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NIGERIA**

**THE ONE HUNDRED AND TWENTY-FIFTH (125TH)
INAUGURAL LECTURE**

“MY ADVENTURE WITH POLYMERS”

BY

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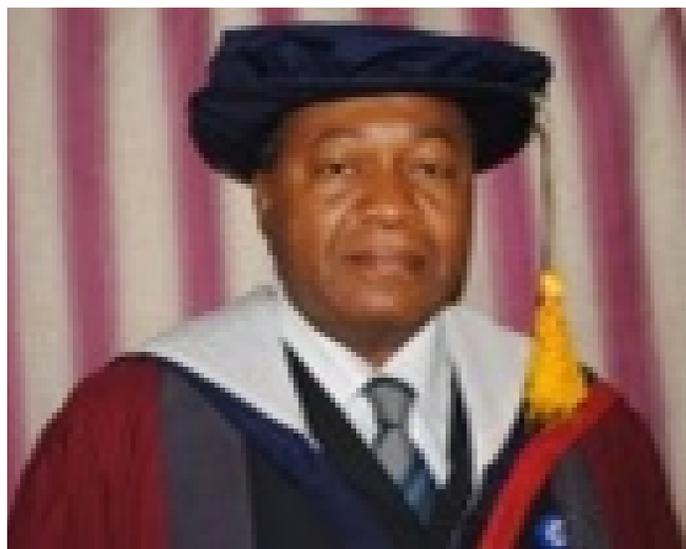
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Distinguished invited guests,
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Students of the University of Ilorin,
Ladies and gentlemen:

Preamble

I give glory to God for the opportunity that I have to deliver this lecture today and I am delighted to welcome you all to the 125th inaugural lecture of the University of Ilorin. Although I had my basic undergraduate training in chemical engineering, I spent about nineteen years working in the department of chemistry. Thus, my interest veered towards industrial chemistry with emphasis on polymers. In many areas of research, it is always difficult to delineate the boundaries of disciplines as there will be some form of convergence at a particular stage: e.g. in areas of physics and branches of engineering. Similarly, there are many areas of convergence in chemistry and chemical

engineering and it may not be surprising that similar researches may be carried out in both departments. In addition, many aspects of polymers are better understood using a multidisciplinary approach. Even in other areas of research, multidisciplinary approach to problems is fast gaining ground.

If I had remained in the department of chemistry, this lecture would have been the third inaugural lecture in industrial chemistry; the first inaugural lecture in industrial chemistry was delivered by Prof Fagbule on 15th December, 1988 while the second inaugural lecture in industrial chemistry was delivered by Prof S.A. Abdulkareem on 10th May 2007. However, being one of the pioneer staff of the relatively young department of chemical engineering, I feel honoured to deliver the first inaugural lecture from this new department and the lecture will describe my adventure with polymers.

Definitions

Some technical terms will be defined as I am aware that some members of the audience are neither chemists nor chemical engineers.

- Polymer: The name polymer is used to describe organic substances consisting of large long-chain molecules that are formed from the covalent combination of small repeat units or molecules. It must be noted that inorganic polymers have also gained prominence.
- Monomer: This is the starting unit of all polymers; a monomer may be described as a small molecule which under suitable conditions of temperature, pressure and catalyst or any combination of these, combines with itself or another type to form a larger

molecule called a polymer molecule. E.g. ethylene is the starting unit of polyethylene. $n\text{CH}_2=\text{CH}_2 \rightarrow -(\text{CH}_2-\text{CH}_2)_n-$

- Polymerization: The process by which monomers join or link together to form large molecules (polymers) is called polymerization. The polymer formed may be linear, branched or network. Also, polymerization requires that each monomer be at least difunctional. A functional group is a particular atom or group of atoms which is capable of being characterized by distinctive chemical reactions.
- Homopolymer is a polymer formed from only one monomer.
- Copolymer is a polymer formed from two monomer species.
- Terpolymer is a polymer formed from three monomer species.
- Degree of polymerization is the number of times a monomer unit repeats itself in one chain of polymer molecule.
- A crosslink is a chemical bond between polymer chains other than at the ends.
- Resin is a term previously used for certain naturally-occurring exudates from trees which are used as hard protective coatings but is now used to refer to synthetic polymers as well.

Other common definitions are available in standard textbooks (Allcock, Lampe and Mark, 2003; Billmeyer, 1984; Cowie, 1973; Flory, 1953)

Historical Background

In the account of creation in the Holy Bible, God created plants and He created living beings and animals

