CHAPTER 1

INTRODUCTION

predominantly organic, consisting of long – chain molecules to a glassy state. Materials in the class of polymers which are **plstics,** at normal temperature, become **rubbery like** as the temperature is raised above their Tg. For this reason their Tg **mark** the *upper temperature limit* of their service properties, or their heat resistance.

1.1: PRIMARILY NOTE ON THE RUBBER PROCESSING AND MANUFACTURING :(2)

The term "*rubber*" is used to convey several meanings and it is unfortunate that the terminology of the industry regarding this one word was not clarified many decades ago. **Rubber**, apart from a turkish—bath attendant, means the raw material produced by the tree, a product for erasing pencil marks from paper, and the generic term for products from rubber; in other words, it covers both the raw unvulcanized materials and the finished product. Designers specify their material requirement as "*rubber*".

So far little mention has been made of any raw polymer other than natural rubber, because for so long it was the only polymer available for elastomer production and much of the technology referred to above was developed for this polymer.

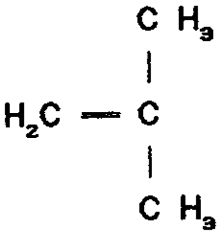
The copolymers, requiring peroxide vulcanization, found only specialized applications. That section of the rubber industry using general purpose rubber is greater to sulphur vulcanization and is reluctant to accept rubbers not capable of this type of cure. The terpolymers, in which the third monomer provides unsaturation for sulphur vulcanization and the possibility of blending with Natural Rubber [NR], Styrene Butadiene Bubber [SBR], Polybutadiene Rubber [BR] and Polyisobrene Rubber [IR] have become firmly established and their production is now greater than that of the copolymer.

Referring to the general purpose rubber, mention should be made at this point of **Butyl rubber**, the copolymer of isobutylene and a small percentage of isoprene.
This rubber become available in the early 1940s and found immediat application as an inner-tube rubber because of its special property of low permeability to gases. At that time, it tended to be classed as a *special purpose rubber*. With the change to tubeless tyres, it main outlet was substantially reduced and , in some ways, it can now be considered as general purpose rubber. Its good resistance to ozone, oxidation, and chemicals has let to its adoption for a number of applications as a replacement for natural rubber. Butyl rubber is now used for engine mounts, cable sheating,tank and reservoir lining and for airbags and similar components in

tyre manufacture. Halogenated butyl rubber have assumed some importance and find application for tyre curing bags, roofing, membranes, pharmaceutical closures and automotive mounts.

1.1.1: ISOBUTENE - ISOPRENE RUBBER [IIR] :(2,3)

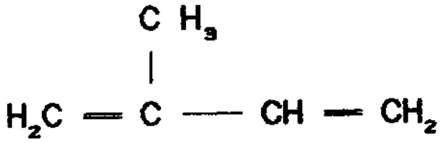
Rubberlike copolymers of isobutene or 2-methylprop-1-ene



$$H_2C - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}$$

Isobutene

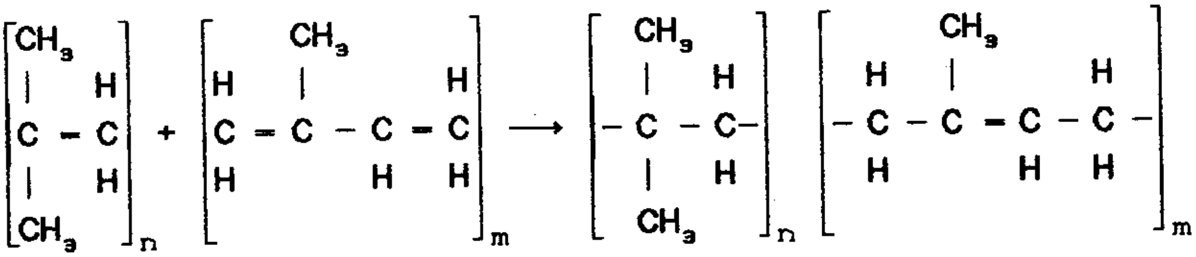
and isoprene were first produced in the USA just before World War II. and known as **butyl rubber [IIR]**



$$H_2C = \overset{\displaystyle CH_3}{C} - CH - CH_2$$

Isoprene

The monemers are polymerized in solvents such as methyl chloride, and at low temperature (− 80°C), using. Friedel-Carfts catalysts such as $AlCl_3$ or BF_3.



