

**PHYSICO-MECHANICAL PROPERTIES OF MODIFIED KAOLIN CLAY
FILLED RUBBER COMPOUNDS**

M.Sc (Polymer Technology)

A.R.M.W.W.K.Ranasinghe



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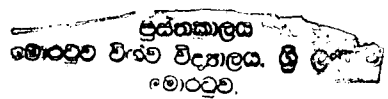


Physico-mechanical properties of modified kaolin clay filled rubber compounds

By

A.R.M.W.W.K.Ranasinghe

This thesis was submitted to the Department of Chemical and Process Engineering of the University of Moratuwa in partial fulfillment of the Degree of Master of Science in Polymer Technology



Department of Chemical and Process Engineering,
University of Moratuwa,
Sri Lanka.

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Supervisors

A handwritten signature in black ink, appearing to be 'P.Y. Gunapala'.

UOM Verified Signature

Dr (Mrs)Olga Gunapala

Department of Chemical
and
Process Engineering

UOM Verified Signature

A handwritten signature in black ink, appearing to be 'P.Y. Gunapala'.

Dr P.Y. Gunapala

Department of Materials Engineering

ABSTRACT

An attempt has made to activate the inert structure of Rubber grade kaolin clays through ion-exchange process. Counter ions absorbed by unsatisfied silicon, oxygen and hydroxyl ions at the edges of planar surfaces of kaolinite mineral to preserve electrical neutrality were replaced with complex organic ions containing active functional groups (amine, hydroxyl, carboxyl) in their organic radicals. Strongly attached to the clay surface these complex ions project their organic aryl or alkyl radicals outwards to suspending medium rubber matrix making inorganic kaolin surface effectively organic and therefore hydrophobic one. Such change in kaolin surface facilitated rubber-filler interaction owing to better wetting of the filler surface with organic rubber polymer and formation of sufficient density grafted polymer layer bonding the rubber matrix to filler.

Carried out physico-mechanical testing of filled rubber compounds showed that modification of kaolin with chosen basic electrolytes ionized in aqueous medium was effective.

Increase in strength characteristics has made possible in commercial practicability of rubber formulation technology the substitution of expensive reinforcing fillers with lowest in cost appropriately modified kaolin Clay.



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NOMENCLATURE

DTA	-	Differential thermal analysis
MEA	-	Monoethanol amine
PVA	-	Polyvinyl alcohol
UF	-	Urea formaldehyde
NMR	-	Nuclear Magnetic Resonance
Mix N ⁰	-	Mix Number
N	-	Newton
MPa	-	MegaPascal
Q	-	Toluene uptake per gram of Rubber hydrocarbon
u	-	Microns
RSS	-	Ribbed Smoked Sheet rubber
HCl	-	Hydrochloric acid
DPG	-	Diphenyl guanidine.
MBTS	-	2,2, Dithiobis benzothiozole
ZnO	-	Zinc Oxide
DEG	-	Diethyleneglycol
PEG	-	Polyethyleneglycol
H ₃ BO ₃	-	Boric acid
NH ₄ Ac	-	Ammonium acetate
NH ₄ Cl	-	Ammonium chloride
Nm	-	Newton meter



Outline of the Thesis

The thesis consists of five chapters. Chapter one is composed with the introduction and the objectives of the research. Chapter two describes the existing background of the fillers, properties of kaolin and its modifications, also justification of the present work. Chapter three describes the materials, experimental techniques and tests used in analyzing the prepared test samples. The results obtained from the research are given in chapter four ,chapter five consists of the discussion of the obtained results, and final chapter consists of suggestions, future recommendations and recommendations for the industry.



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CHAPTER 1

1. INTRODUCTION

A wide variety of particulate fillers are used in the rubber industry to improve the performance of rubber compounds. A general division of filler classes is based on the effect of filler on physico-mechanical properties of rubber. Particularly the fillers, increasing the hardness, stiffness and strength characteristics of vulcanized rubber are called reinforcing fillers. While fillers, which effect on those properties insignificantly and act merely as diluents and extenders are referred to non-reinforcing fillers.

Carbon blacks belong to highly reinforcing fillers because they contain many active functional groups on the surface, which are capable of reacting with polymer molecules to form grafts during processing and vulcanizing. This results in the highest degree of reinforcement coming through high values of tensile strength, tear strength, abrasion resistance and other properties.

A number of mineral fillers are also used in rubber industry to extend or reinforce elastomers, including carbonates, clays, silicates and talc. As compared to carbon blacks non-blacks or mineral fillers are lower in reinforcing effect. Among those mineral fillers kaolin clays are the cheapest and most versatile. They are second only to carbon blacks in this respect. Kaolin clays are unusually inert, temperature stable and disperse well in polymer systems. Because of its inert nature kaolin is not able to form strong interfacial bonds with hydrophobic polymer rubber matrix and can be added in large quantities to many formulations in order to reduce production cost due to diluent effect and slightly improve some performance properties of rubber compounds.

In accordance with general principles of rubber compounding, kaolin is traditionally added with a more expensive active reinforcing filler, that increases



also tensile, shear strength, maximum strength at break, impact resistance, in order to keep balance between performance and compound cost.

New developments in rubber formulation technology aim to increase the replacement value of reinforcing fillers with non-reinforcing ones on score of cost and availability, keeping the performance properties unchanged by means of appropriate activation of the inert fillers. Surface modified clay fillers that are approaching the performance of highly reinforcing fillers such as carbon black and precipitated silica are mostly due to the various types of silane treatments. It has been reported previously, that increase in performance of interfaces in mineral filled polymers could be achieved with silane based coupling agents. Even after silanization, wetting properties can be further enhanced by treatment with amine or functional additives.

The better interaction between surface treated clays and various types of resins which are added to rubber compound (eg. Coumarone indene resin) to enhance composite properties, manifested itself in:

- easier dispersion, leading to higher filler loading and reduced cost.
- improved process ability
- improved uniformity of physical properties.
- higher tensile flexural strength, with greater scratch and impact resistance.
- reduced degradation of physical and electrical properties by reduction of moisture absorbed .

However these modifications are still costly exercised due to high price of silanes, making modifications economically not worth the properties improvement.

Looking at the structural features of kaolin, it consists of crystals of kaolinite. These kaolinites are thin hexagonal plates. In these plates some oxygen and hydroxyl valences are not balanced, and these unbalanced valences are satisfied in practice by external ions that do not form a part of the structure but merely act as

counter ions, that contribute for retaining electrical neutrality of the kaolinite structure. These counter ions, mostly cations, are capable of being exchanged with other cations.

In the disordered kaolinites, additional balancing cations are present because of the lattice substitutions. These additional cations also contribute to cation exchange that occurs with the disordered kaolinites.

Replacing the counter and balancing cations with appropriately selected compounds, can change chemical structure of kaolin surface, making it active towards rubber polymer.

In this connection it was thought that properties of filled rubber compounds could be improved through modification of kaolin by exchanging some cations associated in kaolinite with organic cations containing some active functional groups capable of formation of physical or chemical bonds with rubber polymer

Opposite the silanization the ion exchange process employs electrolytes readily dissolved in water so that they do not need another solvent for ion dissociation that results in modification and product being cost effective.

Therefore the study of activation of inert kaolin clays through ion-exchange process gives rise to interest in both, the development of fundamental investigations in the reinforcement of polymers with fillers and solving a practical task connected with optimization of rubber compound formulation technology.

The aim of the research could be formulated as follows :

- Finding the ion exchange capacity of rubber grade kaolin
- Introduction of the functional groups active towards rubber polymer through ion exchange process to kaolin clay
- Carrying out the series of chemical and physico-mechanical tests and procedures in order to investigate the effect of structure of kaolin on the performance properties of filled rubber compounds

CHAPTER 2

LITRATURE REVIEW

2.1 Types of fillers and their properties

Fillers or extenders are finely divided solids added to polymer systems to improve properties or reduce cost. Fillers can be minerals, metallic powders, organic-by products, or synthetic inorganic compounds. They cover a broad range of particle sizes and shapes and may be under gone surface treatments. Although most fillers are solids, a few silicate types contain air voids to reduce effective filler density .(Barlow,1989)

In classifying the dry fillers used in rubber to increase its usefulness or make a cost effective product; it is convenient to divide them into black and non black fillers or mineral fillers. These non-black fillers are chosen over one or more of three reasons:



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1. The product has to be white or light coloured.
2. Certain unique properties are required like thermal conductivity by using of zinc oxide
3. It is hard to get less cost materials than natural products in good supply like clay or ground lime stone

Non-black fillers have certain features in common compared to carbon blacks. They have higher specific gravities from 1.95 for a precipitated hydrated silica to 5.6 for zinc oxide. At the same loading by weight they have lower tensile values than blacks. For example, in a 50 part loaded nitrile stock with 25 parts of plasticizer, the highest tensile for the most reinforcing non black filler, silica, would probably be 1800-2000 psi; carbon black would range from 1900 to 3000. There is simply not the chemical and physical interaction between filler and polymer that exists with carbon black. For the same reason modulus is lower at

the same hardness. High tensile and modulus are considered as vital components of abrasion resistance. Non black fillers are less abrasion resistant.

Certain differences are shown up in process as well. There is more chance that natural non black fillers will have more oversize particles than blacks. Such particles can easily lower tensile or tear strength as they can well be the points of initial rupture. Normally carbon blacks are aggregates of particles; most non-black fillers are not, they consist of circular, platy, or blocky particles. This difference can be shown up in shrinkage with or cross the grain or calendered or extruded stocks.

There are many ways to classify non black fillers considering the variety of natural sources and various treatments now being used.

Mineral fillers usually have low refractive indexes (1.4 -1.6), in the range of most polymers and binders. Such fillers show little if any hiding power, but are extremely useful in a formulated coating to increase colorant effect, adjust gloss, impart adhesion or other properties, and increase solids content at low cost. In plastics, fillers increase stiffness, affect of electrical properties, improve chemical resistance, and reduce cost. In rubber, reinforcing fillers improve rigidity and tear strength. In liquid systems, such as caulks, sealants, and adhesives, functional fillers control thixotropy, sag, and shrinkage. (Barlow.F.W, 1989)

With the development of polymers in the early 1900s, fillers were needed to meet key functional requirements.

Among the all fillers carbon blacks and mineral fillers play the main roll in rubber compounding. Their industrial uses vary with the required property of the rubber product. Compared with carbon blacks mineral fillers show some interesting characters based on the final rubber product. Some comparative properties of mineral fillers are given bellow.

2.1.a. Calcium carbonate fillers

Calcium carbonate is in many ways a direct contrast to carbon black. In its natural form ground lime stone and ground chalk (Whiting), the particles are coarse , (of the order of 0.5-30um for limestone and 0.2-10um for chalk), off-white (lime stone) or white (chalk) and confer very little, if any reinforcing effect. These carbonates do give some increase in hardness and provide a useful base for light coloured goods. Because of their low cost they are frequently used in non-black compounds of only modest strength specifications.

Some what superior materials may be obtained by calcining the raw chalk to give calcium oxide, slaking it in water, filtering off impurities and bubbling in carbon dioxide to reform calcium carbonate, which is precipitated. Such *precipitated calcium carbonates* are of finer particle size and give compounds of improved properties compared with those based on ground whiting. The precipitated calcium carbonates may be treated with up to 3% of stearic acid or a stearate to aid dispersion. Such activated calcium carbonates are some times used in higher-grade coloured compounds.

It is now recognized that the presence of many small molecules, including stearates, on the particle and rubber molecule surface may interfere with the interaction between filler particle and rubber molecule and thus prevent calcium carbonates from reaching its true potential as a reinforcing filler. In contrast to the silicas and silicates, little success has been achieved by the use of coupling agents as the silane and titanate types

(Barlow.F.W.,1989)

2.1.b.Silicas and silicates

Silicas are used as extenders; they are grouped into crystalline silica, precipitated silica, pyrogenic silica, diatomaceous earth, and silica gel.

Compared with carbon blacks the following features of silicas should be noted.

- The surface of the silica particle is hydrophilic and much absorbed water is present. This causes difficulties in achieving rapid wetting and dispersion. The

longer mixing times may cause excessive heat generation and in the case of IR and NR, polymer break down.

- The particle surface is acidic and active- OH groups on the surface tend to bond and deactivate accelerator molecules. As a result of these effects cure is retarded, and in order to maintain a given cure rate. It is necessary to use a higher level of accelerators than in corresponding black formulations. At one time it was common practice to add a substance which was preferentially absorbed on to the surface of the filler particle at an early stage in the mixing process and before the addition of the accelerator.
- Silicas generally have a greater surface area than a carbon black of the same particle size, thus indicating a greater porosity. This can lead to a greater stiffness for uncured stocks at a given filler loading. Additional plasticizer is therefore required to achieve parity of stock viscosity with the corresponding black compound.

High levels of reinforcement may be achieved with silica fillers, particularly where silane coupling agents are used. Most studies reported concur that the tensile strength of a silica- filled compound is comparable with a reinforcing black (Barlow.F.W,1989)

Some workers (eg Stewart, 1977) stated that replacement of carbon black with a fine silica will adversely affect abrasion resistance and lower the 300% modulus. On the other hand,(Wagner,1977) stated that these properties were comparable with the two types of fillers. He has suggested that the difference was due to the choice, level and point of addition of the coupling agent.

The major use of synthetic silicas is in shoe sole manufacture. There has been some increased use in tyre applications where tear resistance was more important than abrasion resistance, such as in off-the-road earthmover and truck tyres.