(Genesis 1:9-26). Advances in science have since revealed that plants contain carbohydrates while living beings contain protein; both carbohydrates and protein are polymeric. Also, the basket that was used to lower Moses in River Nile was reported to have been coated with tar and pitch which are both polymeric (Exodus 2:1-3). From the foregoing, we may say that polymers have existed since the beginning of time. Although, there had been reports of the existence and use of naturally-occurring polymers from earlier times, polymers were not properly understood. In the 1830's, Henri Braconnot, Christian Schonben and others modified the natural polymer cellulose to obtain celluloid and cellulose acetate (Greenway et al., 1978). Many scientists/inventors modified natural polymers without understanding the underlying science. For instance, it was speculated in some quarters that hard rubber might have been produced accidentally by Bergius in Stockholm (Porrit and Rogers, 1924; Memler, 1934) prior to 1791. By 1832, F. Ludersdorff in Germany had noticed that rubber when dissolved in turpentine and heated with sulphur lost its stickiness and exhibited better stability (Memler, 1934). Similar observations were made by Van Guens in Holland and Nathaniel Hayward in the US but none of those workers recognised the significance of their discoveries and did not attach any practical value to them. Further attempt at modifying natural rubber was made by Charles Goodyear in about 1831 but it was not until 1839 that he discovered that a mixture of rubber, sulphur and lead oxide heated at elevated temperatures gave a product distinctly superior to the raw material both in mechanical properties and in resistance to change of temperature. He did not patent this discovery until 1844 (Stern; 1945, 1967). Also, Thomas Hancock in England was awarded a patent in

1843 for demonstrating that sulphur alone would vulcanize natural rubber.

In continuation of his work, Charles Goodyear in 1851 obtained ebonite by heating natural rubber with excess sulphur. It can be said that his work laid the foundation for the development of thermosetting plastics. The ability of formaldehyde to form resinous materials was reported in 1859 by Butlerov while Adolf Bayer also reported the formation of resin from phenol and formaldehyde in 1872. Around the 1860's, Thomas Graham suggested erroneously that cellulose and other polymers were colloids or aggregates molecules with small molecular mass (Greenaway et al, 1978).

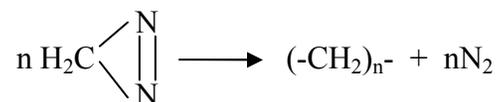
Alexander Parkes made the first attempt to produce plastics commercially in 1862 when he displayed articles moulded from a mixture of cellulose nitrate and castor oil - essentially his process involved a chemical modification of a naturally-occurring polymer to obtain a thermoplastic material. In 1866, Bertholet in France reported that when styrene was heated at 200°C, a resinous material was formed. In 1869, Daniel Spill formed a company to process materials similar to that of Parkes. Later in 1870 John Wesley Hyatt took out a U. S. patent where he used camphor instead of castor oil to plasticise cellulose nitrate, thus producing celluloid (Brydson, 1975). There are reports that synthetic polyisoprene rubber was first synthesized by Bouchardat in 1879 while Friz Hofmann in Germany polymerized 2,3-dimethylbuta-1,3-diene in 1909.(Morton, 1978)

The manufacture of casein formaldehyde was described in a patent issued to Krische and Spitteler in 1897. Arthur Smith also took out a British Patent in 1899 where he described the use of phenol-aldehyde resins as an

ebonite substitute in electrical insulation. Further developments on phenolics were made in 1907 when a Belgian chemist, Leo Baekeland filed his first patent for phenol formaldehyde (called Bakelite); this led to the formation of General Bakelite Company in the U. S. in 1910 (Baekeland, 1909). After the production of Bakelite, urea formaldehyde was synthesised by Hans John in 1918.

Contributions to the development of polymers were not limited to Western Europe and the U. S. A. In about 1912, a Russian Scientist, I. I. Ostromilensky reported the polymerisation of vinyl chloride to obtain poly (vinyl chloride) (PVC); the monomer used, (vinyl chloride) in the process was discovered by von Liebig in 1835. The development of PVC was however held back for about two decades because of thermal degradation at processing temperature. Continued research and development efforts on the stability of PVC have today made it one of the most widely-used plastic materials (Brydson, 1975; Greenaway et al, 1978)

Later in 1930, I. G. Farben in Germany produced polystyrene. Further progress was made on other plastic materials in 1931 by R. O. Gibson, J. S. Swallow and E. W. Fawcett of Imperial Chemicals Industries Limited (I.C.I), England. These workers were investigating the effect of high pressures on organic systems. They noticed that in one of the experiments in which ethylene was being used, a small amount of waxy solid had been formed. This white waxy solid was analysed to be polyethylene while a small amount of oxygen that leaked into the reactor acted as a catalyst (Cowie,1973). There are claims however, that polyethylene was prepared prior to 1900 by the decomposition of diazomethane (Pritchard, 1981):



The storage of diazomethane in ether solution over pieces of unglazed china produced a polymeric powder containing repeating methylene units (Pritchard,1981). This notwithstanding, polyethylene became an important commercial product as a result of fundamental studies undertaken by I. C. I. Polyethylene was found to have many useful properties and this prompted further studies into its nature. The first plant for producing polyethylene came on stream on 1st September, 1939.

