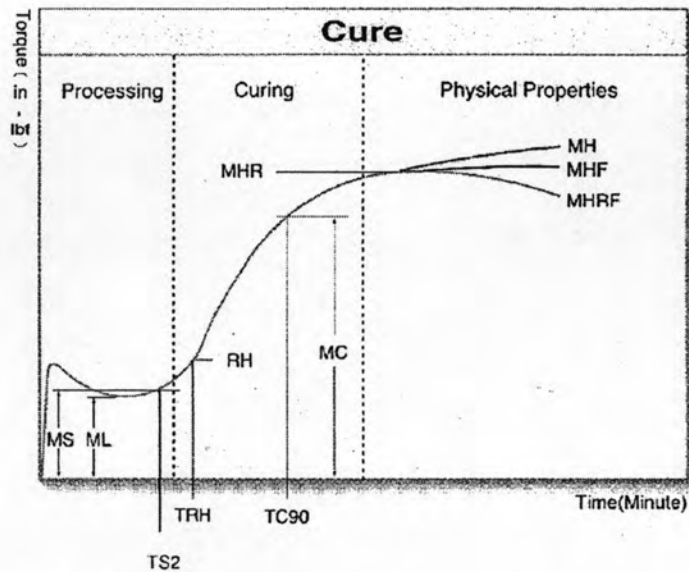
### 2.6.2 Dispersion of filler

The scanning electron microscope (SEM) was used to check dispersion of CB. SEM is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.



**Figure 2.7** Scanning process of SEM

### 2.6.3 Cure characteristic



- ML : minimum torque
- MHR : max. Torque of reverting curve
- MH : maximum torque
- MHF : max. Torque where curve plateaus
- MHRF : final torque of reverting curve
- TS2 : scorch time
- TC90 : cure time to 90% of max. Torque
- MS : torque to the scorch time
- MC : 90% of max. Torque

Figure 2.8 Cure characteristic

## 2.7 Science and Technology of NR/CB compound

NR/CB compound or NR/CB masterbatch had been studied for many years. Two types of compound are also prepared, i.e. solid and latex masterbatch.

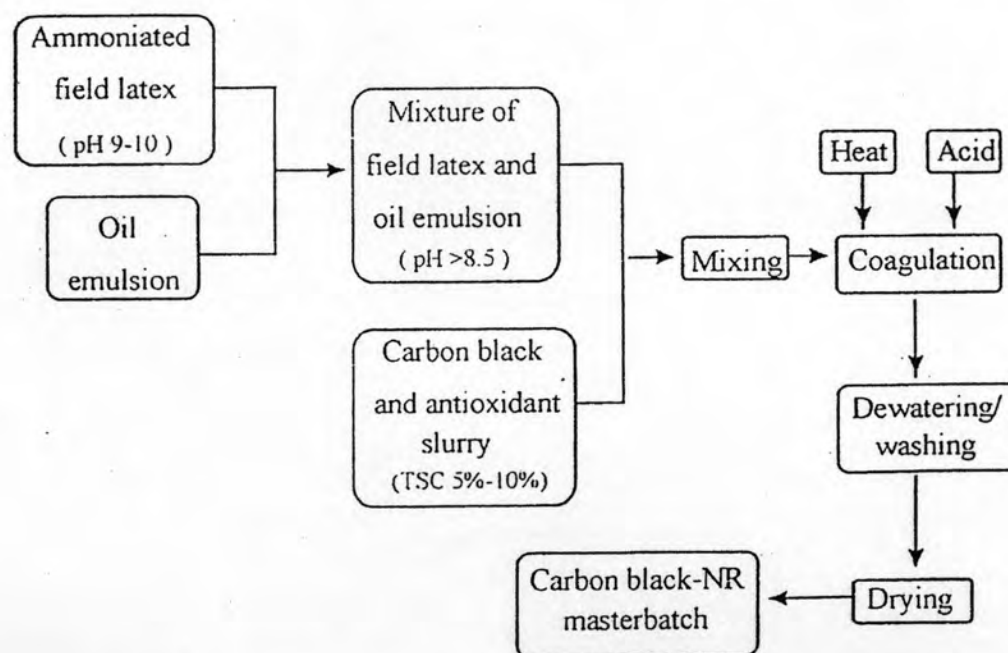
### 2.7.1 NR/CB solid compound

CB powder has been directly mixed with solid in an internal mixer and in an open two-roll mill to prepare NR/CB compound or NR/CB masterbatch [11] for many years. The advantage of this compound is process without loss of CB. Many methods were reported for the modification of CB surface to improve interaction between CB particle and rubber [9], such as oxidation to increase

