

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA.

# THE ECONOMIC POTENTIAL OF NATURAL RUBBER PRODUCTION IN NICERIA

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### PROF. M.A.T. SULEIMAN

ND, B.Sc, Ph.D, FICCON, FCSN **Professor of Chemistry**Deputy Vice-Chancellor (Administration)

**INAUGURAL RECTURE SERIES 12** 

13<sup>™</sup> NOVEMBER 2008



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In the name of Allah the beneficent the merciful I give thanks to Allah (SWT) for making this inaugural lecture a reality. When on the 24th April, 2008 the Chief Servant and Executive Governor of Niger State, Dr. Mu'azu Babangida Aliyu, OON and Talban Minna challenged me to present my inaugural lecture, it was a great task given to me. However, today Allah has made it possible, I therefore feel very highly honored and privileged to present the 12th inaugural lecture of this university which is titled "The Economic Potential of Natural Rubber Production in Nigeria".

Mr. Chairman, there is no doubt that natural rubber production and application in Nigeria has a great economic impact on our day to day life. Natural rubber is a biopolymer and renewable material obtained from Hevea brasiliencies tree which is native to South and Central America but also grown in Asia and Africa including Nigeria. Natural rubber is unique and used for many applications that has no synthetic equivalent.

Natural rubber products have become household materials that hardly between the time one wakes up in the morning and goes to bed in the night he/she does, not use material produced from the rubber tree. Their unique characteristics and properties such as resilience, elasticity, abrasion, impact resistance, efficient heat dispersion of natural rubber products make them outstanding for many applications. For instance, Aeroplanes cannot safely land with tyres made from synthetic rubbers, only truct tyres made from natural rubber are resilient enough to withstand heavy shock and loads; car tyres containing natural rubber are safer than synthetic rubber tyres because of the unique heat dispersion abilities of natural rubber. Natural rubber is used in over 40,000 consumer products, including more than 400 medical devices for instance; disposable syringe, gloves, condoms, and catheters.

Synthetic rubbers derived from petroleum a non-renewable resource offer an alternative to natural rubber production. However, many decades of industrial research have not produced synthetic rubber with similar qualities of natural rubber. Synthetic rubber production is at present about 60% of world rubber production but its production is grossly affected by the global oil production and market prizes. The rapid economic developments in China and India are fueling growth of natural rubber demand, and prices have increased significantly. Incidentally tyre manufacturing companies consume about 70% of world natural production. Evidently, in all the countries where natural rubber is produced, national governments are the major stakeholders because it constitutes a strategic resource for economic development. Without natural rubber many sections of the world economy would experience great difficulties in attaining any meaningful technological development. Nigeria is not an exception; however there has been gradual decline in rubber production due to negligence by the various stakeholders.

Mr. Chairman, it is in line with the above economic importance of natural rubber production and its applications that informed this lecture of today. There is need for Nigerian government to revive the trend in rubber production and develop the local processing techniques to meet the local demand and for export.

My research interest and works reported here centre mostly on the ways of enhancing the properties of natural rubber for wider application of its products. Thus various means of improving the quality and physical performance of natural rubber by modifying its structure and behavior have been the main focus of this lecture.

#### 1.0 INTRODUCTION

#### 1.1 What is Rubber?

The term "rubber "is used exclusively to refer to a natural substance obtained from trees and consists of a hydrocarbon polymer of isoprene units in cis-configuration. Physically, it is elastic in nature, which describes its ability to undergo stretching under stress and upon removal of the stress, to return with force to approximately its original length in a short time. The name rubber was proposed by Joseph Priestly in 1770 because he found small cubes of it useful in rubbing out pencil marks (http;//www.answers.com/rubber, Pavies and Glazer (1955) and Industrial Potentials of the Natural Rubber Tree Laboratory Wednesday 13<sup>th</sup> April, 2005).

With the development of synthetic (man-made) rubbers having rubbery characteristics but differing in chemical structures and properties, an umbrella term, "elastomers" being a contraction of the words "elastic" and "polymer" was introduced. The term elastomer therefore, describes both natural and synthetic rubbers (http://www.answers.com/rubber). Three requirements must be met for rubbery properties to be present in both natural and synthetic rubbers viz: long thread like molecules, flexibility in the molecular chain to allow flexing and coiling, and some mechanical or chemical bonds between molecules.

Natural rubber and most synthetic rubbers are commercially available in the form of latex, a colloidal suspension of polymers in an aqueous medium. Natural rubber comes from trees in this form and immediately ammoniated to prevent coagulation. Many synthetic rubbers are polymers that can be dispersed in water to form latex. Stabilization of synthetic latexes is usually achieved by incorporation of protective colloid, usually a cellulose derivative such as hydroxyethyl cellulose (HEC) or long-chain alcohol e.g.

Polyvinyl alcohol (PV<sub>A</sub>). In the crude state, natural and synthetic rubbers possess certain physical properties which must be modified to obtain useful end products. The raw or unmodified forms are weak and adhesive. They lose their elasticity with use, change markedly in physical properties with temperature, and are degraded by air and sunlight. Consequently, it is necessary to transform the crude rubbers by compounding (addition of additives in order to improve certain properties or overcome some deficiencies) and vulcanization procedures into products that meet specifications (http://www.answers.com/rubber1).

#### 1.2. Historical Antecedents

In its native Central America and South America, rubber has been collected for a long time and used for production of balls, containers, shoes and for waterproofing fabrics. According to Bernal Diaz del Castillo, the Spanish Conquistadores were so astounded by the vigorous bouncing of the rubber balls of the Aztecs that they wondered if the balls were enchanted by evil spirits. The use of rubber to make water resistant cloth was well practiced in Brazil. A story says that the first European to return to Portugal from Brazil with samples of such water-repellent rubberized cloth so chocked people that he was brought to court on the charge of witchcraft (http://www.solarnavigator.net/rubber.htm). The interest of Europeans in rubber was aroused only after reports about it were made (1736-51) to the French Academy of Sciences by Charles de la Condamine and François Fresneau (http://www.answers.com/rubber, Pavies and Glazer, 1955). When samples of rubber first arrived in England, it was observed by Joseph Priestley, in 1770, that a piece of the material was extremely good for rubbing out pencil marks on paper, hence the name rubber (http://www.solarnavigator.net/rubber.htm). In 1790, latex from

rubber trees was successfully preserved by the addition of alkali, thus rendering native processes potentially available to Europeans, although no use was made of this for over a century. In 1791 rubber manufacturing, albeit on a small scale, became commercial when the Englishman Samuel Peal discovered a method of waterproofing cloth by treating it with a solution of rubber intorpentine (http://sreassociated.anu.au/fpt/nwfp/naturalrubber/natural.htm/). The first rubber factory in the world was established near Paris in 1803, the first in England by Thomas Hancock in 1820. Hancock devised the forerunner of the masticator (the rollers through which the rubber is passed to partially break the polymer chains), and in 1835 Edwin Chaffee, an American patted a mixing mill and a calendar (a press for rolling the rubber in sheets (http://www.answers.com/rubber). Some drawbacks however, affected the growing popularity of rubber at that time which included becoming brittle in cold weather, and soft bad smelling in warm whether. To overcome these negative properties, Charles Goodyear in 1839, at Woburn, Massachusetts developed the "Vulcanization process", which gives rubber increased strength, elasticity and decreased susceptibility to temperature change by treating it with sulphur and white lead at a high temperature. His samples of "cured" rubber, with which he tried to raise funds in England, prompted the English inventor Thomas Hancock to make his own "discovery" of vulcanization. discovery revolutionized the rubber industry. Wherever elastic, shock-absorbing, water-resistance, insulating and air steam-tight properties were required, vulcanized rubber was used (http://www.answers.com/rubber; htt://sreassociated.anu.au/fpt/nwfp/naturarubber/naturalrubber.htm/). While the ancient Mesoamericans did not have vulcanization, they developed organic methods of processing the rubber with similar results, mixing the raw latex with varieties of saps and juices of other vines, particularly Ipomoea albá, a species of Morning glory

(http://www.answers.com/rubber). There are wide varieties of trees around the world, mainly in the tropical rain forests, from which natural rubber can be derived. However, there is only one species that is exploited in particular for commercial production, namely para' rubber or Hevea Brasiliensis because this species is indigenous to Brazil (Amazon basin). Despite Brazil restrictions, seeds of up to 70,000 in number were smuggled to England in 1876 by Sir Henry Wickham and planted in Kew Gardens. The resultant seedlings were sent to Ceylon (Sri Lanka) and later too many tropical regions, especially the Malay area and Java and Sumatra, beginning the enormous East Asian rubber industry. Here the plantations were so carefully cultivated and managed that the relative importance of Amazon rubber diminished. As a step toward diminishing foreign control of the supply, American rubber companies enlarged their plantation holdings in Liberia as well as in South and Central America (http://www.answers.com/rubber).