Other research workers at I. C. I. laboratories such as R. Hill and J. W. C. Crawford made notable contribution to the range of plastic materials available. They developed poly(methyl methacrylate) in the 1930's and this was marketed as Perspex. Perspex was especially found useful in aircraft glazing during the Second World War because of its transparency and weathering resistance. Another contribution was made by W. H. Carothers who made nylon as a fibre in 1934 and published papers on condensation polymerisation. This was followed by the synthesis of polyurethanes by Bayer in 1937 and the commercial production of melamine formaldehyde in 1940. In 1941, R. J. Plunkett discovered polytetrafluoroethylene and also, nylon was used as a moulding powder in the same year; Plunkett's process was later developed commercially by E. I. du Pont de Nemours and Company, U. S. A.(Brydson, 1975).

At the end of the Second World War, there was a phenomenal growth of polymer materials. Karl Ziegler in Germany in 1953 used a combination of a transition metal

salt - titanium tetrachloride (TiCl_4) and a metal alkyl, triethylaluminium ($\text{Al}(\text{C}_2\text{H}_5)_3$) to polymerize ethylene under low pressure while in 1954, Giulio Natta in Italy used Ziegler catalysts to obtain isotactic polypropylene. Consequently, various grades of polyethylene, polystyrene, polypropylene and poly (vinyl chloride) were produced on a large scale and low cost which made them cheaply available.

Since the 1950's many variants of the older and established plastics have been developed while speciality plastics with more durable properties are continually being introduced into the market. Also, the Second World War and its end brought about a massive production of different types of synthetic rubber. For those who may be interested, the historical development of polymer science is available in Professor Flory's book (Flory, 1953)

Polymers in modern life

Properties of polymers such as resistance to chemicals, lightness in weight, ease of fabrication and low cost have made them attractive as alternative to metals. In addition, they can be produced in a wide variety of colours. Synthetic polymers, which are predominant, derive mainly from oil-based products.

The importance of polymers could be further appreciated when their numerous uses are considered. Such uses are found in packaging, building, piping and drainage, automobiles, house wares and a host of other uses which are too many to list. Many components of the modern automobile and commercial aircraft are constructed from polymer composites and are run on tyres which are made from rubbers. Paints and coatings are widely used to decorate buildings and are used to protect iron from

corrosion. With the supply of cheap petroleum feedstock and the recycling of polymer scraps, it is anticipated that the production and consequent use of polymer materials will become increasingly important in modern living.

Table 1: Examples of some polymer materials and their uses

<u>Commodity Plastics</u>	<u>Abbreviation</u>	<u>Uses</u>
Polyethylene	PE	Films, sheet ,packaging, electrical insulation, toys, domestic house wares, bottles, containers, pipes and fittings e.t.c
Polypropylene	PP	Carpets, ropes, rugs, hospital sterilisable equipment, luggage, stacking chairs
Polystyrene	PS	House wares, toys, packaging, combs, plastic forks, e.t.c.
Poly(vinyl chloride)	PVC	Films, sheet, floor tiles, pipes and fittings, calendared products
<u>Engineering polymers</u>		
Polyamides	PA	Textiles for clothing, carpets, ropes, tyre cords, bearing.
Poly (ethylene terephthalate)	PET	Bottle for carbonated drinks and water, textiles
Polycarbonate	PC	Electrical and telecommunication, glazing and sheet products, for producing compact discs e.t.c.
Poly(tetrafluoroethylene)	PTFE	Bearings, gears, non-stick coatings, e.t.c

Poly(ether ether ketone)	PEEK	Bearings, piston parts, pumps, e.t.c
<u>Thermosets</u>		
Phenol formaldehyde	PF	Adhesives, knobs and handles
Urea formaldehyde	UF	Adhesives, domestic plugs and switches, electrical fittings
Polyurethane	PU	Foam, shoe soles, coatings, adhesives, fibres e.t.c.
<u>Rubbers/Elastomers</u>		
Natural rubber	NR	Tyres, foot wear and shoe, adhesives, latex products and general rubber goods
Styrene-butadiene rubber	SBR	Tyres, wire and cable, hose, tubes, adhesives, latex products, footwear and general rubber goods.
Nitrile rubber	NBR	Oil seals, O-rings, automotive transmission belts, adhesives, gloves for the healthcare industry
Polybutadiene	BR	Tyres, cable, hose, adhesives, latex products footwear and general rubber goods.
Butyl rubber	IIR	Inner tubes, tyre inner liners, automotive suspension bumpers e.t.c.
Polychloroprene	CR	Adhesives, transmission belts, conveyor belts, profiles e.t.c.

Classification of Polymers

Different yardsticks can be used to classify polymers. Some of these polymers are naturally-occurring e.g. polysaccharides such as starch are found in most of our staple foods; cellulose in the form of cotton is used for clothing; also, cellulose in the form of wood is used for shelter or as fuel. Thus, polymers may be classified according to the basis of origin, method of synthesis, physical properties and/or end use. Also, classification of polymers can be on the basis of chain structure, thermal behaviour, monomer composition, chain configuration and polymerization mechanism (Challa, 1993).

Classification by origin

On the basis of origin, polymers may be classified as (a) synthetic organic polymers (b) biopolymers (c) modified polymers (d) inorganic polymers.