Hydrated calcium and Aluminium silicates are semi reinforcing fillers which may have a slight retarding effect on cure. In recent times these materials have tended to be replaced by the less expensive mixtures of silica and china clay.

2.1.c. Kaolin (China clay)

The china clays are hydrated aluminium silicates resulting from the weathering of feldspars. Like the calcium carbonates they are often considered as low cost inert fillers but grades are available that provide a fair measure of reinforcement at low cost.

Compared with calcium carbonates the basic grades of china clay show the following vulcanizate characteristics:

- Low pigmenting powder;
- Slight reinforcing at low levels;
- Lower resilience;
- The plate like particles can lead to anisotropy in products and also to poor tear resistance;
- Good electrical insulation properties;
- Good resistance to mineral acids.

The china clays are frequently classified into the following groups.



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1. *Soft clays with particle size greater than 2 um.* They have a marginal reinforcing effect and are used mainly in mechanical goods.
2. *Hard clays of finer particle size (less than 2um)* confer a significant reinforcing effect to the rubber. As with other fine particle-size silicates they may have a retarding effect on cure, particularly which at loading;
3. *Calcined clays* . These are hard clays calcined to remove water and which confer higher tensile strength, hardness and electrical resistivity as well as a good white colour. They may be used where colour and good electrical insulation are particularly important. They may have a less retarding effect on cure
4. *Treated clays* . They may be of many types . At one time such diverse material as amines and polyglycols were used but are no longer of much importance. The silane coupling agents, particularly the mercapto- terminated silane which are particularly effective with the calcined clays much more significantly. They function by providing a link between filler and rubber molecule (Brydson,1988)

2.2 Structural chemistry and processing

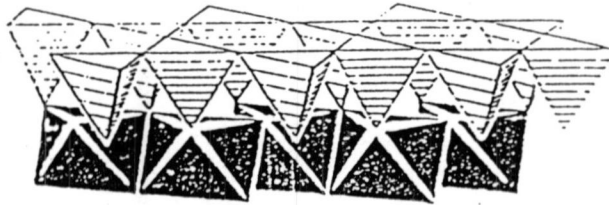
2.2.1 Characteristics of china clay

Kaolin is a hydrated Aluminium silicate mineral of definite chemical composition having the general formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. It is most common of the four polymorphs in the phyllosilicate subclass and applies the same chemistry of other silicates and silica as a filler. (Sutton.D, 1998)

The surface of kaolin is highly polar and hydrophilic as a result of its polysiloxane structure as the presence of numerous silanol groups. The chemically active silanols on the surface of clays (silicates) contain active hydrogen atoms that can react with various chemical groups. If the surface area is high then surface activity is high and this can have a dramatic effect on in-compound reactions, specially sulfur vulcanization.

The silanol groups are acidic in nature and reactive. Silanols show similarities to carboxylic acid groups in their reaction with amine, alcohol and metal ions. At elevated temperatures silanol groups on the surface of the silicates will react with a number of chemical groups present in rubber compounds. If ZnO and stearic acid are added earlier, form zinc stearate and subsequently reacts with silicates or silanol groups and reduce cure properties. (Byers.J.T., 1998)





(Fig 1 .a) Structure of Kaolinite Layer



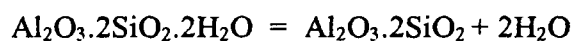
(Fig 1.b.) Microphotograph showing Book-shaped arrangements of hexagonal plates in kaolin (Velde B,1992)

2.3 . Chemical modification of china clay

China clay used in many industries for several purposes and required properties can be obtained through some physical and chemical treatments . Some of those treatments are given below

2.3.1 Calcination

Calcination, the operation of heating or roasting, is useful to pre react materials and provide stable product as improved raw materials. By heating at a suitable temperature, four hours at 800 °C the water of hydration can be removed from kaolinite. (Worrall.W.E.,1986)



2.3.2 Oxime treatment

8-Hydroxy quinoline (oxime) is an almost colourless crystalline solid, with melting point in a range 75-76 °C. It is almost insoluble in water. The reagent is prepared for use in following way to be treated with required metal ion in aqueous medium.

Two grams of oxime were dissolved in 100 ml of 2N acetic acid and ammonium solution was added drop wise until a turbidity began to form.

Oxime having both a phenolic hydroxyl group and a basic nitrogen atom , is amphoteric in aqueous solution. Oxime (C₉H₇ON) forms sparingly soluble derivatives with metallic ions, which have the composition M(C₉H₆ON)₄ If the coordination number is six. (eg: Aluminium, Iron , Bismuth, Gallium)

The usefulness of this sensitive reagent has been extended by the use of masking agent (eg: EDTA, Citrate, Cyanade, Tartarate ect.) and by control of PH (Vogel. A, 1989)

2.3.3 Polar polymer grafting

Kaolin can react with long chain or short chain polar polymers due to the high polarity of silica or silane particles. Reacting or grafting polymer can be tailored for required properties such as better dispersion, reinforcement, whiteness, ect.. Clay can be de watered by flocculating with organic flocculants such as polyacrylamides. This method is more effective than using electrolytes. These organic flocculants may act in several ways by entering the stem layer, by rending the surface of the clay hydrophobic or by linking clay particles via-chain molecules. . (Mark.J.E, 1994).

2.3.4. Surface deactivation by Esterification process

Moisture is readily attached to the silica/silicate surface through hydrogen bonding. Absorbed water on the surface of filler particles reduce the activity of the silanols. If diethylene glycol (DEG) or polyethylene glycol (PEG) is present in the recipe, it can replace the volatilised water and reduce the reactivity of the filler surface with moisture thereby increasing the cure characteristics in sulfur vulcanization. (Byers.J.T,1998)

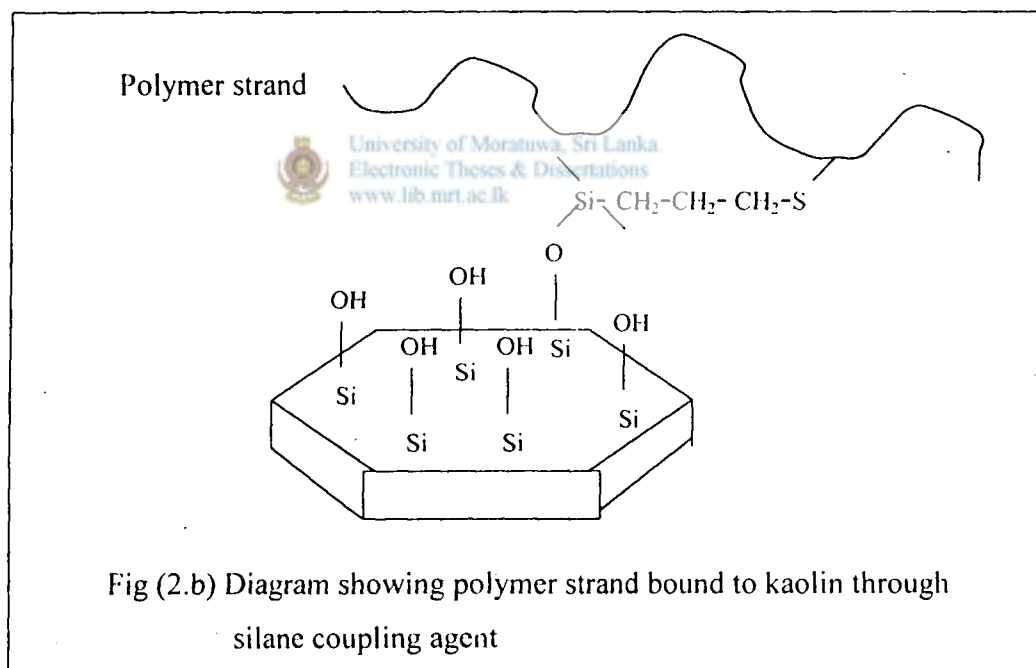
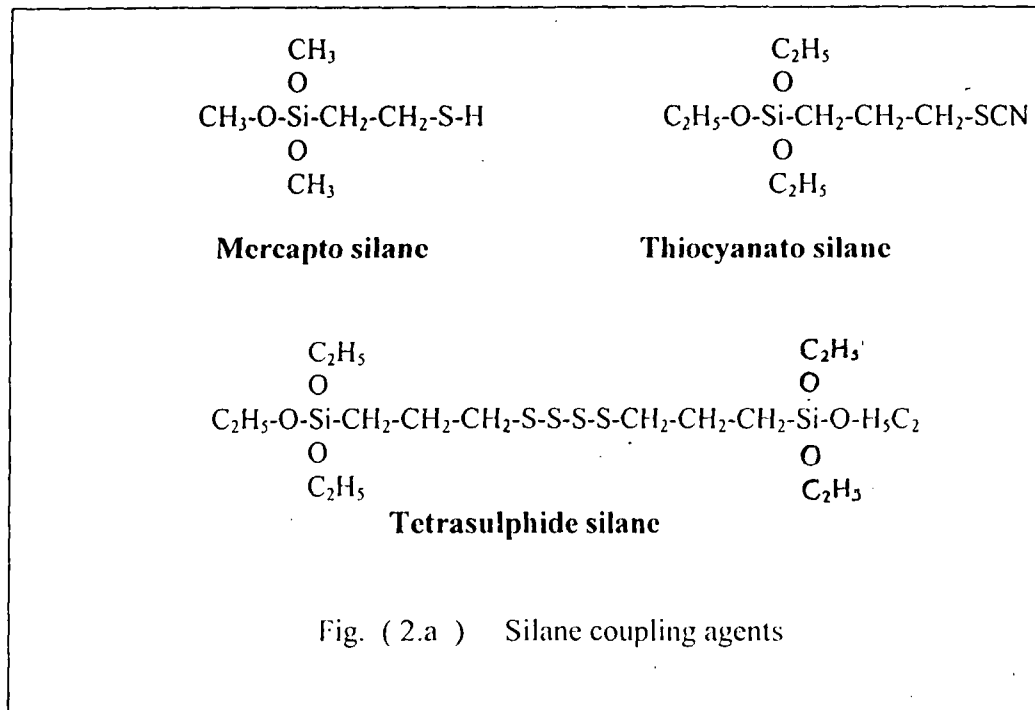
As in the same way by reacting (silica/silicates) with a polyol such as hexadecanol or ethyl methyl alcohol, it was found that with these products the relaxation modulus or stiffness of uncured mixes of chlorosulphonated rubber decreases with decrease of surface activity due to the reaction between polyol present and silanol groups on the filler surface . Thus esterification treatment seems to function as dispersing aid for such elastomers and deactivating agent between polar polymer and the filler

(Roychoudhuri.A,1995)

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2.3.5 Silane coupling

Several coupling agents are commonly used in sulfur cured compounds filled with non-black fillers . Some of them are Mercapto silane, Thiocyanato silane, Tetrasulphide silane. (Fig 2.a) The methoxy or ethoxy groups react during mixing with the silanol groups on the structure of silica, silicate or clay particles and give strong bonds. The sulfur containing group of each structure reacts during vulcanization to give bonding to the polymer. All these silanes probably yield similar final structures for the coupled linkage between the filler and the polymer. (Byers.J.T,1998).



Investigations obtained using NMR spectroscopic analysis give models for these reaction systems. A single siloxane bond is first formed with the silica/silicate surface (primary reaction) it is followed by condensation reactions between silanol groups of silane molecules which are already bound to the silica surface

(secondary reaction). Primary reaction faster than secondary reaction and both become rapid in acidic and alkaline PH ranges. Primary reaction accelerates up to a particular water content after which the rate is constant. But secondary reaction keeps on accelerating with rising water content (Goerl.Udo,1997). The silane loading to a particulate mineral filler depends on the surface area of the filler and the coverage of the specific silane. The level of silane varies from 2-11 by weight for the particular silica/ silicate filler depending on the properties of the final product (Byers.J.T,1998).

2.3.6 Addition of Amine or Aminofunctional derivatives

Amino functional derivatives (Diamine salts of fatty acids) or Amines improve the mechanical properties of silica/silicate filled compounds. From swelling it has been shown that amine or amino functional derivatives improve filler dispersion and also have some effect on cross link density. These amines or amino functional groups give optimum properties with silane coupling agents and can be observed through computer aided image analysis or micro photographs. (Ismail.H)

Most of the accelerators used in sulfur cure systems contain an amine group . Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reaction. This can give slower cure rates and reduced state of cure, therefore addition of amine or amino functional derivatives gives rise to faster cure rates and dispersion properties. (Ismile.H).

Polar oils or aromatic resins generally improve dispersion properties of compounds containing silicates. (Byers.J.T,1998)

2.4 .Physical modification of Kaolin

Kaolin has a low cation exchange capacity ranging from about 2 to 1 Meg/100g and the chief exchangeable ions are H^+ , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . Due to their low ion exchange capacity, china clay requires less amount of deflocculant than sedimentary clay. For kaolin group minerals Na^+ ions favor the stability of deflocculation whilst H^+ and Ca^{2+} ions cause flocculation. In the deflocculation

process, Poly phosphates are said to be more effective and high zeta potential accompanied by deflocculation, can be reduced when only a fraction of the total cation sites have been replaced by sodium. Hence "Calgon" sodium Hexameta phosphate is more effective in deflocculation of china clay (Mark.J.E.,1994)

As mentioned above kaolin can be modified chemically or physically through several processes. The possibilities of such modifications are mainly due to the structural features of the kaolinite particle.