Rubber latex production began in Nigeria in 1955 and was experiencing wonderful growth until this plummeted with the advent of so called oil boom. Nigeria is blessed with about 8 million hectares of land suitable for cultivation of rubber but only about 250,000 hectares are being utilized for this purpose, with greatest concentration around the Niger Delta, near Benin City (RMRDC, 1996). Nigeria, hence, has great potential to revamp economy through optimal use of opportunities lying fallow in the rubber industry. Today Malysia, Indonesia, and Thailand are the major producers of natural rubber, producing around 90% of the work's natural rubber (htt://sre-associated.anu.au/fpf/nwfp/naturalrubber/naturalrubber.hmt/). Nigeria is probably the second after Liberia as major producers in Africa. The problem is finding labour to tap it in the amongst inaccessible forests and ship it to the factories where they are required.

#### 1.3 An Overview of Synthetic Rubber

The synthetic rubber might be viewed to be a "child of circumstance" During the World War I, the spread of natural rubber became so greatly hampered that alternatives needed to be sought after. Germany made a synthetic rubber during this period but it was too expensive for peacetime use. In 1927 a less costly variety was invented, and in 1931 reopening was made, both in the United States. German Scientists developed Buna rubber just prior to World War II. When importation of natural rubber from the East Indies was cut off during World War II, the United States began large-scale manufacture of synthetic rubber, concentrating on Buna S. Today synthetic rubber accounts for about 60% of the World's rubber production (http://www.answers.com/rubber, Allen, 1972; Morton, 1987). The raw materials from which synthetic rubber is derived are petroleum, coal oil, natural gas and acetylene. Many of them are copolymers referring to polymers consisting of more than one monomer polymerized simultaneously. In general, synthetic rubber has the following advantages over natural rubber: better ageing and weathering, more resistance to oil, solvents, oxygen, ozone and certain chemicals, and resilience over a wider temperature range. The advantages of natural rubber on the other hand are less build-up of heat from flexing and greater resistance to tearing when hot. Furthermore, natural rubber is among the strongest, yet lowest cost, of all the members of the rubbers family. Possessing excellent dynamic and resistance to fatigue properties, it is still a highly utilized material having such applications as bellows, booths, bumpers, bushings, shock mounts and wear pads (http:/www.answers.com/rubber; http://www.moldeddimensions.com/capab materials.htm). an agricultural material, natural rubber is environmentally friendly and biodegradable; hence constitute little or no hazards to lives. The present discourse is thus focused on this renewable resource material to which the subsequent report is devoted.

#### 1.4 Description of the Rubber Tree

Typically, the rubber tree is the species known as Hevea brasiliensis (Euphorbiaceae) or Para rubber tree, so called because, originally it is native to Brazil from where Henry Wickham in 1876 took thousands of seeds of the tree for germination in Kew Gardens, England. Subsequently, the seedlings were sent to Colombo, Indonesia and Singapore (http://ww.solarnavigator.net/rubber.htm). The rubber tree is usually tall, sometimes reaching to a height of 30 meters or more. Having a tap root system, the main stem grows vertically upwards and produces relatively slender branches at the top (Fig.1) (htt://sre-associated.anu.au/fpt/nwfp/natural/natural rubber.htm/). Hevea brasiliensis grows best at temperatures of 21-28°C, in areas with an annual rainfall of just under 2000mm. Its prime growing area is around 10 degrees on either side of the equator, although it is also cultivated further north in China, Mexico, and Guatemala (htt:/sre-associated.anu.au/fpt/nwfp/natural rubber/natural rubber.htm/).



Figure 1:Pictorial View of Rubber Trees (Para Rubber)

#### 2.0 PROCESSING OF NATURAL RUBBER LATEX

#### 2.1 Tapping

The first step in rubber processing is tapping referring to the process by which **latex** the milky-like colloid suspension consisting of rubber particles dispersed essentially in water) is extracted from the stem (Figure 2) (http://www.solarnagator.net/rubber.htm). The latex is present in latrex ducts called 'laticifiers', which run spirally down the stem from right to left. The tapping involves using a specialized tool ("jebough knife") to make an incision cutting through as many laticifers as possible. As a result, the latex flows out and is collected in containers strategically positioned (figure 2). In places like Kerala, where coconuts are in abundance, the shell of half a coconut is used as the collection container for the latex. The shells are attached to the tree via a short sharp stick and the latex drips down into it overnight.



Figure 2:Tapping of Rubber Latex

This usually produces latex up to a level of half to three quarters of the shell (http://www.solarnavigator.net/rubber.htm). Tapping is usually done early in the morning, between 5 .00 and 6.00 am, because latex flow is greatest at this time due to a higher turgor pressure. Tapping occurs 4-5 hours a day for six months of the year, with the other six months left to allow the trees to recover (Gomez, 1983). After the latex flow has stopped for a tapping, the laticifers become plugged by coagulum (solid rubber particle) the stimulant edaphron is used as a means of delaying plugging, although its effects are not maintained in the long-term. Because edaphron increases yield in the short-term, it is seen as an ideal way to reduce labour costs as the trees need to be tapped for less regularly. On a reasonable site, a tree which has attained the age of seven years has matured enough to be tapped. The full cycle for tapping starting from this point of maturity can last for 6 to 8 years. Today skilled tappers can tap the same trees for around 25 years because damage to the tree is minimized (Ochigbo, 2005; associated.anu.au/fpt/nwfp/natural rubber/natural rubber.htm/).

Latex is thought to be a defense against insect pathogens and possibly a site for the depositing of metabolic waste of the tree. Chemically, the constituents of latex from <a href="Hevea brasiliensis">Hevea brasiliensis</a> are shown in Table 1 (Pavies and Glazer 1955).

Table: 1: Analysis of Plantation Rubber

Constituents	Percent Composition		
Moisture	0.3	-	1.2
Acetone extracts ('resins')	2.5	-	3.2
Nitrogenous substances (Proteins)	2.5	-	3.5
Ash	0.15	-	0.5
Rubber hydrocarbon (by difference)	92	-	94

Of these constituents, the non-rubber-hydrocarbon components that is acetone-extractable probably the most important matter, which is a complex mixture of sterols and their esters, amino acids, fatty acids, etc. This extractable matter contains carotene (a pigment), natural antioxidants, and fatty acids which functions as softeners, latex stabilizing agents, and as reactants with zinc oxide, necessary in modern accelerated mixings, so that the acetone extract-may have a determining effect on colour, ageing, processing, and vulcanization of rubbers (Pavies and Glazer1955). Not all latexes are elastic, but those that are, including the latex of <u>Hevea brasiliensis</u>, contain long hydrocarbon chains.

2.2 Fabrication Techniques

Immediately after the extraction of the latex from the trees, it is ammoniated to prevent bacterial attack and coagulation. The resulting latex, known as field latex, which is a 35 percent suspension of rubber particles in water is taken to a processing plant to be treated in either of two ways depending on its destination. If it is to be sold commercially as latex, it is concentrated to about 60% dry rubber content (DRC) by centrifuging, creaming or evaporation. The concentrated latex can be used directly after compounding for the manufacture of various useable items such as adhesives, gloves, contraceptive, latex foams and medical tubbing to mention but a few. These processes are termed "latex technology".

Alternatively, the field latex once collected is coagulated in metal pans using a dilute methanoic or ethanoic acid. The resulting cake of raw rubber is then washed to remove any acid and rolled to remove excess moisture. After rolling, the rubber is dried on a rack and smoked over a wood fire to stabilize it, before it is finally sold to rubber manufacturers. At this stage, the rubber (now called a "coagulum") is passed through various processing technologies (Fig. 3) for manufacturing of articles such as tyres, waterproof boots, raincoats, hosepipes, gaskets and oil seals electrical appliances etc. This is called "dry rubber technology". The most striking potential use of rubber at this stage is the possibility of generating plastics from it for production of various items for engineering applications.