Synthetic organic polymers are man-made and constitute the bulk of polymers or macromolecules. They are simply referred to as polymers. Biopolymers, which are naturally-occurring, include protein, polynucleotides, polysaccharides (cellulose, glycogen and starch), wool, silk, natural rubber and several gums. Modified polymers are products of chemical reactions applied to polymers or biopolymers. Examples of modified polymers are esters or ethers of cellulose and vulcanized natural rubber.

Inorganic polymers can be defined as polymers having other atoms than carbon, oxygen and nitrogen in their main chain. In this group are polymers in which organic substituents are placed on inorganic chains e.g. poly (dimethylsiloxane). Some others are completely inorganic and they are based on silicon-nitrogen,

phosphorus-nitrogen or boron-nitrogen chains. (Challa, 1993; Rahimi, 2004)

Classification by chain structure

Some polymers contain linear chains, some contain branched chains, and some contain networks while some are ladder polymers. Asbestos is a typical inorganic ladder polymer.

Classification by thermal behaviour

On the basis of their response to heat, polymers can be further classified as either thermoplastics or thermosets.

Thermoplastics can be repeatedly softened by heating and hardened by cooling. On heating, they become soft and fluid and can be transformed into any desired shape which solidifies on cooling. Because this cycle can be repeated indefinitely, it is possible to recycle thermoplastic articles. There is no chemical crosslink or reaction during or after processing. Changes brought about by heating are physical rather than chemical.

A thermoset polymer is capable of undergoing or has undergone a chemical reaction by the action of heat, ultraviolet light etc. to produce a relatively infusible material. They are prepared from resins which consist of a mixture of reactive, low molar mass compounds. On heating thermoset resins, they transform from a fluid into a three-dimensional, network material owing to crosslinking. In essence, a cured thermoset is highly crosslinked and can no longer be softened by heat; and so cannot be recycled. For example, natural rubber and synthetic elastomers are thermoplastic in the raw state. On curing however, they become thermosetting. As a consequence of the crosslinks introduced, vulcanized rubber cannot be melted and will

not dissolve in any solvent; vulcanized rubber will only swell in a compatible solvent.

Classification by monomer composition

Another classification of polymers is on the basis of monomer composition. Thus we have homopolymers, copolymers and terpolymers; these have been described earlier.

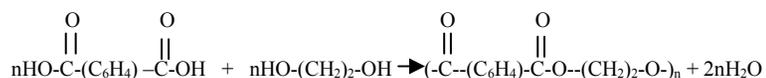
Copolymers can be subdivided further into four main categories: these are a) random copolymers b) alternating copolymers c) block copolymers which comprise of substantial sequences or blocks of each monomer d) Graft copolymers are formed when blocks of one monomer are grafted on to a backbone of the other.

Classification by polymerization mechanism

Polymers can be further classified according to the polymerization mechanism by which they are formed. The two major routes of polymer formation are condensation polymerization and addition polymerization.

Condensation polymerization is characterized by reactions involving the elimination of a small molecule such as water at each step.

An example is the condensation polymerization of terephthalic acid and 1,2-ethylene glycol to produce a polyester:



Addition polymerization involves repetitive addition of monomer units without the loss of any molecule. An

example of an addition polymerization is the formation of polyethylene from ethylene: $n \text{CH}_2=\text{CH}_2 \rightarrow -(\text{CH}_2-\text{CH}_2-)_n$

Classification by chain configuration

There are polymers with the so-called head-to-tail, head-to-head and tail-to-tail structures, which can arise during addition polymerization of olefinic monomers $\text{CH}_2=\text{CHR}$.

Geometric isomerism arises when conjugated diene monomers, like butadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$) and isoprene ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$) are polymerized. The resulting polymers contain C=C bonds in the main chain if the polymerization takes place by 1,4-addition. The C=C double bond can exist in the cis or trans geometric form. Also, some polymers may be isotactic, syndiotactic or atactic.

Classification by application

Polymers can also be classified according to application. Thus, we have plastics (including films and sheets), synthetic fibres, elastomers or rubbers and, coatings and adhesives.

A plastic is a material containing an organic substance of large molecular weight which is solid in its final condition and which at some earlier time was shaped by flow. A plastic is usually below its glass transition temperature (T_g) if it is amorphous. Crystalline plastics may be either above or below their T_g . Examples of plastics have been given earlier.

Synthetic fibres are thin threads produced by extruding a molten polymer through small holes in a die or spinneret. An example of a fibre is poly(hexamethylene adipamide) or nylon-6,6 ($-\text{HN}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_4\text{CO}-$) $_n$.

A coating is used to protect or enclose a layer of any material e.g. varnish. House coatings and paints are based on either oils or latexes. An adhesive is a substance capable of holding materials together by surface attachment e.g. poly (vinyl acetate).