2.4.1.Cause of cation exchange

In the kaolin minerals the oxygen and hydroxyl valences at the planer surfaces of the structure and completely satisfied. At the edges, however there are aluminium, silicon, oxygen and hydroxyl ions that are not satisfied because the lattice is capable of extension indefinitely in the ab plane. These unsatisfied valences , or broken bonds as they are often called, are satisfied in practice by external ions that do not form part of the structure, but merely act as counter ions, preserving electrical neutrality. These counter ions , particularly the cations , are capable of being exchanged for other ions and are one possible cause of cation exchange in clay minerals. ' broken bonds' however are not the only cause of cation exchange in disordered kaolinites, as mentioned previously additional balancing cations are present because of the lattice substitutions. These additional cations probably account for the greater part of the cation exchange that occurs with the disordered kaolinites.

Another possible cause of cation exchange in clays, often quoted in the past is ionization of basal hydrogen groups , to produce a negative charge on the oxygen and a hydrogen ion that is exchangeable for other cations if this were so, one would expect the cation exchange capacity to be strongly dependent on PH, which is certainly not the case. Ionization of hydroxyl groups is of course an important factor in oxides (Worral.W.E,19986)



2.4.2. Cation exchange capacity

For a given clay, the maximum amount of any cations that can be taken up is constant and is known as the cation exchange capacity (Worrall, W.E., 1986), often abbreviated to c.e.c. In principle, the c.e.c. is determined by leaching the clay with a chosen electrolyte, so as to replace all existing cations by one particular cation. The clay is then filtered, washed free of excess of electrolyte (often with alcohol rather than water, to avoid hydrolysis) and the amount of chosen cation is determined. Ammonium acetate is the electrolyte frequently chosen for this purpose, since ammonium can readily be determined by distillation. Instead of an electrolyte, an exchange resin in the ammonium form may be employed. Other electrolytes, in which the relevant cations can be readily determined by chemically, have also been used, such as acetates, sulphates or chlorides of manganese, lithium and sodium. On the whole, values of c.e.c. obtained with different monovalent cations agree reasonably well, but discrepancies have been found when comparing monovalent with polyvalent cations. This discrepancy has been ascribed to the formation of complex ions of type M-OH by polyvalent ions; with calcium for example, it is conceivable that one monovalent [Ca-OH] ion could be attached to every exchange site, resulting in an apparent c.e.c. of twice the normal value if the latter is calculated as Ca²⁺ rather than Ca-OH. Alcoholic solutions of polyvalent cations are said to give normal values of c.e.c. presumably because the complex ions cannot be formed in alcohol.

(Worrall, W.E., 1986)

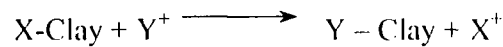
2.4.3. Values of cation exchange capacity

For well crystallized kaolinites the c.e.c. is small, being approximately 2-5 meq/100g. The amount of c.e.c. contributed by broken bonds is probably small, since the crystals are relatively large; moreover, the degree of substitution is small. For the disordered kaolinites, however, the c.e.c. is high, and of the order of 30-40 meq/100g, due to lattice substitution. Many workers have reported that

c.e.c increases with specific surface area. This would indeed be true if c.e.c were associated entirely with broken bonds at the edges, and many authorities have found a linear relationship between c.e.c and surface area for well-crystallized kaolinites (Worrall, W.E., 1986)

2.4.4. Cation exchange reactions

If a clay is placed in a solution of a given electrolyte, an exchange occurs between the ions of the clay and those of the electrolyte:



As indicated, the reaction is a balanced one and the extent to which the reaction proceeds from left to right depends on the nature of the ions X and Y, their relative concentrations, the nature of clay, and on any secondary reactions.

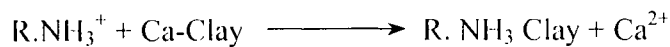
Even for equivalent concentrations, some cations are adsorbed better. One obtained the lyotropic or Hofmeister series:



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2.4.5. Cation exchange reactions with organic ions

It had been investigated that the organic cations also can be exchanged with the associated cations in kaolinite structure as inorganic cations. As might be expected, basic organic compounds that ionize in aqueous solution may also replace other cations on clay surfaces. Amines for example, may react with calcium clays:



In the above equation, R stands for an alkyl or aryl group. Whatever the nature of the original counter ions, replacement of the latter with amine invariably results, in aqueous suspensions, in the clay being strongly flocculated, possibly because the amine is strongly attracted to the stern layer. Another explanation may be that since the amine is adsorbed with the NH_3^+ group close to the surface, the alkyl or aryl group projecting outwards, the surface is therefore hydrophobic; thus, the

solvation energy of the composite clay particle is drastically reduced. Conversely, if the amine-clad clay is dispersed in organic medium, the solvation energy is very high and this alone may account for the deflocculation that occurs.

Because of their organophilic properties, amine-clad clay have many industrial applications. Their compatibility with organic media enables them to be used as paint-thickeners, in polishes, and in treatment of effluents.

It is common experience that when clay is shaken and dispersed in water, the resulting suspension remains cloudy on standing and frequently may be not clear for days or even for weeks. This is because a colloidal solution of clay in water has been formed, the particles of clay are so small that they settle extreme slowly. The stability of this colloidal suspension depends primarily on the nature and concentration of the counter ions

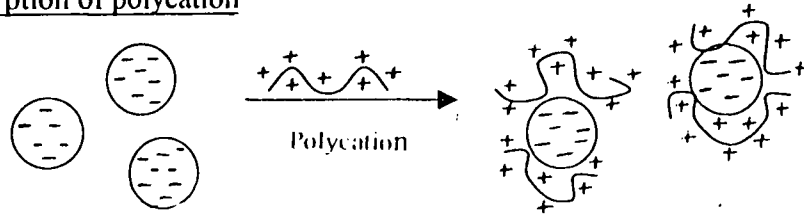
So counter ions favor stability and complete deflocculation, whilst hydrogen and calcium ions cause flocculation to occur. Deflocculated clay suspensions are required for casting slips and in the determination of particle size; flocculated clays, on the other hand may be required for various dewatering processes such as filter pressing. Deflocculated clays have a characteristically lower viscosity than flocculated clays (Worrall.W.E ,1986).

One method of achieving deflocculation is the precipitation and replacement mechanism, in which the displacement is removed from solution by precipitation or sequestration. Thus calcium clays may be deflocculated with sodium carbonate, sodium oxalate, sodium phosphate; hydrogen clays may be deflocculated with sodium hydroxide. There is a class of deflocculants, however, that appears to function differently. Sodium silicate, for instance is a very powerful deflocculant for the majority of natural clays. The mechanism of this instance is not simply the replacement of other ions by sodium, followed by the precipitation of the displaced cations as silicates. Simple measurements have shown that a high Zeta-potential, accompanied by deflocculation, can be produced when only a fraction of the total cation sites have been replaced by sodium. Similar results are observed with other polyelectrolytes such as 'calgon' (sodium hexameta phosphate) and

'Dipex' (sodium polyacrylate). These observations suggest that the anion plays an important roll in deflocculation. Large polyanions such as silicate, polyphosphate and polyacrylate are adsorbed by clay surfaces, in addition to sodium ion. It is not quite clear how this adsorption produces a high-zeta [potential, but it would seem likely that the adsorbed polyanions provide extra negative sites that are strongly ionized, so that the associated cations are at a relatively great distance form the surface. Polyanions are likely to be repelled by the negative planer faces of clay crystals, and it is therefore probable that they are absorbed onto the edges, either by anion exchange or by physical adsorption. Another characteristic of polyelectrolyte deflocculants is that considerable excess can be tolerated without offsetting the deflocculating effect.(Worrall,W.E.1986)

According to G. Petzold and H.M. Buehhammer adsorption of polycation as well as the modification with oppositely charged polyelectrolytes is a useful tool for surface modification. A strong enhancement of the attainable specific cationic surface charge was observed with eg., with poly (diallyl-dimethylammonium chloride) as the polycation and maleic acid-co-methyl styrene) as the polyanion, at a ratio of anionic to cationic charges of $n^-/n^+ = 0.6..0.7$

1. Adsorption of polycation



2. Addition of polyanion

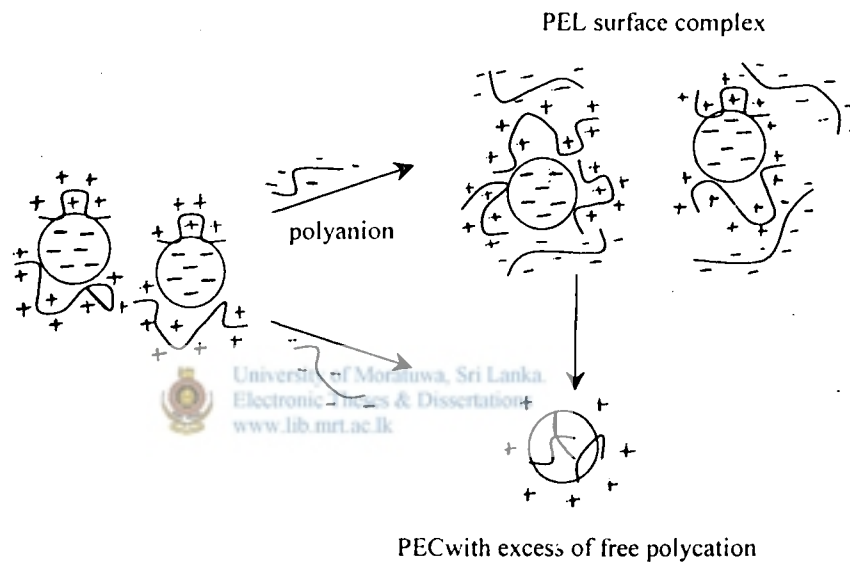


Fig (3) Mechanism of adsorption and modification (Petzold.G, 2000)

According to their study it was concluded the formation of positively charged surfaces is influenced by the adsorption polycation on clay as well as the formation of a non stoichiometric polyelectrolyte complex, with polycation in excess, and reversible interaction , with polyanion in the surrounding solution.

(Petzold.G,2000)

2.4.6. The effect of edge charges

The edges of clay crystals may behave differently from the planer surfaces in having an atmospheric character. It is clearly possible for the edges to carry a net positive charge over a wide range of pH, whilst the faces are permanently negative. In these circumstances, the edges and faces will mutually attract, giving rise to a so-called 'edge-to-face' flocculation, even though the zeta potential may be moderately high. Because of the comparatively small magnitude of the edge charges, they can be neutralized or reversed by small additions of a suitable electrolyte. (Worrall.W.F,1986)

It has been observed that when a hydrogen clay is treated with successive small additions of NaOH, the degree of flocculation, and therefore the viscosity, at first begins to increase markedly until just before the equivalence point, after which deflocculation suddenly occurs and the viscosity drops sharply. This is because the sodium ions first replace H^+ on the faces only, increasing their negative potential without influencing the edges; this results in an increased attraction between edges and faces. On further addition of NaOH, the pH rises sufficiently to reverse the edge charges, so that the clay particles become negatively charged overall and the system is therefore deflocculated.

It has been suggested that the remarkably small additions of polyelectrolyte required to deflocculate clays. It can be explained by supposing that the polyanions are absorbed on to the crystal edges and thus ' mask ' any positive charge on these sites. This explanation cannot be regarded as satisfactory, however, since it does not account for the very high zeta potential that is observed when clays are deflocculated in this way

2.4.7. Other causes of flocculation

Calcium is a predominant exchangeable cation of natural clay that is normally flocculated. The degree of flocculation is in all cases increased by the addition of any electrolyte in sufficient quantity, due to 'crowding' of the stern layer. Salts of polyvalent cations are more effective flocculants than those of monovalent cations. Thus, the deflocculation of natural clay may be inhibited in the presence of soluble salts, notably sulfates of calcium, magnesium or iron. If the clay processing involves filter pressing, much of the soluble salt will be removed; there by otherwise, careful addition of the stoichiometric amount of barium carbonate may effectively remove the sulfates:



The net effect of this treatment, as indicated by equation, is to produce two sparingly soluble substances, the effect of which is thus minimized. Deflocculation can often subsequently be achieved by the addition of sodium carbonate, sodium silicate or both. (Worrall, W.E, 1986)



CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS USED FOR THE EXPERIMENT

(a) Kaolin

Rubber grade kaolin processed in Boralesgamuwa refinery was used for the experiment as a filler.

Kaolin is a rock or aggregate composed of essentially of clay minerals of kaolinite group.

The kaolin minerals consist essentially of a hydrous aluminium silicate having the general formula



Used grade had following characteristics:

- the ion exchange capacity was 4.1 milli equivalents per 100 grams
- PH value was 5.2
- particle size ranged from 0.2 to 1.0 μ
- moisture content was 2.3%

(Other technical data are given in appendix I)

(b) Urea (Carbamide)

-Analar grade urea having Chemical formula $\text{NH}_2\text{-CO-NH}_2$ in granular form with 99% degree of purity was used in experiment.

The impurities are given below

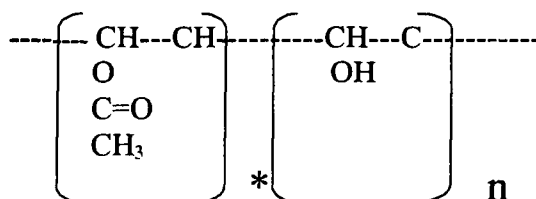
- Sulfated ash content did not exceed 0.1%
- Chloride content did not exceed 0.002%
- Sulfate content did not exceed 0.05%
- Melting point was in a range of 131-134⁰C

(c) Polyvinyl alcohol (PVA)

Commercial grade granular form polyvinyl alcohol ,having molecular weight of 1000 gram , readily water soluble was used.