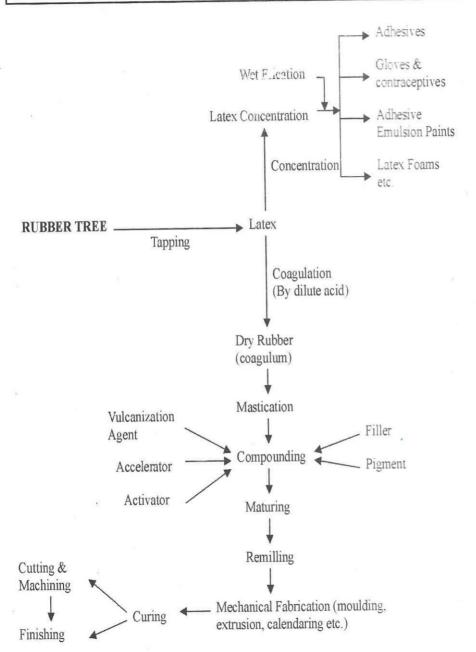


Figure 3: Processing Routes for Converting Rubber to Finished Articles

#### **Table 2: Plastics Derived from Natural Rubber**

Pla 1	astics EBONITE	Applications Lining for acid tanks, insolating roller coverings, pump valves and panels.
2	HALOGENATED RUBBER	Chemical and heat resistant paints, vanishes, slaps and sleeves for thermal insulation and adhesives.
3	HYDRO HALOGENATED	Protective wrapping purposes, protection of engine, adhesive for metal, glass and wood.
4	OXIDIZED RUBBER	Ingredients for paints, vanishes, printing ink, bonding agents, cartones for packing food stuffs, insulator for electromagnetic coils.
5	CYCLISED RUBBER	Insulators, water proofing, corrosion resistant, paints, and thermoplastic moulding materials.

#### 2.3 Natural Rubber Production and Consumption

The annual worldwide natural rubber production is estimated close to 0,800,000 tons (http://www.rubberstudy.com/statistics-quarstat.aspx), almost all of it from one biological source: the Brazilian rubber tree (Hevea brasiliensis). Asia countries such as Malaysia, Indonesia, and Thailand together produce nearly 94%, followed by Africa with only 4% of the world supply (fig.4a). In terms, of consumption Asia still leads with 65%, followed by European Union, North America and Africa with 14%, 12% and 1% respectively (fig. 4b). The yield of rubber varies from 500 kg ha<sup>-1</sup> y<sup>-1</sup> in smallholder plots to more than 1500 kg ha<sup>-1</sup> y<sup>-1</sup> in large plantations (Balsiger et al., 2000). In experimental plots with new Hevea brasiliences, yields of up to 3000 kg ha<sup>-1</sup> y<sup>-1</sup> have been obtained. Natural rubber from H. Brasiliensis mainly consists of cis-1, 4-polyisoprene, with many minor additional components that are key to the superior properties of this material compared to all synthetic rubbers.

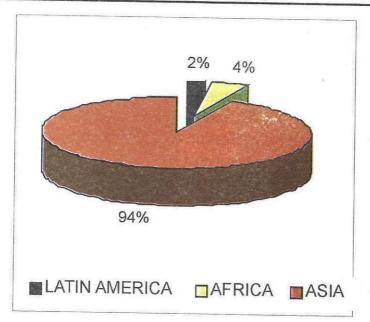


Figure 4a: Natural Rubber Production 2007

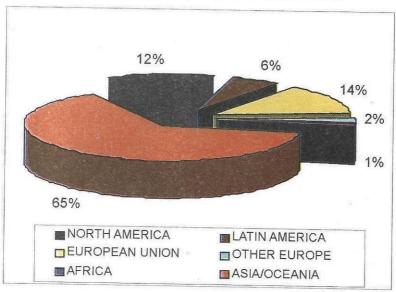


Figure 4b: Natural Rubber Consumption 2007

#### 2.4 Hevea Rubber Market and Applications

Natural rubber is a highly valuable biomaterial: in contrast with most other biopolymers it is essential for many applications and cannot be replaced by synthetic materials. For example, heavyduty tyres for trucks, buses, and airplanes, as well as many latex products for the medical profession (fig. 5), cannot be made with synthetic rubber, or only at great cost.

About 10% of the latex harvested from Hevea trees is manufactured into latex products. Latex films form an excellent barrier to pathogens, including viruses: condoms and gloves provide excellent protection from infection. This is largely due to the excellent film-forming nature of natural rubber latex. In this aspect, natural rubber latex is vastly superior to vinyl films and to most other competitive materials.



**Heavy Duty Tyre** 



Boots



Yoga Mat



**Baby Teeth (Feed)** 



Rubber Gloves & Syringe
Figure 5: Plastics Materials Derived from Natural Rubber

Natural rubber films are also very strong and are closely fitting (tactile performance is not impaired and may even be enhanced). Gloves made from this material protect both the wearer and the object (scientific samples, objects, drugs, foodstuffs, electronic components, etc) or the person being handled. The latex harvested from the tree is concentrated by centrifuging, removing some of the water and much of the proteins, and is preserved with ammonia. Products such as gloves and condoms are produced by dipping a porcelain or glass former into the latex. Usually, the latex is prevulcanized by mixing with sulphur and accelerators. In the subsequent steps, the coated former is dipped into a coagulant (typically calcium nitrate) to gel the latex, and then heated in a continuous oven, which dries and vulcanizes the latex films.

The remaining 90 % of latex is coagulated and converted into dry rubber. Usually smallholder rubber has been coagulated prior to sale, already in the tapping cup. The coagulated rubber is milled and washed to remove contaminants introduced by collection and transportation. Most of the natural rubber is dried by using fossil fuel, which, as a rule of thumb, consumes about a tenth of the fossil fuel required to produce synthetic rubbers. Rubber sheets can also be dried by solar heating.

Most of the dry natural rubber is used in tyres, especially those, which call for high performance, notably aircraft and truck tyres (more than 70 % in the USA). The ability of natural rubber to dissipate heat makes these tyres much safer than those made from synthetic rubber. The rapid economic development in Asia, especially in China (the world's largest rubber consumer imported 1.5 million tons in 2005) and India is resulting in strongly rising prices. According to the International Rubber Study Group (http://www.rubberstudy.com), the production deficit for 2006 was around 250,000 tons. After a low point in 2000, the price of natural

rubber has increased 5-fold to €2.30 per kg in June 2006. It then becomes extremely volatile, losing ground to €1.70 per kg in September 2006. An increasing oil price is likely to act in two directions: while it makes natural rubber a better competitor for synthetic rubber, it also reduces demand for natural rubber by the producers of heavy-duty tyres for aeroplanes and the car industry.

#### 2.5 Rubber Wood

An important side product of Hevea rubber production is rubberwood (Killmann, 2001), which was originally perceived merely as a useful by-product for drying and smoking rubber and to provide a source of charcoal for local cooking. Rubberwood can be easily steam-bent, or stained to resemble any other timber, depending on consumer demand. Its favourable qualities and light colour make it a good timber for furniture making and other applications. The natural colour of rubberwood is one of the principal reasons for its popularity in Japan, where it is increasingly used to replace more traditional timbers. In 1998, Malaysia exported rubberwood furniture with a value of \$ 683.3 million, and in general rubberwood is one of the most successful export timbers of Southeast Asia. Hevea is sometimes being grown primarily for timber harvesting, with the latex as a co-product.

## 2.6 Economic Threats to Natural Rubber Production from Hevea

Threats to natural rubber production from Hevea include competition for land by palm oil plantations: the palm oil acreage in Malaysia increased in only three decades from less than 100,000 hectares to almost 2,000,000 hectares, which is more than the rubber tree acreage. Together the two crops account for more than 70% of the total agricultural land use of that country. Similar developments are taking place in Thailand and Indonesia.

Strongly increasing labour costs are especially an issue in Malaysia, as latex harvesting is very labour-intensive, and the Malaysian economy is shifting to an industrial basis. As with all agricultural commodities the effects of climate change, pollution, economic development, and population growth are unpredictable Factors, which may induce major changes in available acreage, yield, and demand for natural rubber.