Elastomers or rubbers are amorphous polymers that have the ability to stretch out and spring back to their original shapes i.e. they are capable of recovering from large deformations quickly and forcibly. These polymers must have a modest amount of crosslinking (a crosslink is a structure bonding two or more chains together) to prevent the chains from slipping over one another i.e. they can be or are already modified to a state in which they are essentially insoluble but can swell in boiling solvent such as benzene or methyl ethyl ketone. A rubber in its modified state, free of diluents retracts within 1 minute to less than 1.5 of its original length after being stretched to twice its length and held for 1 minute before release. Elastomer chains must have irregular shape to prevent crystallite formation. When stretched, the randomly coiled chains straighten out and orient along the direction of the pull. Elastomers are amorphous and exist above their glass transition temperatures.

Generally, a polymer chain is expected to have three basic properties: i). the molecular weight and molecular weight distribution of the molecules ii) the conformation of the chains in space or the different arrangement of atoms and substituents of the polymer chain brought about by rotations about single bonds. iii) the configuration of the chain. The term configuration refers to the organization of the atoms along the chain.

The study of the science and technology of polymers is important as it forms the basis of industries

such as plastics, rubbers, adhesives, fibres, inks and paints. It is believed that a multidisciplinary approach gives better information and understanding. Indeed, anyone studying polymers must have some knowledge of chemistry, physics, mathematics, biology, and engineering.

Basics of Polymers

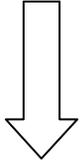
Raw material sources

The sources of raw materials for synthesizing polymers are from vegetable origin and from petrochemical feedstock. Natural rubber, cellulose and other vegetable materials can be modified into a variety of products.

The key petrochemicals for polymer synthesis (ethylene, propylene, styrene, vinyl chloride monomer and others) are produced largely from naphtha, one of the distillation fractions of crude oil. Naphtha can be cracked to obtain petrochemical feedstock such as ethylene, propylene e.t.c. Also, natural gas is a major raw material for polymer synthesis. Once polymer materials are produced, they are passed to major consuming industries such as textiles or paints or the building, packaging, agriculture, automobile, furniture, electrical and general engineering industries.

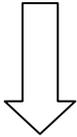
Primary Resources for Synthetic Polymers (Hall, 1981)

e.g. Crude oil, Natural gas, Air, Chlorine, Nitrogen



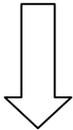
BASIC PETROCHEMICALS

e.g. Ethylene, Propylene, Styrene, Vinyl Chloride, Butadiene, Cyclohexane, Acetylene, etc.



POLYMER MATERIALS

e.g. Polyethylene, Polypropylene, Polystyrene, Poly(vinyl chloride), Polyurethane, Polybutadiene, etc.



POLYMER END PRODUCTS

e.g. Plastics, Elastomers, Fibres, Composites, Adhesives and Coatings

Differences between low-molecular weight and polymers. (Sperling, 2006)

- Most low-molecular weight compounds can be synthesized to obtain homogeneous substances but this is not possible with polymers.
- A polymer is characterized by a distribution of molecular weights while a low-molecular weight

compound is characterized by a single molecular weight.

- Low-molecular weight compounds will dissolve instantly in suitable solvents but swelling precedes the dissolution of polymers in compatible solvents.
- Polymer melts and solutions have high viscosities and are shear-rate dependent; solutions or melts of low-molecular weight compound have low viscosities.

Synthesis (Challa, 1993; Allcock, Lampe and Mark, 2003)

The requirements a molecule must meet in order to be able to polymerize as a monomer are (1) a monomer must have a functionality of at least two (2) it must be pure and reactive and (3) the thermodynamics must be such that the monomer will polymerize.

The methods of polymerization are by step-growth polymerization, free radical polymerization, cationic and anionic polymerization, co-ordination polymerization, metallocene polymerization and a host of others.

Step-growth/Condensation Polymerization

Condensation polymerization is used for monomers with functional groups such as -OH, -COOH, -COCl and it is often a series of condensation reactions. The term "condensation" is used generally in organic chemistry to refer to reactions in which molecules combine together with the elimination of a small molecule such as water.

A characteristic feature of condensation polymerization reaction is the elimination of a small molecule such as water at each step; this makes the majority of polymers formed in this way to differ slightly

from the original monomers because of the elimination of a small molecule. Consequently, the molecular weight of a condensation polymer is not always an integral multiple of the formula of the monomer molecule.

Condensation reactions take place by a step reaction mechanism i.e. stepwise intermolecular condensation of functional groups and are more generally referred to as step-reaction or step-growth polymerization; the kinetic process being of greater importance in classification. It is because of this that polyurethanes and other polymers, which grow by a step-reaction mechanism but without elimination of a small molecule or a by-product, are also classified as step-growth polymers.

Poly (ethylene terephthalate) is an example of condensation polymerization. It can be prepared in the melt by reacting terephthalic acid with ethylene glycol with the elimination of water.