Degree of purity corresponded to 95% and degree of acetyl group substitution corresponded to 12 %

Chemical structure is given bellow.



(d) Monoethanol amine (MEA)

Commercial grade monoethanolamine in a liquid form having Chemical formula $\text{NH}_2\text{---CH}_2\text{---CH}_2\text{OH}$ with 96% degree of purity , 1.07 g/cm³ specific gravity and 170^oC boiling point was used for the experiment.

(e) Rubber and additives

All experimental procedures were carried out using ribbed smoked natural rubber of grade I (RSS I) The typical characteristics of raw rubber and black filled vulcanizate properties are given in table I.

Table I: Properties of natural rubber

Type	Source	Dirt content % Weight	Mooney Viscosity	Tensile Strength (mN/m ²)
RSS I	Co-agulated field Latex	0.0 -0.08	60-100	2.1 -2.8

Vulkanizing agent

Sulfur was used as a vulkanizing agent in its elemental form as finely ground rhombic crystals with 99.5% degree of purity and ash content of 0.5 %

Activators

Zinc oxide (ZnO) :

Zinc Oxide was used as an activator being coarse white in colour with degree of purity 99.9%.

Particle size of used zinc oxide did not exceed 1.0 u

Product contained impurities as follows:

Lead (Pb) content did not exceed 0.005%

Sulfur (S) compounds content did not exceed 0.01%

Calcium (Ca) content did not exceed 0.05%

Potacium (K) content did not exceed 0.01%

Iron (Fe) content did not exceed 0.001%

Sodium (Na) content did not exceed 0.05%

Magnesium (Mg) content did not exceed 0.005%

Stearic acid :

A fatty acid having chemical formula $C_{17}H_{35}COOH$ was used in a powdery form as a dispersing and activating agent, present in the non hydrocarbon constituents of natural rubber . In standard practice stearic acid is added to compound for a precaution against possible deficiencies of the accelerators of vulkanization in the raw rubber.

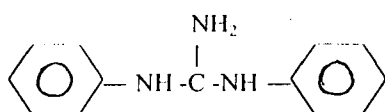
Used stearic acid was of 95% degree of purity with melting point in a range of 67-69 °C

Accelerators

Diphenyl Guanidine (DPG) :

DPG is a typical amine type accelerator, that acted as a secondary accelerator in natural rubber compounds.

-The chemical structure is given bellow.



- Product was of 97% degree of purity with melting point in a range of 177-180 °C



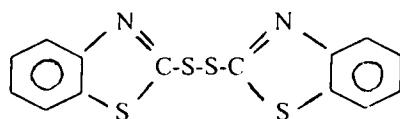
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2,2 Dithio bis benzothiozole (MBTS) :

MBTS belongs to thiozole type accelerators .It was used in a powdery form, being of light yellow colour.

MBTS acted as a primary accelerator and scorch modifying secondary accelerator in natural rubber compounds .

The chemical structure is given bellow:



Used MBTS had degree of purity - 99.0% with melting point ranging from 159°C to 170 °C and density of 1.51± 0.3 Mg / m³

3.1.1 Rubber compounding

The standard formula used for compounding of the rubber is given in table 2.

Table 2 : The standard formulation of filled natural rubber based compound

Ingredients	Weight, g	Weight, %
Rubber	100.0	70.82
Zinc oxide	5.0	3.54
Stearic acid	2.0	1.41
Filler	30.0	21.24
MBTS	1.5	1.06
DPG	0.2	0.16
Sulfur	2.5	1.77

Five compounds were prepared according to given formula, so as formula N 1 included standard rubber grade kaolin as a filler, while in formulae N N 2-5, standard kaolin was completely replaced with kaolin modified respectively with carbamide (urea), polyvinyl alcohol, monoethanol amine and urea formaldehyde resin. Modification procedure was developed and described in an experimental part



3.2 EXPERIMENTAL PROCEDURES

3.2.1 (a) Finding the ion exchange capacity

In order to determine the ion exchange capacity, i.e the number of valence sites available in kaolin structure, Kjeldahl method was proceeded. The method included following steps.

- Weighed portion of rubber grade kaolin of approximately 10.0 g was mixed with 200.0 ml of 0.1 N ammonium acetate solution in order to replace all counter cations attached to the kaolin surface with ammonium cations.
- Then this portion was distilled with 2.0 g of Magnesium Oxide powder (MgO), so as to replace ammonium ions with magnesium ions Mg^{2+} from kaolin.
- The ammonium liberated at high temperature in the gaseous form was trapped in to the Boric acid.
- Complex containing boric acid and ammonia was titrated with 0.1 M hydrochloric acid (HCl) using Bromocresol green as an indicator to find ammonium acetate concentration.
- The results obtained from the titration were used to calculate the number of equivalents that participated in cation exchange reaction.

3.2.1. (b) Treatment of kaolin

Water soluble amines were selected for modification of kaolin on account of their capability of being exchanged with cations associated with kaolin and on economical reason, as they did not require expensive solvent for dissociation.

(a) Treatment of kaolin with urea

The relevant concentration needed for treatment of kaolin, was calculated using the value of ion exchange capacity of kaolin obtained experimentally.

A portion of kaolin weighed about 100.0 g was treated with 200 ml of 0.025 mol / dm³ carbamide (urea) solution by keeping them in contact for 12 hrs while stirring, to ensure better ion exchange. Then the mixture was filtered off, precipitated suspension was dried under normal atmosphere until permanent weight was achieved.

(b) Treatment of kaolin with Poly vinyl alcohol (PVA)

It was difficult to find equivalent number of PVA as it belongs to polyelectrolyte compounds. In this connection, the optimum concentration of PVA, needed for treatment of kaolin was determined experimentally as described below.

The samples treated with PVA solutions of following concentrations 1.0 g/dm³, 4.0 g/dm³, 8.0 g/dm³, 12.0 g/dm³, 16.0 g/dm³ were ground easier. The PVA solution of highest concentration that corresponded to 16.0 g/dm³ was selected for further experiment

Other procedures were carried out similar to those, developed for treatment of carbamide described earlier.

(c) Treatment of kaolin with Monoethanolamine (MEA)

The relevant concentration of MEA needed for the activation of kaolin was calculated in order to keep equality of equivalent number to cation exchange capacity of kaolin obtained experimentally

Weighed portion of 100.0g kaolin was immersed in 200.0 ml of $0.025 \text{ mol/ dm}^{-3}$ monoethanolamine solution. Few drops of 0.1 M HCl solution were added to ensure the stability of formed cations . Composition was left for 12 hours to provide better ion-exchange. It was stirred time to time

The rest of experiment was proceeded similar to that of treatment of kaolin with carbamide.

(d) Treatment of kaolin with urea formaldehyde resin

Synthesis of urea formaldehyde in a water soluble form

A pyrex glass beaker was filled with 270 ml of 37 % formalin .The PH was adjusted to 4.6-5.3 using aqueous solution of NaOH. Then 100 g of urea was added to formalin , by portions while heating , At time all urea had been introduced, reaction mixture was brought to boiling at $90-100^{\circ} \text{C}$. In 30 minutes heating was stopped and reaction mixture was cooled.The PH of the reaction mixture was increased to 7-8 using ammonium hydroxide. Freshly prepared resin was used for treatment of kaolin according to the procedures discribed earlier.

3.2.2 Rubber compounding

The compounds were prepared on an open two- roll mill of laboratory size, having circumference milling speed 5 rpm and friction ratio 1.4 at a temperature ranging between 40°C and 60°C . Formulae N N 1-5 were performed according to mixing cycle given in table 3

Table3 : The mixing schedule for 5 mixes on an open two -roll mill

Ingredients		Time on mill (min)
1.	Rubber	0
2	ZnO	8
3.	Stearic acid	10
4.	Filler (kaolin)	12
5	MBTS,DPG	18
6.	S	20
		24 Unload



3.2.3 Determination of vulcanization characteristics

(a) Vulkanization characterics

This test was carried out to determine the vulkanization characteristics of rubber compounds. The effect of heat on compound caused changes in the viscosity and scorch characteristics were determined from initial portion of the curve of torque versus time.

The vulcanization times of all prepared compounds for determination of tensile properties and tear resistance were found from rheological or cure curves obtained with Mooney Viscometer and Monsanto Rheometer

Mooney Viscometer test was carried out according to ASTM 2084 – 95.

A specimen of a specified shape was sheared by a rotor having diameter corresponding to 1.5 inches. Speed developed by rotor was 2 rpm and temperature was maintained at 160⁰C

Monsanto Rheometer test was carried out according to ASTM 5289-95.

A standard shape specimen was sheared by the rheometer disk making 30 rounds per minute. Temperature was maintained at 160⁰C

The following standardized values were taken from the obtained rheological curves and used to calculate cure time:

- Minimum torque in Nm
- Maximum torque where curve plateaus in Nm
- Minutes to one lbf inches rise above minimum torque used with 1⁰ arc, minutes to two lbf inches rise above minimum torque used with 3⁰ arc
- Minutes to 90 % of maximum torque

3.2.4 Physico- mechanical tests

3.2.4 (b) Tensile test



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Tensile properties of vulkanized rubber were determined according to ASTM D 412- 92, using 'D' type dumb bell test specimens of about 2 mm thickness. Standard mould was used for press curing of test samples under temperature of 140⁰C for period of time, determined for each compound from rheological curves. Dumb bell test specimens were tested with a tensometer at 28⁰C to take following readings:

1. Modulus at 100% elongation
2. Modulus at 300% elongation
3. Tensile strength at break
4. Elongation at break

3.2.4 (c) Ageing test

The dumb bell test pieces were kept at 100⁰ C for 72 hours and tested with tensometer to find the tensile strength values and elongation at break. Testing procedures were carried out at 28⁰C

3.2.4 (d) Abrasion resistance test

This test was performed according to ASTM D 1630- 94 standard using the instrument called “ Din Abrador “ .The test specimen of 16 mm diameter and 8 mm height was subjected to wearing by rubbing with the abrasive held on the rubber

Three test specimens were run in order to obtain average value of abrasion resistance

3.2.4 (e) Flex cracking test

This test was done according to ASTM 4482-85 standard by De Mattia flex cracking experiment .The flexing machine provided 300 bending cycles per minute.

The number of cycles at crack initiation was measured.

For crack growth a single cut of 1 mm was introduced using a razor blade .The direction of the cut growth followed in groove along the specimen centreline.The cut length and number of cycles were recorded . The results reported were the average of three samples tested.

3.2.4 (f) Bound rubber content

This test was performed on filled raw rubber compounds to find the bound rubber or gel content corresponding to the amount of rubber sufficiently strongly attached onto the filler surface. This test was carried out to establish certain correlation between bound rubber content and strength characteristics of filled rubber compounds.

Several samples of approximate dimensions 10 x10 mm were prepared from rubber compounds N N 1-5, loosely packed each in its own prior washed and dried pure cotton bag of approximate dimensions 30x 35 mm. The open ends of the bags were stiched . In a such manner prepared bags were immersed in to 100 ml of toluene for 96 hours at room temperature. To intensify the extraction of rubber from a specimen , toluene was replaced with a fresh portion in every 24 hours. After extraction, bags were taken out of toluene and dried at ambient temperature untill constant weight of residue was achieved. The bound rubber content was calculatrd as a percentage of insoluble polymer

3.2.4.(g) Swelling test

The swelling test was performed with vulcanized rubber, in order to get some useful information about density of cross links of chemical bonds. From each vulcanized compound the specimens having approximate volume of 0.2 cm³ were prepared and weighed. The weight of each specimen was recorded using an electronic balance having 0.0001 g accuracy.



In this study the weight of toluene uptake per gram of rubber hydrocarbon (Q) was calculated according to the expression derived by Park and Brown as shown bellow

$$Q = \frac{\text{Swollen weight} - \text{Deswollen weight}}{\text{Dry weight} \times 100} \times \text{Formula weight}$$

Where formulation weight was the total weight of the rubber plus compounding ingredients based on 100 parts of rubber. Dry weight was the original weight of the sample



3.2.3 Differential Thermal Analysis (DTA)

This test provides the information about enthalpy changes reflecting a chemical or physical changes occurring under heating or cooling of tested samples at permanent rate.

Two specimens were tested:

1. A sample of kaolin treated with MEA
2. A sample of rubber compound, filled with kaolin treated with MEA



CHAPTER 4

RESULTS AND CALCULATIONS

4.1 Results obtained from the Kjeldahl experiment

Amount of HCl required for titration of ammonium cations (NH_4^+) removed from kaolin structure is given in table 4.