## 3.0 OUR CONTRIBUTIONS IN THE DEVELOPMENT OF NATURAL RUBBER PROCESSING TECHNOLOGY

#### 3.1 Study of the Effect of Local Materials used as Compounding Filers on Some Physical Properties of Vulcanised Natural Rubber

Natural rubber is a high molecular mass polymer. In its raw state, natural rubber is a tough material, which deforms easily and has little or no useful application. It crystallizes readily at low temperature below 0°C and become soft and sticky when warm (Lindley, 1992). On the other hand, processed natural rubber obtained by incorporation of various compounding agents has been used successfully in engineering applications, and remains the preeminent elastomer for springs and mountings. Hence the search for compounding ingredients such as reinforcing fibers and fillers to modify the physical properties of polymers continue to attract much attention; (Manson and Sperling, 1976 & Nielsen, 1974). There are various kinds of these compounding ingredients used today in the polymer industries.

The compounding agents used mostly in rubber include substances such as vulcanizing agents, sulphur, zinc oxide, carbon black, fibers, fillers, pigments, accelerators, antioxidants, blowing agents, etc, depending on the area of application intended for the

products. The main reason why so much emphasis has been placed on the development of modified polymeric based substances rather than the creation of new polymers is largely due to cost (Dyson, 1990). It is much easier to modify an existing elastomeric material than to create new one.

In this work, the comparative effects of various local and imported compounding materials, that is, sulphur and carbon black on some physical properties of vulcanized natural rubber has been reported (Ajayi et al 2001). The use of local raw materials in our industries is the thrust of Nigerian government today. The government has since recognized that the low pace of growth of the manufacturing sector is due to its dependence on foreign sources for raw materials and equipment inputs.

The activities and programmes of the Raw Materials Research and Development Council (RMRDC) have encouraged immensely the development of local resources of raw materials to substitute the imported ones (Okonkwo, 2000). It has been realized that most of these compounding ingredients can be sourced locally (Eperokum.1989).

The effectiveness of Local and imported materials on the physical properties on the vulcanized natural rubber were investigated and results compared, in table 3 (Ajayi et al 2001).

Table 3: Comparative Effects of Local and Imported Compounding Materials on the Physical Properties of Vulcanized Natural Rubber.

Parameter	Vulcanized Natural Rubber with		
	Local	Imported	
	materials	materials	
Modulus at 100% (Mpa)	4.06.	2.81	
Modulus at 300% (MPa)	16.85	13.85	
Elongation at Break (%)	900.10	460.50	
Tensile Strength (MPa)	31.04	24.13	
Resilence (%)	58.50	54.50	
Hysteresis (x10 <sup>-2</sup> per)	1.71	1.83	
Rubber Hardness (IRHD)	67.30	63.50	
Force of Punch (KN)	5.60	5.32	
Source: Ajai, et al (2001)			

From the results obtained it is pertinent to state that the properties of the locally available sulphur and carbon black compounding materials compared favourably with those of the imported ones. Therefore, the local fillers could be exploited and used as substitutes for imported ones. This will have great economic value and will save the nation's hard-earned foreign currency Normally used to import these materials.

#### 3.2 Preliminary Studies on the Effects of Concentration, Temperature and Diluents (Methanol) on the Viscometric Properties of Dilute Solution of Natural Rubber.

When a polymer dissolves in a liquid, the interaction of the two components results in increase in polymer dimensions over that in the unsolvated state. Because of the vast difference in size between the solvent and solute (the polymer molecules) the frictional properties of the solvent in the mixture are intrinsically altered and an increase in viscosity occurs which reflects the size and shape of the dissolved solute, even in dilute solution (Cowie, 1973).

Measurement of viscosity of polymer solution has become very important from academic and technical viewpoints. Apart from being a ready tool for characterization of polymers, the technique, because of its simplicity is often used in the investigation of interactions (compatibility) of dissimilar polymers (Dondos and Benoit, 1975; Bohmer Berek, and Florian, 1970 and Vasile and Schneider 1971). Besides, information derived from such studies is useful as a guide in quality control assurance of both components and final products (Goodwin, 1990).

There are many solvents that are used for different polymers depending on the polymer/solvent interaction parameters particularly the solubility parameters. Some common solvents include n-hexane, carbon tetrachloride, and 2-Butanone, for the polymers; polyethylene, polystyrene and poly (methyl methacrylate), respectively (Billmeyer, 1962). Availability and toxicity of the solvents however, are factors that can determine which solvent may be used for a particular polymer at a particular time. Each of the various solvents affects the flow properties of the corresponding polymer solutions differently. A "good" solvent, which is highly compatible with the polymer produces liquid-polymer

interaction resulting into the expansion of the polymer coil from its unperturbed dimensions in proportion to the extent of these interaction, whereas a "poor" solvent gives fewer interactions and molecular chain expansion is restricted (Billmeyer, 1962). Both types of solvents affect the viscosity of the solution differently with the good solvent producing higher solution viscosity than the poor solvent.

The viscosity of a liquid is a measure of the intensity of work done in maintaining the flow (irreversible deformations) of a liquid (Malkin, Askadsky and Kavriga, Chalykh, 1983). It is also referred to as a measure of a fluid resistance to flow. The greater the viscosity therefore, the more slowly the liquid flows (Chang, 2000). The effects of varying the concentration of natural rubber in petroleum spirit and temperature with and without diluents (MeOH) on the viscosity has been studied with a view to providing some insight into the characteristics of the local natural rubber, obtained from Benin city in Nigeria (Suleiman, et al 2003)

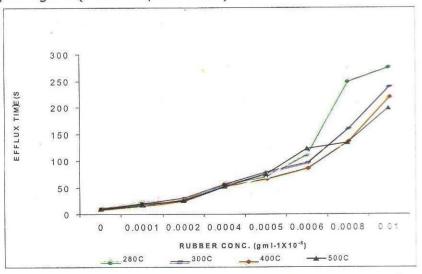


Figure 6: Effect of Varing Concentration and Temperature on the Viscosity of the Natural Rubber Solution

Plots of efflux time against concentration are shown in Figure 6. It is observed from the plots that increase in concentration result in increase in efflux time, which implies that the viscosity of the solution also increases with increasing concentration. This observation can be justified theoretically, in that increase in solution concentration yield more of the rubber molecules per unit volume than will be found with solutions of lower concentrations. Aggregates of rubber molecules in concentrated solutions tend to increase intermolecular associations resulting in corresponding increase in viscosity of the solution. This is evidenced by the fact that liquids with strong intermolecular forces have higher viscosities than those with weak intermolecular forces (Chang, 2000). Weak intermolecular forces are usually characteristic of very dilute solutions because molecules are usually far apart from one another. Also from fig. 6, it can be seen clearly that temperature is a critical factor to efflux time.

At 0.01 concentration level, the mean efflux times of 282.0, 245.0, 225.0 and 198 seconds were recorded for 28°C, 30°C, 40°C and 50°C respectively. This means that the efflux time reduces, in other words, the viscosity decreases in magnitude with increasing temperatures. This trend is in agreement with the observation by Chang, (2000). It is suggested that increase in temperature weakens intermolecular attractions: hence leads to decrease in efflux time, or decrease in viscosity correspondingly.

Suleiman et al. 2003 also studied the effect of addition of methanol (50%) on the viscosity of the various solutions at room temperature (28°C) and the results are shown in fig. 7. In earlier studies the effect of methanol (50%) on the viscosity of water-based coatings had been examined (Achi and Nwankwo 1994). It has been reported that a sharp change in viscosity occurred upon dilution with 50 percent alcohol at 80 percent solid content (Suleiman et. al 2003).

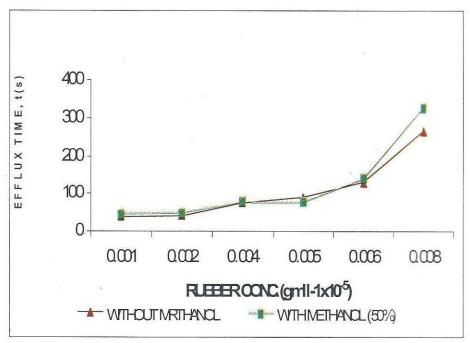


Figure 7: Effect of Methanol on the Efflux Time of the Rubber Solution

As seen from fig. 7, the efflux time for the solution of a given concentration in presence of 50 percent methanol is higher than the efflux time for the same solution in the absence of methanol. A key conclusion from this work is that methanol can act as diluents in both water-based and solvent-based coatings of Natural rubber dispersion. It is reasonable to state that besides concentration, and temperature of a natural rubber solution, use of additives, which have groups capable of engaging in specific interactions such as hydrogen bonding, can always modify the viscosity of natural rubber solution formulations, as observed with methanol in this work. An effective control of these parameters is therefore, going to be helpful in the development of dilute solution of natural rubber in coating applications. Since natural rubber is a readily available

and renewable resource material in Nigeria, studies such as this, which is aimed at discovering its potentials, should be considered as a worthwhile venture, which can attract some benefits to the national economy.