Chain Addition Polymerization

Addition or chain-reaction polymerization is possible only for unsaturated monomers and it involves chain reactions in which the chain carrier may be an ion or a reactive substance with an unpaired electron called a free radical. Thus we have "free radical" and "ionic" polymerization; ionic polymerization is further subdivided into "cationic" and "anionic" polymerization. Chain addition polymerization is used for vinyl monomers such as $\text{CH}_2=\text{CHX}$, e.g. styrene, vinyl chloride, vinyl acetate, acrylonitrile etc. Some vinylidene monomers are also polymerized by this method e.g. methyl methacrylate, vinylidene chloride. Also, some fully substituted ethylenes like tetrafluoroethylene, trifluorochloroethylene are also polymerized by this method. There is no intermediate

species between monomer and high-molecular weight polymer. In addition polymerization, reaction proceeds through the stages of initiation, propagation and termination, and it may be susceptible to retardation and inhibition if extraneous substances are present.

Free - radical Polymerization

A free - radical is usually formed by the homolytic decomposition of a relatively unstable material called an initiator. Its formation involves the sharing of the two pairs of electron making up the labile bond of the initiator such that an unpaired electron remains associated with the new structure. The free radical is capable of reacting to open the double bond of a vinyl monomer and add on to it with an electron remaining unpaired, thus forming an active centre which propagates the chain and in a few seconds, it is eventually terminated.

Polymerization by Ziegler-Natta Catalysts

Ziegler-Natta catalysts are generally formed by the interaction of the alkyls of groups I-III metals with halides and other derivatives of transition metals.

Sometimes, they are referred to as coordination catalysts because they polymerize via the formation of a catalyst-monomer coordination complex. It is possible to have many variations of a catalyst mixture but a typical example of a Ziegler-Natta catalyst can be prepared from titanium tetrachloride and aluminium triethyl.

Generally, these group of catalysts have the remarkable ability to polymerize a wide variety of monomers to linear and stereoregular polymers (i.e. a directing force governs the orientation with which a monomer approaches the growing end.) (Billmeyer, 1984)

It arose from the discovery of Karl Ziegler and co-workers that mixtures of titanium tetrachloride and aluminium alkyls polymerize ethylene at low pressures and temperature; and also from the discovery by Guillo Natta that Ziegler catalysts can produce stereospecific polymers from monoolefins. (Billmeyer, 1984)

Miscellaneous polymerization methods

Several polymerization methods have been developed that cannot be classified in the earlier examples and only a few of these polymerization methods will be mentioned.

Metallocene-induced polymerization is a major development since the advent of Ziegler-Natta catalysts. They have the advantage that they can be used to produce polymers of specific tacticities.

The metathesis polymerization method is one that can be used to synthesize polyalkenamer elastomers through the ring-opening polymerization of cycloolefins like cyclobutane (Breslow, 1993; Fried, 1995)

Although “living” polymerization is usually carried out by anionic polymerization, it can be effected through group transfer of some acrylates and methacrylates at a temperature higher than what is used in conventional systems.

Plasma polymerization is widely used in coating applications. It involves the polymerization of gaseous monomers and subsequent reactions to form crosslinked layers on suitable substrate.

Although polymers are generally known to have insulating properties, there are some organic polymers with the ability to conduct electricity or they can be made conductive and they are referred to as conductive polymers.

Examples of conductive polymers include polypyrrole, polyacetylene, polyaniline e.t.c .

Rubber Technology

Looking back at the different types of polymers, it would be found that rubbers or elastomers constitute a class and it is with this class of polymers that I have carried out some studies. Rubber can be broadly classified as natural and synthetic; both types will be briefly described.

Rubbers

Natural rubber (NR) is a high-molecular weight polymer of isoprene and most of the isoprenes have the cis-1,4 configuration; hence the name cis-1,4-polyisoprene.

Rubber latex is obtained from the milky juice of the tree *Hevea Brasiliensis*. Other trees and shrubs are also known to be capable of producing rubber latex (e.g. guayule shrub) but they do not compare with *Hevea* in terms of yield and commercial significance. The latex which exudes when an incision is made on the bark of the *Hevea* tree is an aqueous dispersion of rubber containing 25 - 40% rubber hydrocarbon, stabilized by a small amount of protein material and fatty acids. The latex is gathered, coagulated, washed and dried. Dry natural rubber is commercially available in one of three grades: these grades are smoked sheets, pale crepe, and crumb rubber.

Synthetic rubbers are a group of rubbers or elastomers that are synthesized. Methods of synthesis may be by free radical polymerization, coordination polymerization, cationic and/or anionic polymerization. Examples of synthetic rubber are styrene-butadiene rubber, nitrile rubber, polybutadiene rubber, butyl rubber e.t.c.

Rubbers in their raw forms are of little use. However, they become useful when they are mixed with particulate fillers, rubber chemicals, crosslinking agents and the resulting compound vulcanized at elevated temperature.