Table 4 : Required amount of 0.1 N HCl

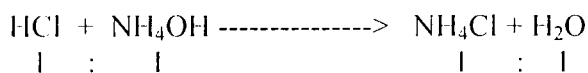
Trial	Required amount of HCl, ml
1	3.8
2	4.1
3	4.1
Average	4.0

Finding the ion exchange capacity

Average amount of the 0.1 M HCl for the titration is, 4.0 ml

Number of moles of HCl required to neutralize NH_4OH is, $\frac{0.1}{1000} \times 4.0$

$$= 4.0 \times 10^{-4} \text{ mol}$$



According to the stoichiometry; number of Ammonium moles present in the titration medium is equal to number of HCl moles required for the titration, that is $4.0 \times 10^{-4} \text{ mol}$

Hence the number of milli equivalents per 100 grams is - 4.0

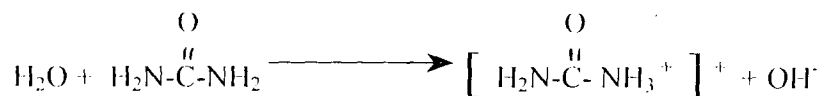
Number of moles of each chemical required for the treatment of 100.0 g of kaolin was equal to the number of milli equivalents of exchangeable cations present in 100.0 g of kaolin

Obtained value of cation ion exchange capacity was used in further calculations, required for preparation of the solutions for the treatment of kaolin.

Calculation of modifiers' concentrations, required for treatment of kaolin.

1. Carbamide

According to (Morrison & Boid) dissociation of carbamide is given by reaction:



So the amount of carbamide that could be involved in ion exchange reaction with 100 g portion of kaolin was equal to

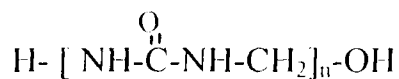
Cation exchange capacity of kaolin in equivalence \times *molecular weight of carbamide:*

$$4 \times 10^{-3} \times 60 = 0.24 \text{ g}$$

Amount of carbamide obtained from the above calculation was dissolved in 100.0 ml of water to get the final concentration. To prepare the solution for treatment of kaolin an excess of carbamide was taken to obtain 2.5 g / dm³.

2. Urea Formaldehyde

Water soluble resin of the second stage polymerization is a linear polymer with a structure



Where: $n = 6-8$

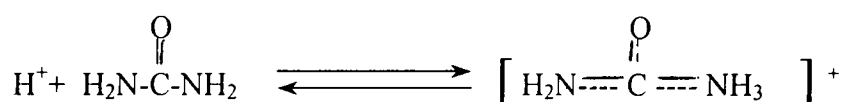
Number of moles of each chemical required for the treatment of 100.0 g of kaolin was equal to the number of milli equivalents of exchangeable cations present in 100.0 g of kaolin

Obtained value of cation ion exchange capacity was used in further calculations, required for preparation of the solutions for the treatment of kaolin.

Calculation of modifiers' concentrations, required for treatment of kaolin.

1. Carbamide

According to (Morrison & Boid, 1996) dissociation of carbamide in acidic medium is given by reaction:



So the amount of carbamide that could be involved in ion exchange reaction with 100 g portion of kaolin was equal to ,

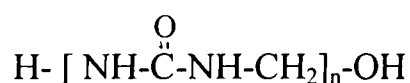
Cation exchange capacity of kaolin in equivalence X molecular weight of carbamide;

$$4 \times 10^{-3} \times 60 = 0.24 \text{ g}$$

Amount of carbamide obtained from the above calculation was dissolved in 100.0 ml of water to get the final concentration . To prepare the solution for treatment of kaolin an excess of carbamide was taken to obtain 2.5 g / dm^{-3} .

2. Urea Formaldehyde

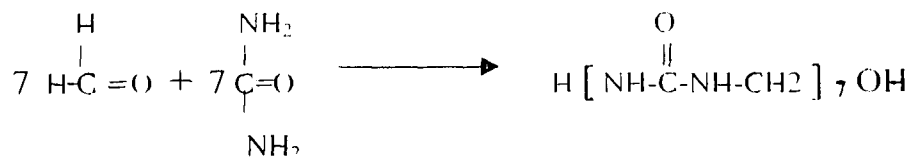
Water soluble resin of the second stage polymerization is a linear polymer with a structure



Where; $n = 6-8$

Approximate amount of urea formaldehyde resin for kaolin treatment was calculated as follows:

Assume, that 100 g of urea was reacted



$$100 / 60 = 1.67 \text{ moles of urea reacted}$$

Amount of formaldehyde reacted has to be 1.67 moles too

$$1.67 \times 30 = 50 \text{ g of formaldehyde reacted}$$

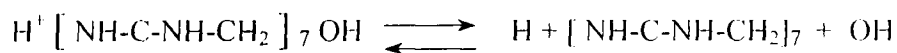
Approximate weight of resin produced would be :

$$100 + 50 = 150 \text{ g}$$

Total weight of solution (determined experimentally) was 400 g, so approximate resin content ratio is ,

$$(150 / 400) \times 100\% = 37\%$$

Proceeding from a common mechanism of dissociation of amines



at least 4×10^{-3} moles of resin participated in cation exchange reaction with 100 g of kaolin.

$4 \times 10^{-3} \times$ molar weight of resin = $4 \times 10^{-3} \times 548 = 2.2$ g of resin involved in ion exchange reaction with 100 g of kaolin.

Minimum amount of 37 % resin solution required for treatment of 100 g kaolin is calculated as:

$$\frac{2.2 \times 100}{37} = 6 \text{ g}$$

This amount was diluted with water to get 100 ml of resin solution.

3. Monoethanol amine

The amount of Monoethanol amine that could be involved in ion exchange reaction with 100g of kaolin was equal to:

Molecular weight of monoethanol amine X Cation exchange capacity of kaolin in milli-equivalents

As monoethanol amine was available in a liquid form at market, volume required for treatment was calculated as:

Weight / Density

Since the specific gravity of monoethanol amine is 1.07 g / dm³, required volume containing 59 g was taken as 60 ml to ensure better ion-exchange reaction.

The calculations were done as follows:

$$60.0 \text{ ml} \times 4.0 \times 10^{-3} = 2.4 \times 10^{-1} \text{ g / dm}^{-3}$$



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4. Polyvinyl alcohol

On the reasons given in experimental part 1.6 g of polyvinyl alcohol were dissolved in 100.0 g of water to get a solution with 16 g / dm³ concentration.

4.2 Results obtained from the Mooney Viscometer and Monsanto Rheometer

Values of scorch time and cure time of all samples were calculated from the rheographs obtained from the Mooney Viscometer (Table 5 , Graph 1).

Table 5 : Results obtained from the Mooney Viscometer

Mix N ⁰	Scorch time, Min	Cure time, Min
1	6.0	11.5
2	6.0	11.0
3	6.0	10.5
4	4.0	7.0
5	6.0	10.75



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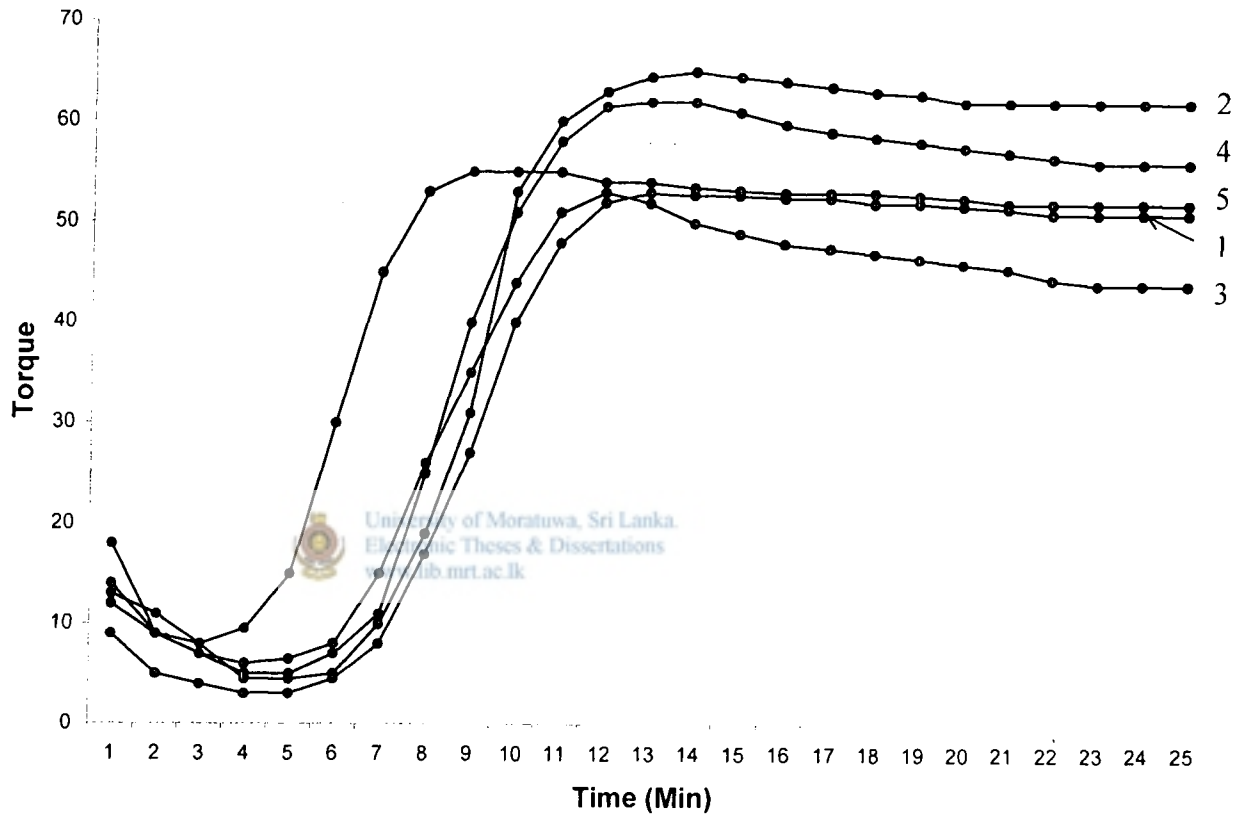
Scorch time and cure time values for all five samples were obtained from rheographs obtained from the Monsanto Rheometer (Table 6, Graph 2)

Table 6: Results obtained from the Monsanto Rheometer

Mix N 0	Scorch time, Min	Cure time, Min
1	6.0	11.0
2	6.5	11.0
3	6.0	10.5
4	3.0	6.0
5	5.5	11.5

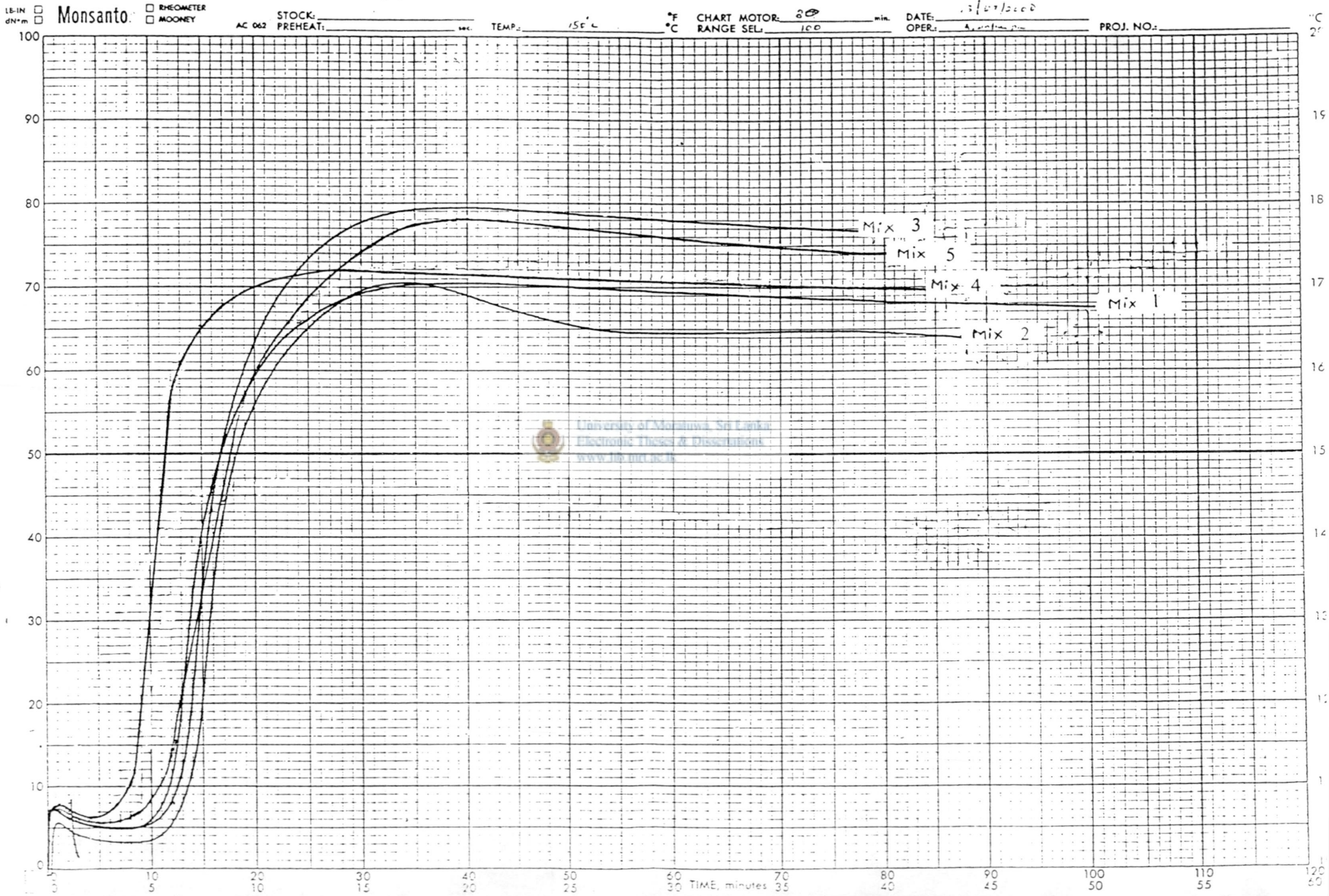


Graph 1 :Curing curves obtained from the Mooney Viscometer



- 1.....Curing curve of Mix 1
- 2.....Curing curve of Mix 2
- 3.....Curing curve of Mix 3
- 4.....Curing curve of Mix 4
- 5.....Curing curve of Mix 5

Graph 1: Rheograph obtained from Monsanto rheometer



4.3 Tensile properties of vulcanized samples

Obtained results were the average of 5 trials for each sample. The tensile strength and the moduli are given in MPa, and calculated as follows;


$$\text{Tensile strength} \quad - \quad \frac{\text{Required force to break the dumb bell sample}}{\text{Surface area of surface to that force applied}}$$

Eg: For specimen N 1

$$\text{Obtained force at breakage} \quad - \quad 83.6 \text{ N}$$

$$\text{Surface area that force applied to} \quad - \quad 4 \times 1 \text{ mm}^2 \quad = \quad 4 \times 10^{-6} \text{ m}^2$$

$$\text{Tensile strength} \quad - \quad \frac{83.6 \text{ N}}{4 \times 10^{-6} \text{ m}^2} \quad = \quad 20.4 \text{ MPa}$$



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$$\text{Modulus } 100\% \quad - \quad \frac{\text{Force required to elongate the sample by 100 \% of its original length}}{\text{Surface area of the surface to that force was applied}}$$

$$\text{Modulus } 300\% \quad - \quad \frac{\text{Force required to elongate the sample by 300 \% of its original length}}{\text{Surface area of the surface to that force was applied}}$$

Table 7 I: Tensile properties of mixes extended with modified and standard kaolin before aging.