#### 3.3 Some Effects of Various Organic Compounds on the Tensile Strengths of the Peroxide Vulcanized Rubber Samples.

The formation of crystallites at room temperature in stretched rubber, vulcanized and unvulcanized has been the subject of considerable studies, Bakkedhal and Wood, (1954). The tendency of elastomers to crystallize on stretching is associated with the presence of nuclei acting as crystallization centres within the material. These crystallization centres are often introduced by chemical modification brought about by vulcanization or by incorporating similar impurities in the form of small particles into the rubber network. By controlling these nuclei centres, the network structure can be suitably modified and stress crystallization elastomers with very high tensile strength and tear strength can be obtained and polymeric materials of scientific and technological importance produced (Hammer et al 1959; Starkweather and Brooks, 1959). Many attempts have been made to improve some of these properties by controlling the amount of crystallization centres.

The relationship between the nucleates and the host polymers have not been fully understood (Cole and Pierve 1978) thus the selection of active materials as crystallization centres is usually empirical. Liquid crystalline materials are used as nucleating agents because of their ability to be oriented by various means while in mesophase structure and yield polymers with modified morphological structure of the mesophase (Perplies et al 1955, Blumstein et al 1975 and Strzelechi and Liebert 1973). In order to

understand the nucleating ability of liquid crystalline materials, Suleiman 1998, studied the crystallization effects of different organic compounds with structural similarity some capable of exhibiting liquid crystalline mesophase Lut others do not (table 4).

Table 4: Selected Compounds used as Nucleating Agents

COMPOUND	SIRICIURALFORMLAR	DELECTRIC (ANIISOTROPY) NEGATIVE	
Azoxyanisole	HCC N=N COH		
Azoxychenetole	HGO N=N OGH	NEGATIVE	
Azoxyphende	HD N=N CH	NEGATIVE	
1-n- xyloxycyarchiphenyl	HCON N=N CNCH	POTIVE	
oxybarære	O N=N	POTIIVE	

Table: 5 Effect of various organic compounds on the tensile strength of the peroxide vulcanized natural rubber samples.

Additives	% Update	Load at Break	Ultimate
		(Mpa)	Tensile Strength (Mpa)
4;4'-n-hexyloxy			And the second s
Cyanobiphenyl	0.9	47.0	4.0
P-Azoxyanisole	0.8	60.7	5.2
P-Azoxyphenetole	1.1	64.8	5.5
P-Azoxyphenol	3.0	54.0	4.5
Azoxybenzen	2.9	51.2	4.3
Control without	0.0	50.0	4.1
(Additive)		8	

Source: Suleiman, 1998

It can be seen from table 5 above that the liquid crystalline materials, that is, P-Azoxyanisole and P-Azoxyphenetole which has the ability to be oriented and in turn cause alignment of the molecular chains in natural rubber are more effective and give higher tensile strength materials. Other additives that are not liquid crystal, even at a higher uptake level recorded lower tensile strength.

Figure 8 shows the effect of varying temperature on the tensile strength of vulcanized natural rubber modified with and without P-Azoxyanisole. It is evidently clear that the tensile strength of the vulcanized natural rubber increases with increase in temperature until a peak is reached above which the strength decrease with further increase in temperature. This observation is similar in the modified and unmodified rubber samples but the effect is remarkably higher with the samples containing P-Azoxyanisole which is a liquid crystalline material.

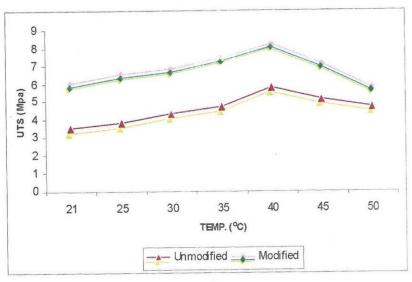


Figure 8: Effects of Varying Temperature on the Tensile Properties of Natural Rubber Containing P-Azoxyanisole

It has been reported by Suleiman 1998, that P- azoxyanisole a liquid crystalline material has remarkable effect on the properties of peroxide vulcanized natural rubber by accelerating the crystallization process presumably by promoting crystal nucleating centers on stretched peroxide vulcanized rubber samples. This observation is analogous to the well- known effects of foreign particles in stimulating the crystallization of super cooled liquids (Gent, 1954). Similar effects have been anticipated theoretically (Morgan, 1954) in the crystallization of long chain polymers. In this study it has been observed that the effects caused by different liquid crystals depend on the dielectric anisotropic characteristic of the additive.

#### 3.4 Physio-Chemical Properties of Blends of Poly (Vinylacetate) and Natural Rubber Latexes Tensile Strength Properties

The effects of blend compositions on both tensile strength and elongation at break for each of the pure PVAc and NR materials and of their blends were investigated by Suleiman and Ochigbo 2006

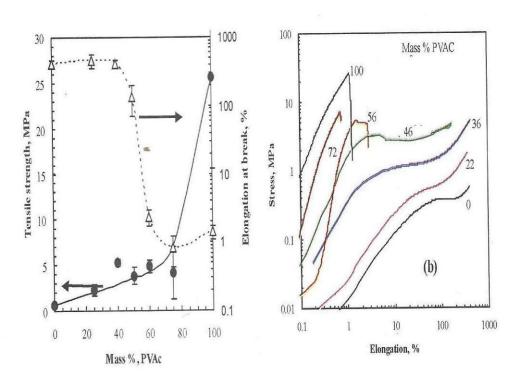


Fig. 9 (a): The Effect of PVAc Content on Tensile Strength and 10(b): Elongation-at Break;

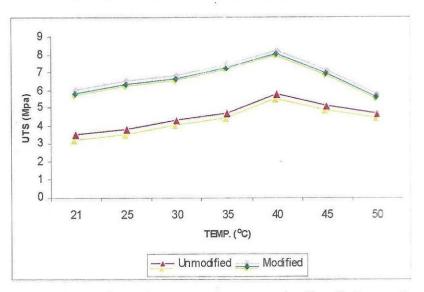


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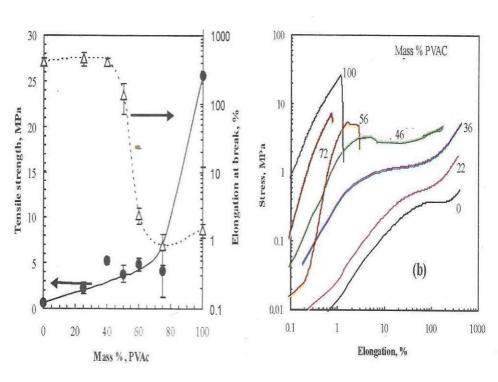


Fig. 9 (a): The Effect of PVAc Content on Tensile Strength and 10(b): Elongation-at Break;