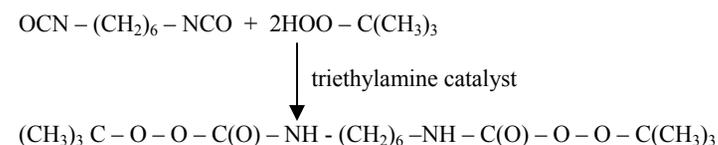
Research Contribution

Historical records indicate that natives of areas where natural rubber trees were in abundance had been using rubber for waterproofing (Semegen, 1981). However, it was European explorers who observed that rubber articles suffered from stiffness and brittleness in cold weather and were sticky in hot weather. It was to overcome the variableness in properties that led to rubber being vulcanized. The historical development of rubber technology had earlier been mentioned and credit for the discovery of vulcanization is shared by Thomas Hancock in England and Charles Goodyear in the U.S. As part of my adventure with polymers, rubbers to be more specific, I studied some aspects of rubber vulcanization and technology. This involved the evaluation of some hexamethylene-N,N' bis(tert butyl peroxy carbamate) as crosslinking agent for both natural and synthetic rubbers.

Preparation of bisperoxy carbamate

Hexamethylene -N,N' bis (tert butyl peroxy carbamate) was prepared by modifying the method described by Pedersen (Pedersen, 1958). It involved reacting hexamethylene-1,6-diisocyanate with tertiary butyl hydroperoxide in toluene medium and in the presence of triethylamine as catalyst. Extent of reaction was monitored by observing the disappearance of the characteristic isocyanate absorption band ($-NCO$ at 2270cm^{-1}) on the

infra-red spectrum with time. The reaction was completed after eight hours; afterwards, some hexane was added to the thick slurry formed to complete the precipitation of the product. The slurry was filtered and the precipitate washed twice with hexane; the filter cake was dried under vacuum at room temperature, giving a yield of about 90%. The reaction equation is shown below:



Using a differential thermal analyser, the melting point of the HBTBP was found to be 93°C while the decomposition peak temperature was 142°C . Also, the infra red spectra of the dry sample gave the following peaks: O-O, 860cm^{-1} ; C-O, 1198cm^{-1} ; $-\text{C}(\text{CH}_3)_3$, 1380cm^{-1} ; and 1395cm^{-1} ; C=O, 1720cm^{-1} ; C-H stretching 2280 , 2980 and 2995cm^{-1} ; N-H, 3360cm^{-1} ; $-(\text{CH}_2)_6$, 720cm^{-1} . Also, the elemental composition determined for HBTBP agreed closely with the theoretical structure written for the compound.

Evaluation of Crosslinking ability of HBTBP

Having prepared HBTBP, I evaluated it for its ability to crosslink various elastomers. Most evaluations were carried out using both gum and filled vulcanizates to test whether HBTBP was suitable as a crosslinking agent for a particular elastomer. Also, limited compounding studies were carried out to enable the comparison of physical properties of vulcanizates cured with the product (HBTBP) and those cured with conventional vulcanization

systems. Some of the elastomers used included natural rubber, styrene-butadiene rubber, nitrile rubber, polychloroprene, and fluorocarbon rubber.

Rubber was mixed on a two-roll mill and it was compounded with fillers, acid acceptors, calcium hydroxide and crosslinking agents. The cure characteristics of the compounds were studied with the aid of a Monsanto Oscillating Disc Rheometer (ODR), after which compression moulding techniques were used to obtain vulcanized rubber sheets of 2mm thickness. After conditioning the sheets, the tensile stress-strain properties were determined using a tensometer and according to standard testing methods. The cure trace obtained using HBTBP in nitrile rubber is compared with those of conventional systems (used as controls) in Figure 1 while a formulation for nitrile rubber cured by HBTBP and controls along with their aged and unaged physical properties is shown in Table 2. (Ogunniyi and Hepburn, 1994).

Table 2: Comparison of physical properties of vulcanizates obtained using HBTBP curing agent and 'controls' for various elastomers (Ogunniyi and Hepburn, 1994)

	<u>Sulphur</u> (phr)*	<u>Peroxide</u> (phr)	<u>HBTBP</u> (phr)
NBR Breon 1042	100	100	100
SRF Black (N762)	30	30	30
ZnO	5	5	-
CaO	-	-	4
Ca(OH) ₂	-	-	6
Stearic Acid	2	-	-
TMTD	1.5	-	-
MBTS	1	-	-
Flectol H	1	0.5	-
Sulphur	1	-	-
Dicup 40C	-	1.5	-
HBTBP			6
Mooney Scorch at 120°C	24mins	>40mins	5mins
Cure Conditions (mins/Temp °C)	12/160	16/170	10/160
<u>Unaged properties</u>			
Tensile Strength (MPa)	14.26	21.07	4.61
300% Modulus (MPa)	10.27	3.61	2.96
Elongation-at-break (%)	350	850	575
Tear Strength (kN/m)	24.75	30.02	34.6
Hardness IRHD	47	42	36
Resilence %	21	31	39
<u>Aged Properties (24 hours at 100°C)</u>			
Tensile Strength (MPa)		12.79	20.41
300% Modulus (MPa)		9.18	4.25
			4.02

Elongation –at-break	325	750	600
Tear Strength (kN/m)	22.39	24.46	44.39
Compression Set (%)	8	25	72
(24 hrs @100°C, 25% strain)			
% Retention of Tensile Strength	90	97	164

*phr – parts per hundred rubber

The ODR traces of other elastomers were obtained but are not shown because constraint of space. In diene-containing elastomers (nitrile rubber, styrene-butadiene rubber and natural rubber), sulphur vulcanization systems gave the best cure response while HBTBP gave the least cure response; peroxide vulcanization systems were intermediate.