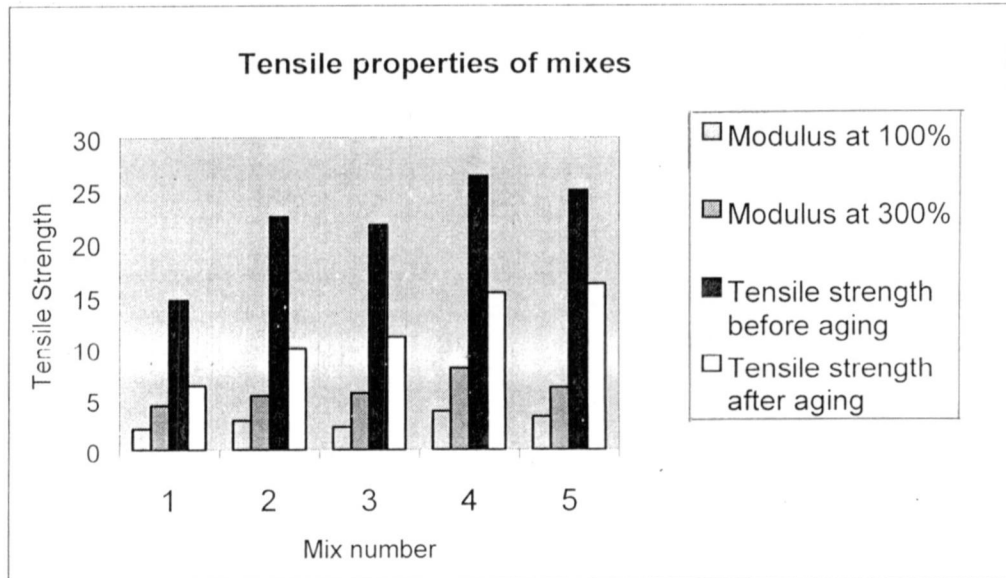
Properties	Mix N ⁰				
	1	2	3	4	5
Modulus at 100%, M Pa	2.03	2.86	2.24	3.78	3.26
Modulus at 300% ,M Pa	4.33	5.31	5.51	7.98	6.08
Tensile strength, MPa	14.6	22.5	21.7	26.3	24.97
Elongation at break, %	1649	1540	1440	1352	1401

Tensile strength and elongation at break of aged specimens were calculated as it was shown in previous test

Table 7 II: Tensile properties of the mixes, extended with modified and standard kaolin after aging

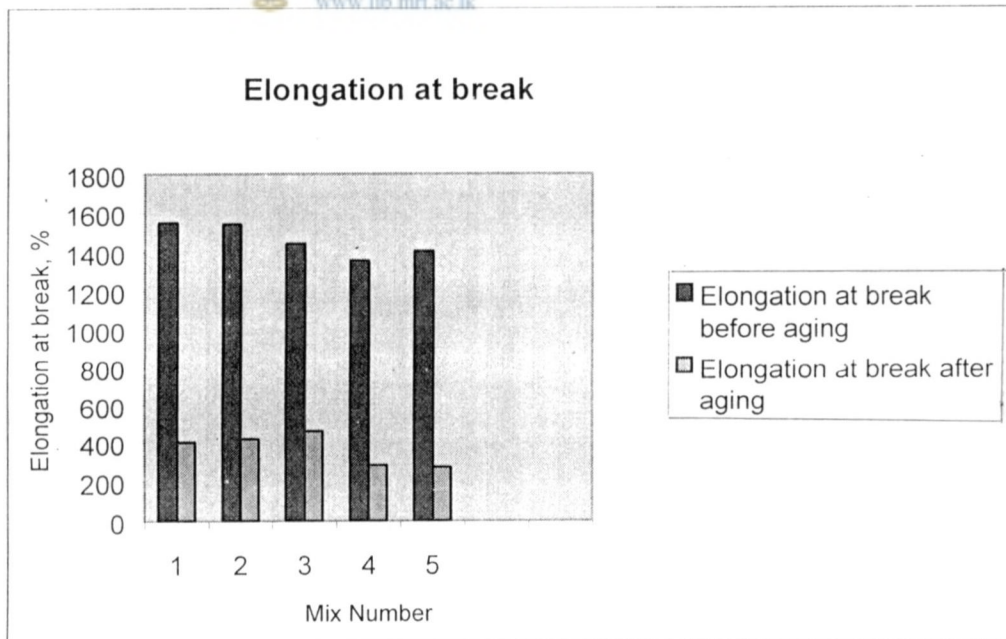
Tensile properties after heat aging at 100 °C during 72 hours	Mix N				
	1	2	3	4	5
1. Tensile strength, M Pa	6.25	9.91	11.04	15.25	16.12
2. Elongation at break %	401.5	421.8	461.0	282.0	273.4

Graph 3 : Graphical comparison of Tensile properties obtained for vulcanized samples



Graph 4 : Graphical comparison of results, obtained for elongation at break.

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4.4 Abrasion resistance test results

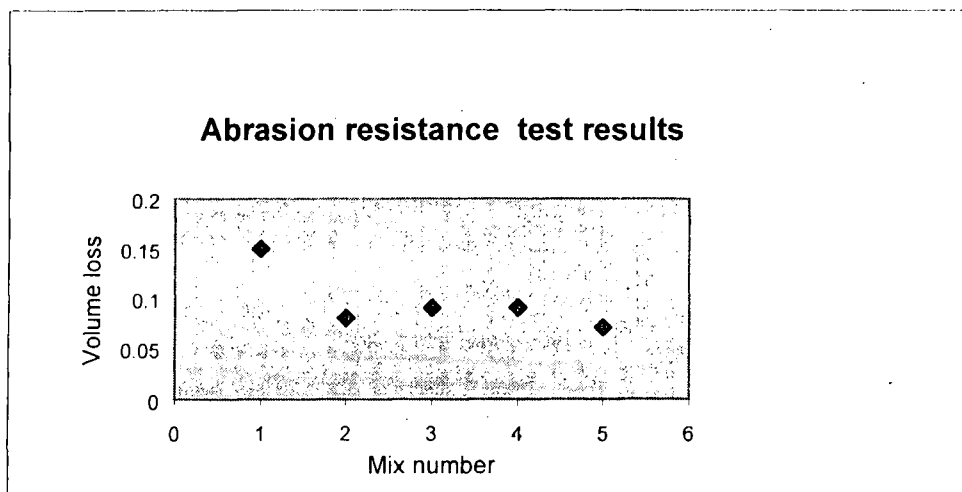
Finalized results were the average of five trials for each samples and the results were expressed as weight loss after abrasion in grams.

Table 8: Abrasion resistance test results

Mix N ⁰	Initial weight, g	Weight after abrasion, g	Weight loss ,g
1	1.25	1.10	0.15
2	1.51	1.43	0.08
3	1.43	1.34	0.09
4	1.52	1.43	0.09
5	1.46	1.39	0.07

Weight loss = Initial weight of sample – weight of the same sample after wearing

Graph 5: Graphical comparison of abrasion resistance test results



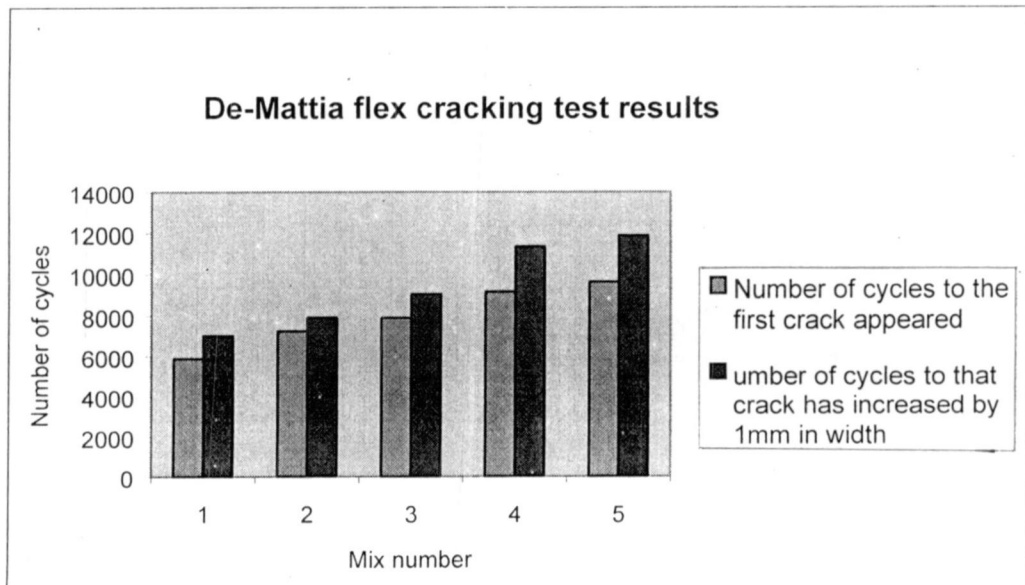
4.5 The Flex cracking and crack growth test results

Obtained results were the average of four trials done for each samples. Results were expressed as the number of cycles passed to the appearance of first crack and the number of cycles required to increase the crack width by 1mm.

Table 9 : Results of De-Mattia flex cracking test

Mix N ^o	Number of cycles to the first crack appearance.	Number of cycles to that crack has increased by 1 mm in width
1	5872	6501
2	7218	8313
3	7881	9017
4	9125	11337
5	9579	11864

Graph 6 : Graphical comparison of flex cracking and crack growth test results



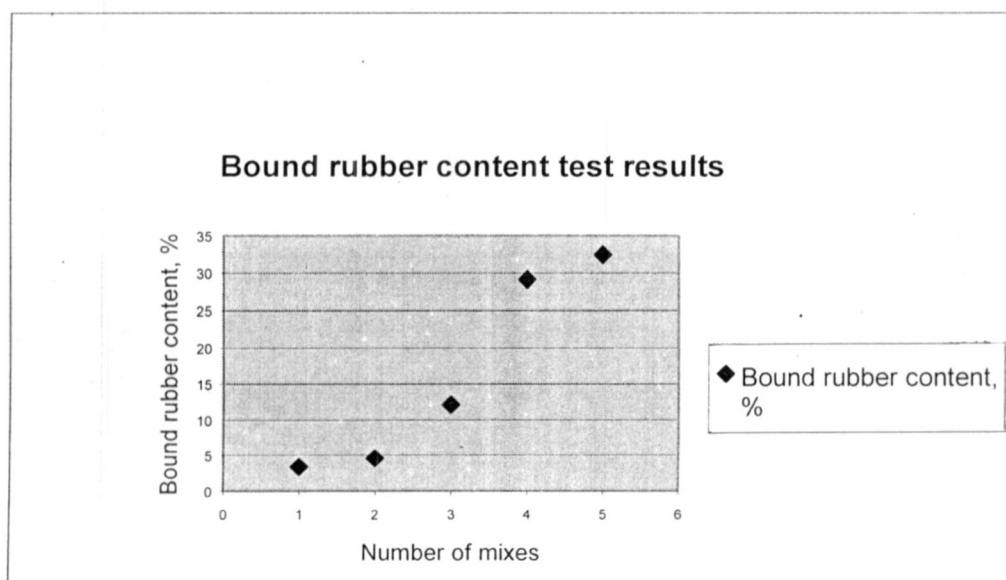
4. Bound rubber content test Results

Results were expressed as a percentage of remaining rubber to the initial weight. Obtained results were the average of two trials.