It can be observed from Fig. 9(a) that the tensile strength increases exponentially with increase in concentration of PVAc. The elongation-at-break is high (> 600%) for all samples containing from 0 % to 46% PVAc. At 100% PVAc the elongation-at-break is a little just above 1%. Tensile strength on the other hand increases gradually with increase in concentration of PVAc until 72 % PVAc was reached, from which point a steep sharp increase was observed in the tensile strength behaviour. Consequently, pure PVAc is stiff and inflexible and gave the maximum tensile strength of 25 MPa. The pure NR (0% PVAc) gave the lowest value of tensile strength of 1MPa. These extreme behaviours of both pure PVAc and pure NR can also be justified theoretically. Given the chemical structure of the PVAc molecule, the alternate acetate groups on the chain impose steric hinderance to free movement of the molecules. Consequently, the polymer is stiff and brittle, (Jaffe et al, 1990). Under the same ambient conditions, NR on the other hand, which essentially is cis-polyisoprene, exists in a coiled conformation due to rotation about single bonds (Young, 1981). As rubber is subjected to stress, the molecules must uncoil, elongate and undergo alignment along the direction of the applied stress before manifesting stiffness character. Consequently, rubber has low tensile strength. According to Jaffe et al, 1990, the need for more flexible versions of PVAc has been realized, being especially required in packaging applications. This has resulted in either compounding PVAc with an external plasticizer or copolymerizing it with a suitable monomer. When plasticizer is externally used to obtain flexibility in a homopolymer, the effect is only temporary because of plasticizer migration, but when PVAc is flexibilized internally with a comonomer, the plasticization is permanent and nonmigratory. Suleiman and Ochigbo 2006 reported that similar level of flexibility into PVAc was also achieved by blending PVAc with NR. From Fig. 9 (b), it is clear that blends containing PVAc above 46 % PVAc behaved as stiff plastic, with elongation falling between 1 % and 2 %, while blends containing this level of PVAc content and below, showed stress/strain curves typical of elastomers. It is surprising that blends containing 22 % and 46 % PVAc demonstrated slightly higher level of percent elongation than 100% NR (i.e. PVAc 0). As there was no compatibility between the blends' components, it was assumed that these synergistic effects were due to the PVAc, acting as reinforcing filler to the rubber matrix. In order to check the reliability of this assumption, samples were prepared in which the natural rubber was filled with titanium dioxide, TiO, and carbon black to the same volume fraction filler (30 %) as the 36 % PVAc blend. From the results obtained (Fig. 9), it was observed that the two pigment-filled natural rubber samples showed similar stressextension behaviours. The stress curves were many folds higher than that of natural rubber at low extensions. However, at higher extensions they approached asymptotically the pattern shown by pure rubber. This contrasted with the performance of the natural rubber containing the same volume fraction of PVAc whose stressstrain curve was observed to lay some order of magnitude higher. These blends of PVAc/NR thus demonstrate significant tensile property improvement, and it is suggested that the observed behaviour points to semi-compatible blends (Fox and Allen, 1991).

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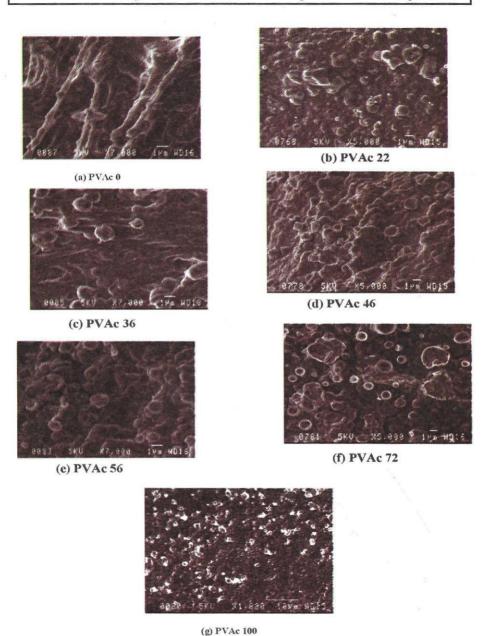


Fig. 10SEM of the Fractured Surfaces of PVAc/ $N_{\scriptscriptstyle R}$  Blends

As seen from the above fig. 10 (g), the SEM of the fractured surface of pure polyvinyl acetate (PVAc100) revealed a honeycomb-like morphology. The honeycomb structures seen might be due to imperfect coalescence of film particles during the curing period. This arises when the minimum film forming temperature is not completely reached in the curing process (Pizzi, 1983). The observed vesicular walls in this micrograph are assumed to be relics of the polyvinyl alcohol used as protective colloid in the PVAc emulsion.

Fig. 10 (a) represents the micrograph of the pure natural rubber sample with the elastic and the extended rod-like structures characteristic of typical elastomer molecule being clearly seen while, fig.10 (b-f) represent the micrographs for the blend systems. Each one of the latter actually represents a three-phase system, made up of the two-phase polyvinyl acetate emulsion/polyvinyl alcohol stabilizer systems and, the natural rubber latex particles. It appears that the original emulsion droplet dimensions determine the polyvinyl acetate domain size. This is not unusual in view of the immiscibility of the three polymers present; the higher consistency of the polyvinyl acetate, the low sharing mixing method that was employed in the blending process and the fact that, volumetrically the PVAc is the minor phase. Normally, the polymer present in the higher ratio would form a continuous phase while the one present in the lower ratio should appear as a discrete or discontinues phase. However, this is not observed as, for example, in the micrograph representing 72% PVAc, structures reminiscent of the parent emulsion droplets including the vesicular wall remains of the polyvinyl alcohol stabilizer used in the polyvinyl acetate emulsion are still clearly obvious. Fig 10c confirmed the earlier observation that the PVAc/NR blends at 36% PVAc show a significant effect on both tensile strength and elongation observed can be attributed to the PVAc acting as reinforcing filles to the rubber matrix. It was, therefore, reasonable to conclude that all the blends examined were actually in each case a three-phase system and each contributes positively on the physical properties of the blends.

# 3.5 Relationship between Rubber Particle Morphology and Crack Tip Craze Behaviour of High Impact Polystyrene (Hips).

Improvement in the mechanical properties of rubber toughened polymers such as high impact polystyrene (HIPS), and rubber toughened poly (methyl methacrylate) (RTPMMA), has stimulated considerable interest in the engineering and technological applications of these materials. It is therefore very important to investigate the role of incorporated rubbery particles in order to further our knowledge and increase our understanding of the toughening mechanisms of these materials.

Suleiman et al, 1990, has established that the significance of dispersed rubber particles is to enhance the strain energy dissipation so that the stress transmitted to the crack tip is greatly reduced and typical catastrophic failure associated with unmodified parent matrix polymers avoided. Energy absorption takes place near the particlematrix interface where the stress concentration is highest, about 1.9 to 3.05 MPa for HIPS materials. The presence of rubbery particles promotes the initiation and growth of crazes and/or shear bands which are the primary means of energy dissipation in the rubber toughened polymers. Thus the strain energy required for breaking toughened polymers is appreciably higher than that responsible for breaking unmodified materials tested under the same conditions (Suleiman et al 2006). High impact strength polystyrene, samples containing rubber particles of various sizes and morphologies as shown in Table 6 below were used to investigate the effect of rubber particles on the mechanical properties of the toughened polystrgrene materials.

Table 6: Showing Rubber Particles Morphologies and Particle Sizes

Material	А	В	С	D	Е
Rubber	MI	DCS 3	SCS	MI ·	MI
Particles					
morphology	<b>®</b>	0	0	000	00000
Particle Size	0.4	0.3	0.4	1.6	1.8
(µm)					4

Source:Suleiman et al 2006

**KEY:**MI = Multiple inclusion, SCS Single Core shell, and DCS Double Core shell.

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Particle Size (µm)	0.4	0.3	0.4	1.6	1.8

Source:Suleiman et al 2006

**KEY:**MI = Multiple inclusion, SCS Single Core shell, and DCS Double Core shell.

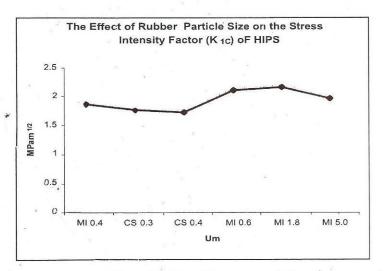


Figure 11:The Effect of Rubber Particle Size on the Stress Intensity Factor  $(K_{1c})$  of HIPS

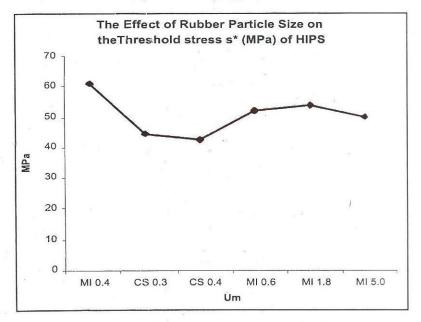


Figure 12:The Effect of Rubber Particle Size on the Threshold Stress O\* (MP<sub>4</sub>) of HIPS

Figures 11 and 12 show the effects of rubber particles size on the stress intensity factor (K,c) and threshold stress (O\*) of rubber toughened polystyrene materials (HIPS)- respectively. evidenced from Fig 11 that increase in rubber particle size lead to increase in stress intensity factor. However, the multiple inclusion particles (Mi) tend to have higher K<sub>1</sub>c values than those having core shell particle structures (CS). This observation is further illustrated in Fig. 12 where the CS particles has lower threshold stress  $(\sigma^*)$ values as compared to those containing Mi particles. Perhaps this particle morphology effect can be better demonstrated by making a relative comparison between the samples A (Mi) and C (DCS) each having the same particles size of 0.4Nm but different morphologies. It has been observed that samples A having Mi particles morphology has both higher K1c and  $O^*$  values than that found in sample C with These remarkable variations in the CS particle structure. mechanical properties between the behaviors of the two different rubber particles morphologies can be better understood by the two effects exhibited by the Mi particles: (i) stress enhancement at a particle is decreased, thus O\* is increased and the probability of damage initiation at a given applied stress is decreased and (2) damages that are initiated are more efficient in dissipating mechanical energy and bearing load without failing (Suleiman et al 1990).