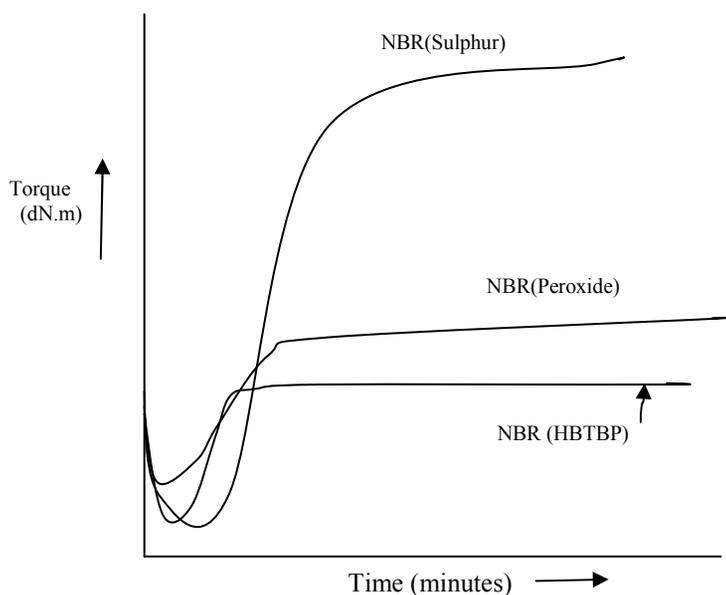


Figure 1: Monsanto ODR Cure Traces of Nitrile Rubber using different Crosslinking Systems

In polychloroprene rubber, metal oxide curing system gave the best response, followed by peroxide curing system and HBTBP curing system. From the ODR traces, we can say that HBTBP was used successfully to crosslink the following elastomers: natural rubber, styrene-butadiene rubber, nitrile rubber, fluoroelastomers, silicone rubber, polychloroprene, epichlorohydrin. However, HBTBP was not found suitable as a crosslinker for ethylene propylene diene monomer terpolymer and it was not suitable for chlorosulphonated polyethylene and butyl rubber.

It was further observed that compounds needed to be cured longer than the estimated cure (t_{95}) times to ensure that the carbon dioxide evolved during HBTBP cure was sufficiently absorbed by the calcium hydroxide included in the formulation. In most of the elastomers, the physical properties of vulcanizates cured with conventional crosslinking agents were better than those obtained from vulcanizates cured with HBTBP (Ogunniyi and Hepburn, 1994; 1995).

Crosslinking of Viton fluoroelastomer by HBTBP

An interesting aspect of my adventure was the good cure response obtained when HBTBP was used to cure fluoroelastomers with the trade name Viton (Viton is a trade name of E.I. du Pont de Nemours, U.S.A.) Most fluoroelastomers are co- or terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene or chlorotrifluoroethylene. Fluoroelastomers are well known for their outstanding heat and fluid resistance. Heat resistance is especially important since fluoroelastomer vulcanizates are able to withstand service temperatures of about 200°C: a service condition well beyond the limit for other common elastomers. Compounding was as previously

described; however, in addition to press curing, Viton vulcanizates were postcured for 24 hours in air oven at 250°C unless otherwise specified. From the results obtained, HBTBP was found to give good cure response in Viton B, Viton E and Viton GF but the best cure response was in Viton GF. The properties of HBTBP-cured Viton GF fluoroelastomer vulcanizates were compared with those cured by a standard vulcanization system and the results are shown in Table 3.

Also, the crosslink density measurements of the gum vulcanizates that were press-cured and those that were postcured in hot air oven were obtained. Volume fraction of rubber at equilibrium swelling was calculated by assuming simple additivity of volumes while the experimental crosslink density $(2M_c)^{-1}$ was estimated from the Flory-Rehner equation

$$-[\ln(1-V_r) + V_r + \chi V_r^2] = \rho V_o M_c^{-1} (V_r^{1/3} - V_r/2)$$

where V_r is the volume fraction of polymer in the swollen gel, χ is the polymer-solvent interaction parameter and it was estimated from a relationship given by Fogiel (Fogiel, 1975), ρ is the density of the elastomer, V_o is the molar volume of the swelling liquid, and M_c is the molecular weight between crosslinks. Network imperfections due to chain entanglements are neglected while the correction for loose chain ends was made by replacing M_c^{-1} by $M_c^{-1}(1 - 2M_c M^{-1})$ where M designates the number-average molecular weight of the non crosslinked elastomer (100,000, in the case of FKM-G).