Table 10 : Results of Bound rubber content test

Mix N ⁰	Initial weight,g	Final weight,g	Bound rubber content %
1	0.98	0.033	3.4
2	0.95	0.044	4.6
3	1.00	0.121	12.1
4	0.96	0.279	29.1
5	0.98	0.375	32.4

Graph 7 : Graphical comparison of the results obtained from bound rubber content test



4.7 Results obtained from the swelling test

Results obtained from this test were expressed as the percentage increment of weight of samples after keeping them in toluene. The finalized results were the average of two trials carried out for each sample.

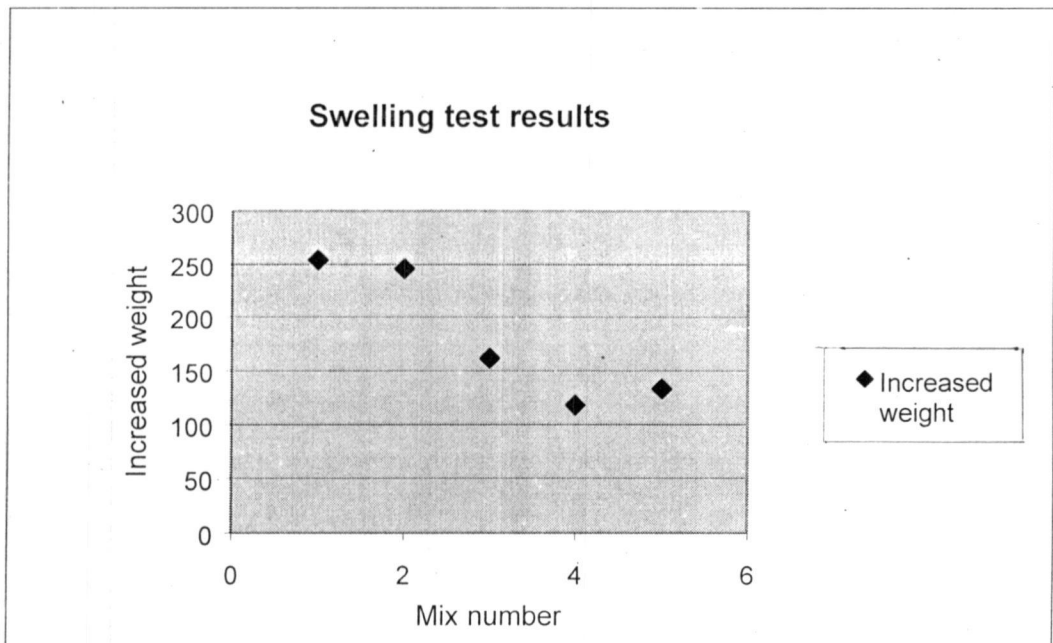
Table 11: Results of swelling test

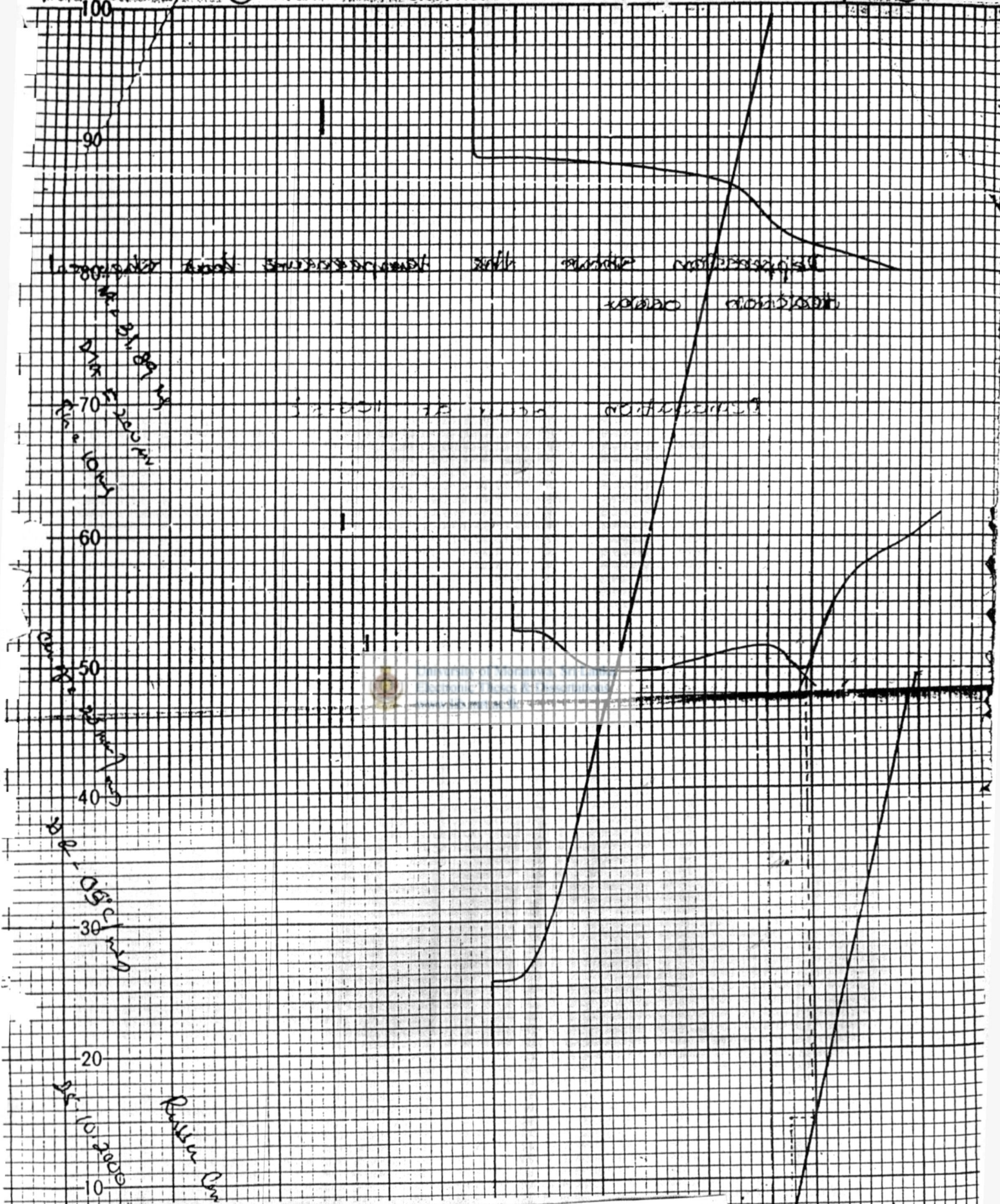
Vulcanizate (Compound Number)	Increased weight %
1	253.9
2	246.1
3	161.2
4	117.7
5	133.0



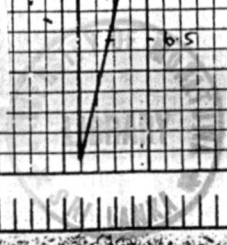
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Graph 8 : Graphical comparison of the results obtained from the swelling test of raw rubber





Graph 9 : DTA of raw rubber filled with kaolin treated with MEA



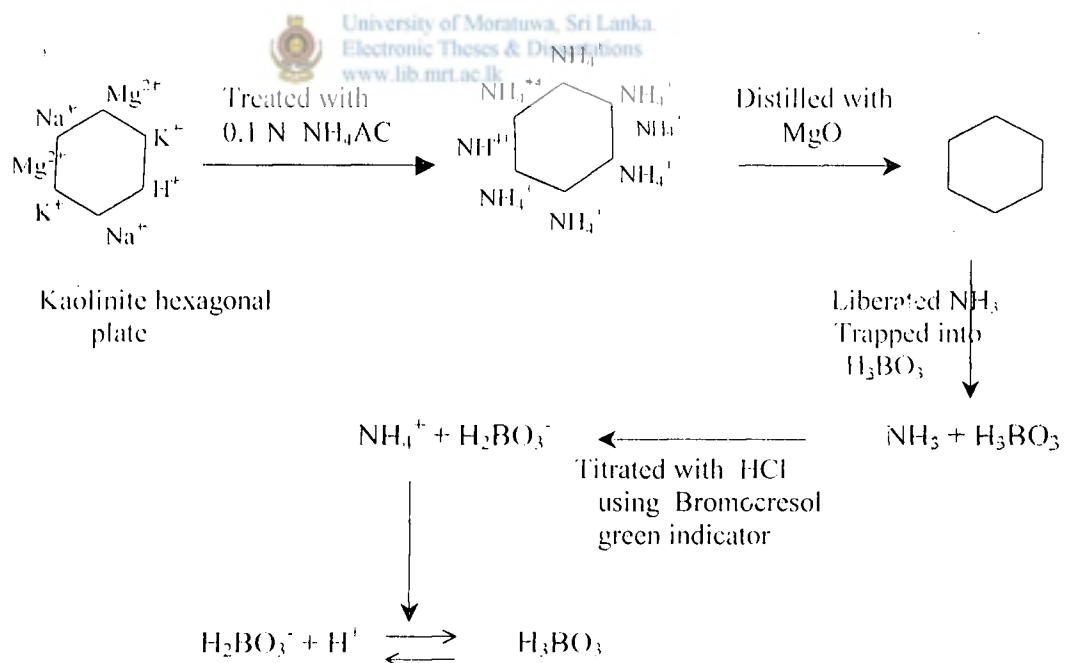
CHAPTER 5

5.1 DISCUSSION

The modifications of kaolin in this study were based on the ion exchange capacity and the adsorption ability of kaolin surface.

Ammonium cations were introduced using Kjeldahl method to occupy the equivalence points on the clay surface through an ion exchange process. This was done in order to determine the exact amount of the chemical concentrations needed for the treatment and verify whether the ion exchange process could be practically applicable for the modification procedure, i.e. to confirm whether the ion exchange would take place.

The reactions carried out by the Kjeldahl method are shown in a simple schematic diagram bellow.



The solution contained H_3BO_3 and NH_4Cl at the equivalence point. The PH of the solution was in a range of 5-6

It was found that the ion exchange phenomena could be applied to kaolin modifications. Concentrations required for treatments were calculated keeping equality of modifying cations to ion exchange capacity. A slight excess of each chemical was taken to ensure a better ion exchange.

The benefit of modification of kaolin with basic organic compounds, dissociated in water medium, gave evidence, when comparing physical properties of filled rubber vulcanizates.

Tensile test results given in table 2 showed higher (at least by 11%) tensile strengths as well as moduli at 100% and 300% elongation for all specimens containing modified kaolin (N^o N^o 2-5) if compared to strength value specified for specimen filled with non-activated standard kaolin (N^o 1)

Aging test followed the same trends, indicating that modification had developed certain resistance of rubber to prolonged action of high temperature (72 hours at 100 °C).

Thermal degradation of course brought down tensile strength for all specimens, but standard one was affected to a greater extent.

Increase in strength characteristics could be related directly to rubber-filler interaction that was promoted by active functional sites introduced to the inert kaolin structure by ion-exchange process. Reinforcing effect came according to generally accepted theoretical conception through a particular attraction between these active sites and reactive points on the rubber-polymer chains, stemmed from weak double olefin bonds and broken under mechanical action of shear force paraffin bonds. Polymer chains even rubber fragments attached to the filler surface formed a grafted layer, held on the kaolin surface by various types of physical, hydrogen and chemical bonds with a wide range of magnitude of their respective bond energy from 0.08 KJ/mol to 1000 KJ/mol.

Examination of flexibility of tested specimens did not reveal within the experimental errors any significant change in elongation at break. However a

Molecular-mechanical or adhesion-deformational hypothesis of friction of polymers suggested the reduction in energy of adhesive bonds as a measure against intensive wearing. From this point of view physical or so-called secondary Van-der Waals bonds, which prevailed in a spectrum of adhesion bonds, established across rubber-filler inter face, were of a great importance.

Being of low energy by nature they could be easily destroyed under force action, permitting chains desorbed and slipped on the filler surface, so that break of a polymer chain did not occur. Such aim of physical bonds was efficient to a certain extent, but did not fully guard against seizure. Constant stresses and heat finally destroyed interface and wore a specimen out.

Analogous behavior was exhibited by the specimens in flex cracking test. Results obtained from DE- Mattia flexing machine are given in table 9



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Vulcanizates with modified filler displayed better flex resistance, than ones with non-modified filler. Similarly the crack growth became slower.

Behavior of a polymer that was repeatedly bent to a double position agreed well with previously considered hypothesis of disorption of the polymer chains from the filler surface and "stress softening effect".

Vulcanized rubber always contained micro irregularities of its structure in the form of cracks, mechanical inclusions. Density of cross-links was also not even through out the rubber matrix, because of snarls and entanglements of macromolecules.

These irregularities experienced higher stresses, than the average one in a specimen, facilitated mechanical destruction and a specimen failed under the effect of stress lower than ultimate strength. As chains desorbed from the filler surface, they regrouped themselves such a way to pass over into the most

slightly expressed tendency to reduction of flexibility was observed in the row-unmodified kaolin, kaolin modified with urea, kaolin modified with polyvinylalcohol, kaolin modified with monoethanolamine and ureaformaldehyde, that could be associated with restriction of chain mobility owing to the increase of the cross link density in the same sequence.

Another aspect involved in reinforcing mechanism of modified filler referred to some degree of ordering or orientation of the chain portions close to the filler surface due to physical adsorption. Active centers, which are believed, amine, carboxyl and hydroxyl groups in organic radicals of exchangeable cations being strongly attached to the filler surface, influenced the electron density of double bonds of rubber polymer caused them displaced, so as arisen inductive dipole interaction culminated in crystallization.