The study leads to the following general conclusions: (Suleiman 1990 and Suleiman et al 2006).

 The stress intensity factor K<sub>i</sub> can be related at any time to the size of the damaged zone through a fundamental material property: the damage initiation thereshold, stress σ\*, which is proportional to the yield stress in materials with high particle volume fractions.

- At 17% rubber particle volume fraction, the HIPS samples containing CS particles has lower ó\* values than those containing stiffer MI particles, which are less efficient in concentrating stresses. This means that damaged zones are smaller in MI HIPS than in CS HIPS.
- 3. Despite of the differences mentioned above, the toughness is identical in both MI and CS HIPS at low rates. As a matter of fact, MI particles initiate higher densities of damages than CS particles. This morphological effect is due to the inhomogeneous internal structure of MI particles, as opposed to the spherical symmetry of CS particles.
- 4. An optimum particle size exists where the fracture toughness is maximum. The reason for the existence of this critical particle size is yet to be elucidated. It is likely to be connected with a critical size for damages which are more likely to fail when they grow in size. Bucknall et al, 1986 also proposed similar explanation based on the kinetics of crazing.
- The influences of particle size and internal morphology are difficult to separate even at a given particle volume fraction because of their interdependency.

# 3.6 Optical Interferometer Study of Crack-Tip Craze of Toughened Polystyrene

Deformation zone of a brittle transparent plastic constitutes mainly of either isolated crazes or a craze at a moving crack-tip. These crazes are formed resulting from the effects of stress concentration in front of the crack-tip. The molecular chains of the polymer are drawn out of their amorphous arrangement in the bulk material into bundles under the action of the principal tensile stress component acting normal to the crack plane. Crazing as a normal

yielding phenomenon thus differs significantly from conventional plasticity in the other materials where it is essentially a volume-conserving shear phenomenon (Beahan et al 1976).

Owing to their structure, crazes have a lower specific gravity and a lower refractive index than the bulk polymer. Thus it is possible to measure their sizes and shapes using optical interference provided that:

- the separations involved are comparable and in order of magnitude to the wave length of light.
- ii. the refractive index of the craze is significantly different from that of the bulk material.
- iii. the boundary between the two regions is sharp, and
- iv. the material is transparent.

The pioneering works of Kambour, (1973) and Bessenov and Kuvshinskii, (1961) have led to a significant development in the optical interference method which is now widely used to determine characteristic craze dimensions and critical displacements at the crack-tip before and during polymer deformation processes. The ability of the molecular chains at the crack-tip to resist the applied stress is determined by both the maximum length of the stretched molecular bundles and the maximum bearing load which the bundles can sustain.

Similarly the plastic zone models derived by both Dugdale, (1960) and Bavenblatt, 1962) show that quantitative information on the craze stress can be derived from measurement of optical interference patterns. Hence, the connection with fracture mechanics has made the optical interference method a powerful

technique in the determination of those properties of materials in the micro region around the crack-tip which directly relate to the fracture or deformation process (Brown and Ward 1973, Vavakin et al 1976 and Weidmann and Doll 1976).

Suleiman et al 1990 assessed the role of various rubber particle morphologies in a toughened polystyrene material on the stress dissipation mechanism in front of crack-tip craze deformation process, using optical interference technique developed locally.

The optical interferometry observations Figs 13 and 14 and additional revelations by the SEM patterns, Fig 15 and 16 suggest that the fundamental toughening mechanisms in rubber particle toughened polystyrene material are highly influenced by the particle size and most especially by the particle morphology, which of course is also a basic function of size. The crack-tip crazes are able to absorb small particles and are noticed mainly by the markings on the fracture surface as revealed by SEM. The increase in stress intensity factor, K<sub>1</sub>, with increase in crack-tip craze formation is observed in both polytyrene material toughened with rubber particles having either CS or Mi morphology. However, the Mi particles than with the CS particles as clearly revealed by the interferanetry photographs in figures 13 and 14.



Fig 13: Showing Movement of Crazes Infront of Crack Tip of a High Impact polystyrene Containing CS Rubber Particle

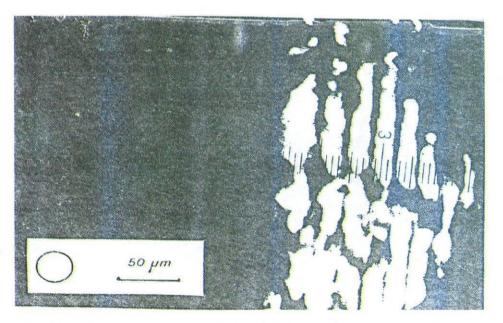


Fig 14: Showing Movement of Crazes Infront of Crack Tip of a Impact Polystyrene Containing Mi Rubber Particle.

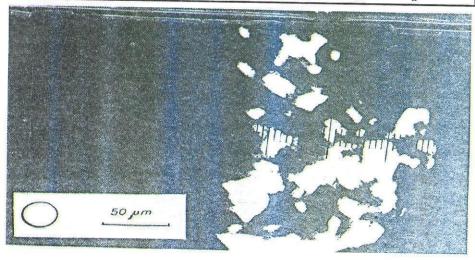


Fig 13: Showing Movement of Crazes Infront of Crack Tip of a High Impact polystyrene Containing CS Rubber Particle

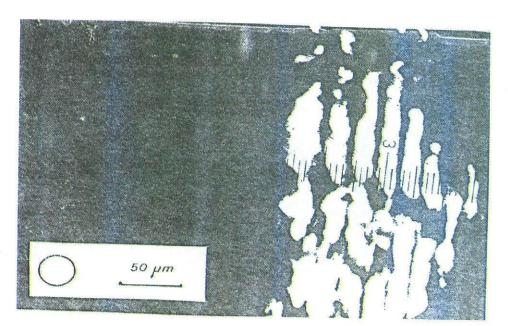


Fig 14: Showing Movement of Crazes Infront of Crack Tip of a Impact Polystyrene Containing Mi Rubber Particle.

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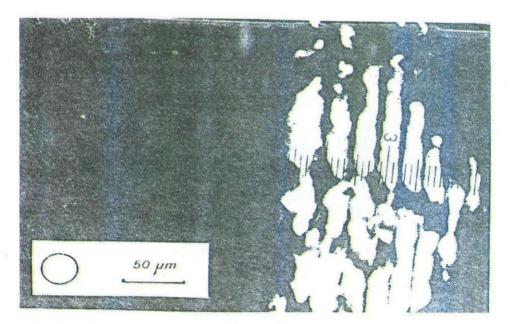


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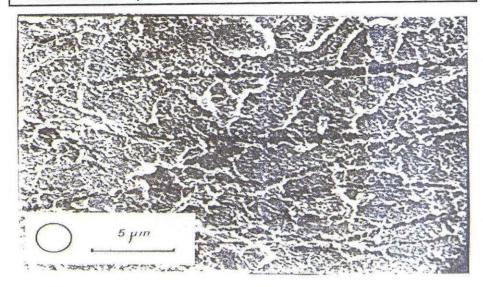


Fig: 15 SEM of Fractured Surface of High Impact Strength Polystyrene Sample Containing CS Rubber Particle Fig 17a:

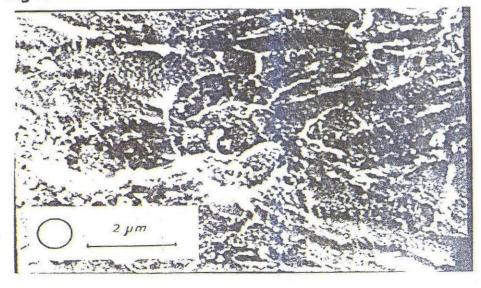
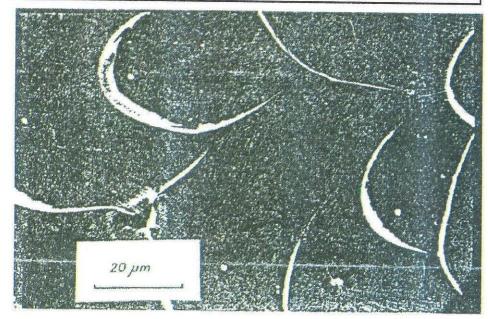


Fig: 16 SEM of Fractured Surface of High Impact Polystyrene Sample Containing Mi Rubber Particle.