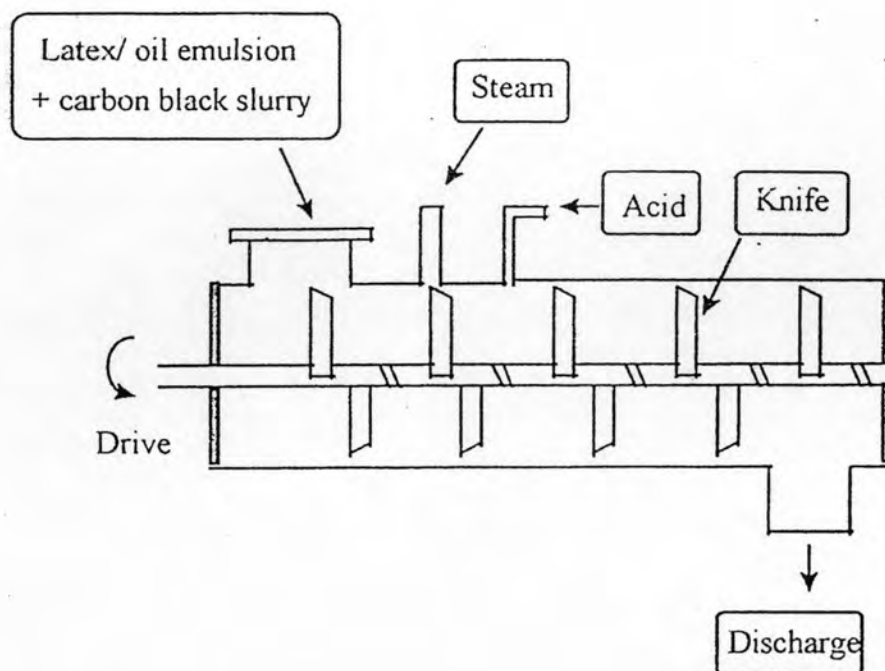
acidic group on the CB surface. Moreover, modified NR such as epoxidized NR (ENR) was studied. The strong reinforce of modified CB and modified NR was better than without modification.

### 2.7.2 NR/CB latex compound

CB powder directly mixed with NR latex was attempted to prepare in 1960 [9]. Problems such as poor dispersion of CB and partial coagulation of latex were reported. Coagulation of NR latex-CB mixture was usually performed by adding acid solution such as acetic acid [27, 40]. Many researchers modified the CB dispersion by many kinds of surfactants to get better CB dispersion [3], and modified the latex by oil to obtain NR/CB compound [13, 14, 15]. Preparation can be done by two methods, batch process [40, 5] and continuous process [6].



**Figure 2.9** Batch process for NR/CB masterbatch preparation [12]



**Figure 2.10** A continuous process for NR/CB masterbatch preparation [12]

## 2.8 Literature review

Medalia, [41] signed patent US 3,294,733 on CB mixed rubber masterbatch process by preparing CB slurry and then mixed with latex. Coagulation agent was then added. Other steps include passed leaching and drying process to obtain the masterbatch of rubber and CB composites.

Wahab, [5] reported 2 methods of CB/NR masterbatch preparation; batch process and continuous process. Batch process started with the preparation of latex-oil mixture, mixed oil with NR latex. Next CB slurry was mixed into the latex-oil mixture. Precipitation of the mixture was carried out by 2%vol formic acid, followed by leaching with water and drying. The other was continuous process by added carbon black slurry in latex-oil mixture together and precipitated by spray water steam and formic acid [6].

Thongnoi [4] studied the preparation of carbon black N330/natural rubber masterbatch in bead form from NR latex by using acid precipitation technique. The 2% w/w<sub>CB</sub> concentration of non-ionic surfactant (Nonidet P40) was used

minimally for preventing the coagulation of CB/NR mixture. This concentration was selected for the latex masterbatch preparation of CB/concentrated NR (CB/CNR), CB/prevulcanized NR (CB/pNR) and CB/vulcanizing ingredients-mixed NR (CB/vmNR) beads. The morphology of beads by SEM showed that CB was entrapped and well dispersed in the NR matrix. It was also found that the interaction between NR and CB are physical and chemical interaction. Shearing beads by internal mixer led to a reduction of Mooney viscosity, resulting in a rubber composite that was easier for molding. This in fact was energy and time saving whereas the tensile properties of the sample prepared from CB/CNR were still good.

A patent by Goodyear Tire and Rubber [17] signed patent US 0158325 A1 reported a method preparing NR/CB composite in tire industrial by mechanical coagulation. Started with mixed CVB aggregates in non-compacted form and rubber processing oil in ratio 90/10 to 50/50 called 'pre-form oil/CB aggregate composite'. Moreover, pre-formed elastomer composite prepared from pre-form oil/CB aggregate mixed elastomer emulsion or diene-based elastomer with the ratio of 30/70 to 70/30 by continuous process was reported. The NR latex flowed into the pipe with strong circulation and created shear-induced coagulation of latex.