Crystallization on the filler surface functioning in that case as crystallization nuclei, could reduce degree of crystallinity in rubber matrix, but no serious negative effects on the strength of rubber were reported, because of cross links density generally increased



Abrasion resistance test results given in table 8 favoured also the compounds filled with modified kaolin. These compounds lost weight on wearing, but much slower, than standard ones filled with non modified kaolin.

Abrasion resistance of vulcanized rubber according to general laws of wear in friction depends on the nature of adhesive bonds formed across contact zone (interface).

In abrasion test under periodical action of external force these bonds deformed repeatedly, strained, hardened and softened again. Process normally involved heat, oxidation and structural changes (reorientation, recrystallization) that together wore a specimen out.

probable state with minimum free energy, reducing the stress concentration level. Structure of vulcanization network became more even and stronger each time after a repeated load applied, so number of cycles to first crack appeared and achieved 3/4 inch in width increased significantly.

Non-activated kaolin also held certain amount of polymer owing to mechanical interlocking of the rubber in the micro irregularities on the porous structure of kaolin or absorption to the active sites on the planar surfaces of kaolinite mineral.

Suggested reinforcing mechanism of activated kaolin, that came through facilitated absorption of rubber polymer to the filler surface was confirmed by bound rubber content test results [Table 10].

The amount of rubber strongly attached to the filler, was significantly more for mixers containing modified kaolin (N⁰N⁰ 2 - 4).

As ion-exchange process touched only upon chemistry of kaolin keeping unchanged its surface geometry, obtained increment in bound rubber content attributed just to intensified attraction of rubber polymer to filler with establishment of sufficiently strong intermolecular bonds capable to withstand prolonged action of solvent.

The claim of improved interfacial activity with polyvinylalcohol as modifying agent was based on enhanced compatibility of inorganic filler with organic rubber. Polyvinylalcohol an amphipathic agent by nature, being applied to the filler surface prior to compounding promoted intrinsically wetting, increased adhesion, dispersion and distribution of kaolin particles through out the rubber matrix.

Comparing the efficiency of chosen basic organic electrolytes, mix N⁰ 4, containing kaolin modified with monoethanolamine attracted attention in virtue of exceptionally high strength characteristics obtained by all test procedures and

bound rubber content. The beneficial effect of monoethanolamine as modifying agent related in all probability to following:

- The discrepancy in the degree of substitution due to large size of polyvinylalcohol molecule leading to steric hindrance, when arranged on the silica sheet was not concerned with monoethanolamine
- Even for equivalent concentrations, monoethanolamine ions could be absorbed more strongly, than carbamide ions, because of their higher activity in the lyotropic or Hofmeister series
- It could not also be ignored, that monoethanolamine effected on vulcanization of rubber, acting as accelerating agent.

Analysis of rheographs showed the reduction in scorch time and cure time nearly two times. It would be too early to state about the formation of additional crosslinks in the network of chemical bonds, because high bound rubber content could be originated from chemical as well as physical adhesion bonds, established across rubber-filler interface. However clearly expressed endothermal peak on the thermograph curves obtained by DTA at 142 °C gave definite support to chemical reaction occurred between rubber and modified kaolin with evolution of low molecular weight byproducts.



5.2 CONCLUSION

Inert structure of rubber grade kaolin was activated through an ion-exchange reaction to match active fillers in their reinforcing capability.

It was suggested that treatment of kaolin with basic organic compounds dissociated into complex ions containing amine, carboxyl and hydroxyl functional groups in aqueous medium, facilitated rubber-filler interaction owing to better compatibility and grafting of rubber polymer to the filler surface.

Physico-mechanical properties of rubber compounds extended with activated kaolin showed definite improvement in performance characteristics, confirming that modification of kaolin with selected compounds was effective.



CHAPTER 6

6. SUGGESTIONS AND FUTURE RECOMMENDATIONS

1. As Monoethanol amine performed the ability of accelerating the curing rate and reducing the cure time, it can be tested as an accelerator for room temperature vulcanization
2. The filler concentration was only 30 parts per 100 parts of rubber in this study. It will be useful to continue this study to investigate the effect of modified filler concentration on properties of filled rubber compounds and compare the variation in properties with properties of carbon black loaded compounds.
3. In addition kaolin has some sites occupied with anions, that can be involved in ion-exchange process also. So ion-exchange capacity of kaolin could be increased and investigation of this increment on properties of rubber would be interesting
4. Since Urea in water medium can be introduced to the kaolin surface it will be useful to study whether there is a possibility of any chemical synthesis, starting from urea, attached to kaolin surface so as to bind rubber to kaolin particles as well as kaolin particles distributed through rubber matrix in to continuous network of chemical bonds
5. Melamine formaldehyde, in its water soluble form can be used to treat kaolin also. It may display some useful effect on filled rubber compounds by means of carefully selected curing system.

6. Activity of Carbon black is normally attributed to large amount of COOH groups on its surface and if there is a possibility to introduce –CN groups to kaolin , that can be converted further chemically in to –COOH acting as pendent groups present in carbon black, activity of inert kaolin could be increased
7. As monoethanol amine being attached to kaolin surface accelerated cross linking the filled rubber, this fact is worth to be studied in details too.
8. Cation exchange capacity of kaolin varies, depending on physical modification. In this connection it would be useful to investigate effect of modified kaolins, of various cation exchange capacities on physico-mechanical properties of rubber.



In spite of preliminary nature of obtained results the certain recommendations to rubber processing industry can be given from carried out research

1. As treatment of kaolin with selected compounds improves its distribution through out the rubber matrix, mixing cycle on two roll mills or in an internal mixer can be reduced significantly.
2. Treatment of kaolin improves tensile strength, abrasion resistance, flex cracking, and thermal stability of natural rubber based compounds.
3. Replacement value of kaolin to carbon black can be increased as some reinforcement will be brought by modification, that is of low cost. So introduction of modified kaolin will reduce cost of rubber compound.

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Appendix I

Technical Data of China Clay

Rubber grade clay was refined in Boralessgamuwa refinery.

Technical data were obtained from Sri Lanka Ceramic Ltd. Piliyandala.

Colour (Raw colour) : Creamish white

Chemical Analysis

SiO₂ : 45.82 %

Al₂O₃ : 38.78 %

Fe₂O₃ : 0.39 %

TiO₂ : 0.79 %

CaO : 0.13

MgO

Na₂O

Loss on ignition : 13.19 %

Specific Gravity : 2.59

pH : 5.6

Brightness less than : 78 %

Moisture content : 2 %

General plasticity : Good

Particle size distribution

Larger than 25 microns : 0.20 % by weight

Between 25-2 microns : 29.90 % by weight

Smaller than 2 microns : 70.00 % by weight

Smaller than 8-5 microns : 6.70 % by weight

Smaller than 5-3 microns : 9.30 % by weight



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Smaller than 3-2 microns	: 8.00 % by weight
Smaller than 2-1 microns	: 16.20 % by weight
Smaller than 0.5 microns	: 40.80 % by weight

Rotational analysis

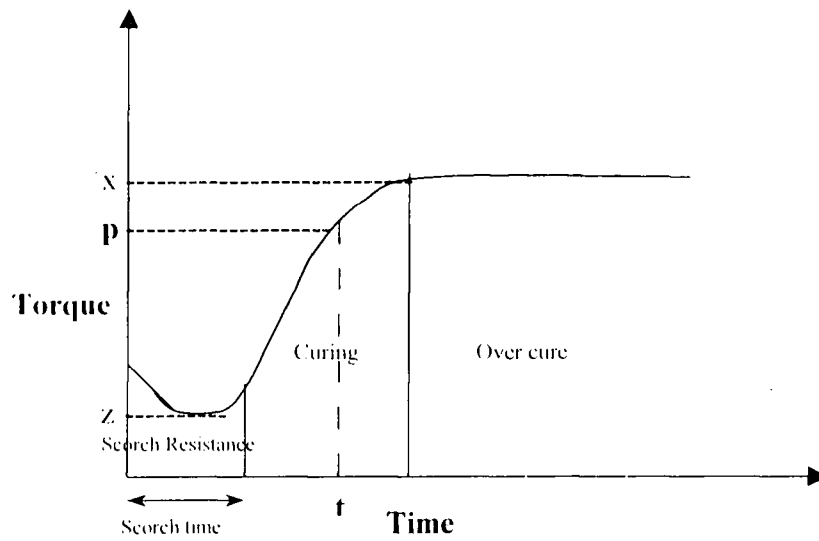
Clay substances	: 94.8 %
Feldspar	: 2.0 %
Alumina	: 0.8 %
Other impurities	: 1.9 %



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APPENDIX II

Characteristics and measurements of curing



(Fig 4): Characteristic Curing cure

Calculations of the curing time; $(X - Y) \times 90 / 100 = P$

The corresponding value of P, in the X axis (t) taken as the cure time.



APPENDIX III

Sketch of an Oscillating disk rheometer, used to monitor the cure characteristics (Fig III.a)

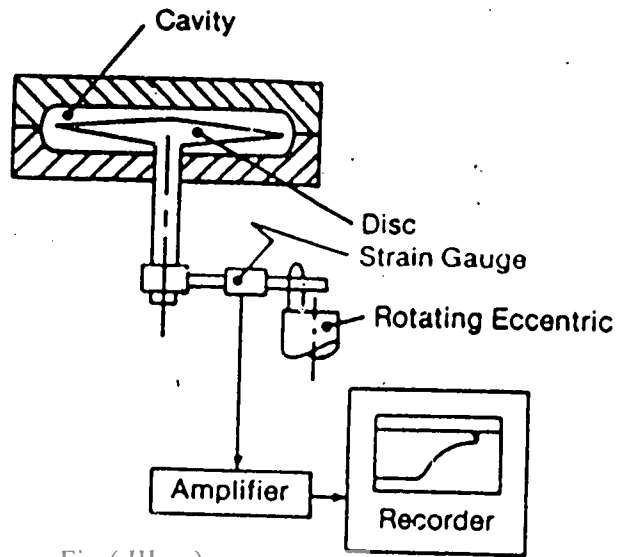


Fig (III .a)



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Sketch of a Din-abrader used to measure abrasion resistance (Fig III b)

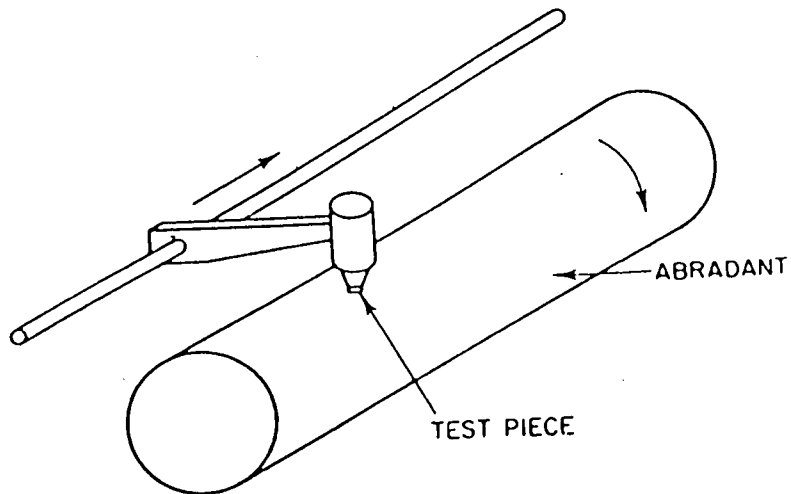


Fig (III b)

A Pendulum/general type tensile strength tester, to measure force and elongation at specified time or at break (Fig III. C)

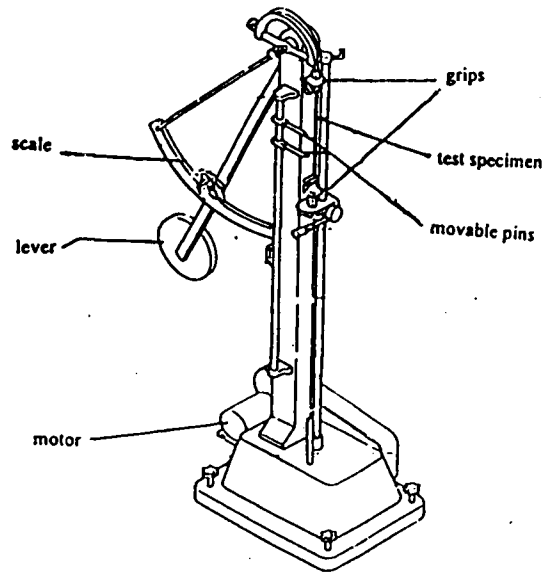


Fig (III c)

The mechanism of the De-Mattia flexing machine used to find the crack initiation and the rate of crack growth s(Fig.III d)

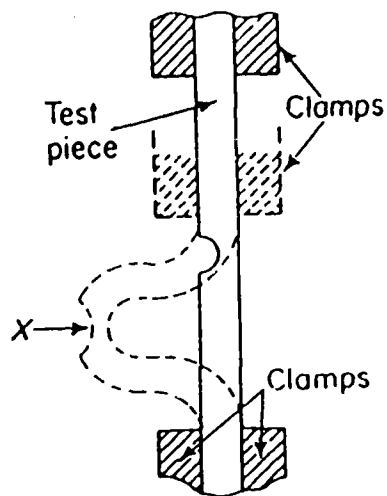


Fig (III d)