SEM examinations of the damaged zones of the rubber particles toughened polystyrenes give typical effects as shown in figures 17a and 17b respectively. The CS particle has the ability to initiate single and continuous crazes which appeared to be very difficult to arrest. Whereas the Mi particles tend to be more effective in initiating short and multiple crazes by deforming inhomogeneously with evidence of internal cavitations. It has also been observed that both the Mi and CS particles still show some elements of satisfactory interfusions adhesion by remaining fairly bonded to the matrix by few ligaments. From the foregoing observations, it is evidenced enough to state that the fundamental toughening mechanisms in HIPS materials are highly influenced by the rubber particle size and most especially by the rubber particle internal morphology. The differences observed in the craze length can be associated with transition from a single craze in the case of CS particles to that of a bundle of crazes as with MI particles (Suleiman and Mann, 2000). In general therefore, optical interferometry technique has been found to be adequate in studying basic phenomenological changes of transparent plastic materials. This is more advantageous where guick and meaningful results are required for further understanding of the toughening mechanisms in plastic materials undergoing deformation process under cyclic loading.



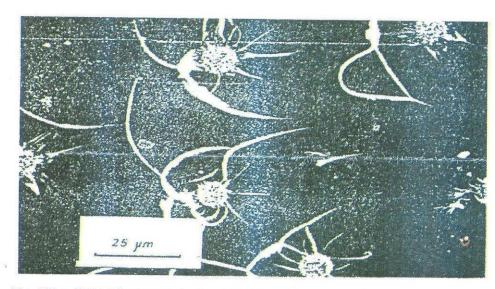


Fig 17b: SEM Photography's of Rubber Toughened polystyrene Damage Zones Showing (CS) and (Mi) Rubber Particles Fig 17a and b respectively.

# 3.7 Predictive Micro Mechanism Theories of Toughening Rubber Particle Polymer Multiphase Systems

Various SEM micrographs of the fractured surfaces of rubber toughened polystyrene and their subsequent image analysis has been examined by Suleiman, 1999. The interpretation of the results obtained lead to proposing different toughening micro-mechanisms prevailing in plastic deformation processes. It was assumed that damages in HIPS consisted of crazes initiated in the matrix near the rubber particles. In all four types of micro-mechanisms can be advanced as follows; (Suleiman, 1999).

#### Mechanisms:

### 1. Effective particle size

Isolated particles with sizes 1.0mm and volume fraction less that 5-10% are too small and rigid to initiate damages and are absorbed by the crack-tip craze thickness. The resulting effects on toughness are much similar and not very different from the case of unmodified polymer matrix. Thus a critical or optimum rubber particle size exist in the case of HIPS for significance effect on toughness to be observed.

# 2. Craze Branching

Smaller particles less than crack-tip craze thickness (about 0.2µm although unable to initiate damages, the crack-tip craze cannot slip between them. This can result into craze branching and causing crack-tip blunting. Clearly the rubber particles size of about 0.2µm seems not to have any significant effect on the toughness. This may be due to an apparent increase of the modulus of the rubber particle modified samples under the testing conditions resulting into clean single crazes at the crack-tip similar to those obtained in pure polystyrene.

#### 3. Influence of Particle Structure

Big multiple inclusion (MI) particles deform inhomogeneously and can initiate more than one craze each, whereas small and homogeneous CS particles initiate one craze only. The larger MI particles act as more favorable sites for craze initiation, and have themselves undergone large deformations with the generation of internal voids and fibrillation of the craze. This enhanced behavior can be adequately associated with the ability of the MI particles to stretch and extend up to about 500% over its original dimension and thus tend to absorb more deformation energy over that of CS particles.

## 4. Influence of particles/matrix adhesion

Adhesion between particle and matrix determine the extent of void formation and internal cavitations. Good adhesions are characterized by strong ligaments between the particle and matrix. This type of linkage can enhance craze initiation and propagation resulting into a lot of internal cavitations and larger volume of damage regions. In this way better energy dissipating can occur within a large area in the multiphase system and preventing catastrophic failure as often obtained in a pure polymer matrix. The particles remain fairly stable and tend to split into several branches. In the case of poor adhesion these particles tend to pull out towards the crack-tip craze under the action of the strong gradient of dilatational stress. Here the smaller particles tend to initiate only large craze and inability to terminate its growth. Thus the low deformation energy and catastropheric failure associated with polymers modified with CS particles is a factor of the particle morphology which in turn depends on the internal structure.

In general the micro-mechanisms in toughing of rubber modified polymers can be said to be rather complex. However, the nature of interfacial bond between matrix and particles and the particle morphology are of crucial importance. Suleiman (1990), reported that interphase between the matrix and rubber contributes to the areas of defects and acting as active sites from which failure almost begins. The rate of craze and crack growth depends strongly on the degree of microscopic inhomogeneity which characterizes the region surrounding the particle.

A strong interface can first subject the applied stress to the matrix and enhance crazing and then help share with matrix crazing; a weak interface will tend to permit easy cavitations at the interface rather than crazing in the matrix, and would be expected to lower the fracture-energy. In addition an ill defined boundary may serve to blunt or slow down growing cracks more effectively; in general, the fracture path tends to proceed through the interfacial region. Thus the role of the rubber interphase is to protect the main inclusion from the effect of the stress waves developed due to the crack propagation process. The degree of protection depends on the quality of adhesion and the degree of capability of the constituent materials.

Attempt has been made to model the toughening mechanisms of rubber particle modified polymer materials on the particle morphology and interfacial bonding. That is the mechanisms where particle debounding or cavitations relieves the negative pressure and promote craze initiation and propagation. These effects are in turn interdependent on rubber particles size.

#### 4.0 CONCLUSION

The plastics derived from natural rubber constitute an important sector of economy and requires necessary attention in terms of building the foundation for the achievement of self-sufficiency in local raw natural rubber production and processing to various products. If this sector of economy is given adequate attention desired Nigeria stand to benefit enormously from reducing dependency on importation of raw rubber materials from abroad. It will also create employment opportunity to teaming unemployed youth and preserve our natural environment which has been seriously under threat.

The critical raw material required for natural rubber based plastics are obtained from the natural rubber tree grown in tropical areas including Brazil, Malaysia, Indonesia, India and Nigeria. There is an obvious need for increasing and sustaining the local production and supply of this basic natural raw material if the rubber plastic industry is to survive. Significant achievement can be made if government can encourage the plantation and conservation of natural rubber trees in Nigeria.

Nigeria has the potentials to achieve self-sufficiency in latex and crumb rubber production. Although the country is presently exporting the raw materials, its economic potentials has not fully been exploited for the local production and processing of these rubber into useful products. Considerable efforts have been made to sustain locally production of rubber latex in Nigeria but this fall short of satisfying both local and export demands hence importation of basic rubber materials are still being done at high cost to the nation. Government must come out with deliberate policy to support the production of natural rubber latex and reduce importation of these commodities.

In order to achieve these noble objectives there will be need to boost rubber production by establishing more rubber plantations and close monitoring of the production process. Public Private Partnership linkages to develop the rubber sub-sector should be encouraged and promoted. A target must be set to attain level of sustainable rubber production and reduce dependence on imported raw materials. If all necessary support and policies are correctly put in place Nigeria should be able to provide adequate latex materials, for domestic and industrial applications to produce finished plastic goods and still export for foreign currency by the year 2020 the Nigerian dream year for technological development and advancement attainment among the top industrialized Nations.

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I have tried to put across my thoughts, ideas, research trials, observations and suggestions towards harnessing the potentials of natural rubber in Nigeria for sustainable economic development. My contributions are just a scratch at the tip of the ice berg generating further interest on the topic.

Ladies and Gentlemen, I will conclude by saying thank you and may Allah reward you all for listening patiently to my lecture.

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