$$[C(CH_3)_2-CH_2]_n + [CH_2=C(CH_3)-CH=CH_2]_m \longrightarrow [-C(CH_3)_2-CH_2-]_n\,[-CH_2-C(CH_3)=CH-CH_2-]_m$$

Although the catalytic system is not essentially sterospecific, the isobutylene units polymerise entirely head-to-tail, and the polymeric chains contain a very regular structure, owing to the symmetricl nature of the isobutene monomer. The isoprene units enter the chain in a mixture of cis – and trans – 1.4 structures, [Van Tongerloo and Vukov, 1979].(4) Hence butyl elastomers are self– reinforcing, with a high pure gum tensile strength (25 MPa).

The use of butyl in such products as Bag-O-Matic bladders, steam hose, and hot materials belts indicate the degree of heat resistance inherent in butyl(5). In compounding for heat resistance some factors should be taken into account. For example, a highly unsaturated grade of polymer is necessary in order to form a tight network of cross links. Fillers loading usually employed in high concentrations should be of the furnace or thermal type of carbon black. The mineral fillers can be utilized, but extensive deterioration of the stok may be encountered under severs conditions. Low sulphur is beneficial since large amounts contribute to reversion. High loadings of zinc oxide tend to overcome this.

1.1.2: FILLERS :(2,6,7)

The use of fillers in rubber is almost as old as the use of rubber itself. As soon as rubber-mixing machinery was developed, fillers such as ground whiting, barytes or clay, were added to cheapen the products and were found, in natural rubber, not to detract too much from the final vulcanizate properties.

The interaction of particulate fillers with an elastomer is dependent on a number of factors that can be classified as *extensity, intensity, and geometrical* factors.

The extensity factor is the total amount of surface area of filler per cubic centimetre of compound, in contact with the elastomer.

The intensity factor is the specific activity of this solid surface per square centimetre of interface, determined by the physical and chemical nature of the filler surface and, to some extent, of that of the elastomer.

Geometrical factors are: (a) the "structure" of the filler, which can be determined by its void volume under standardized packing conditions; and (b) the porosity of the filler, usually a minor factor, which can be varied over a wide range with carbon blacks. Because the weight of individual spongy particls is lower than that of solid particles, the number of particles per cubic centimetre of compound at a given weight loading is greater for spongy than for solid particles.

1.1.2.a: Carbon Black

Carbon blacks are essentially elemental carbon and are composed of aggregated particles. The particles are partly graphitic in structure and are of colloidal dimensions. The carbon atoms in the particle are in layer planes which, by parallel alignment and overlapping, give the particles their semi-graphitic nature. The outer layers are more graphitic than those in the centre. The particles range in size from **10nm** to **400nm** in diameter, the smaller ones being less graphitic. Carbon blacks are produced by converting either liquid or gaseous hydrocarbons to elemental carbon and hydrogen by partial combustion or thermal decomposition.

The ultimat particles of carbon black have considerable quantities of foreign atoms at the surfaces of the fragments or particles. These particles do not generally occur singly, but in aggregates. These may include primary fused structures or chains, which are very resistant to disintegration, and secondary structures less strongly held together.

The *five* most important properties of carbon blacks are: (a) particle size, or surface area, (b) structure, (c) physical nature of the surface, (d) chemical nature of the surface, and (e) particle porosity.

The most obvious factor which influences the resistivity of the rubber is the particle size [or number of particles per unit volume, or specific surface area] of the carbon black.
For closely related types of carbon black the resistivity shows a fairly regular decrease with increasing surface area.

Different carbon blacks, when pressed into pellets, have somewhat different resistivities. The differences can be attributed to (i) the degree of graphitization of the carbon, (ii) the amount of gas, particularly oxygen, which has reacted with the surface, and (iii) any significant amount of other impurities in the carbon.

Most of the carbon black used today is made by the *furnace process.* This process consists of the incomplete combusion of natural gas or heavy aromatic residue oils from the petroleum or coal industries in refractory–lined steel furnaces, ranging in length from 1.5 m to 6 m and in diameter from 0.15 m to 0.75 m.

Blacks produced from natural gas are a very small proportion of the total furnace black output.

A further process is the **LAMP black** one, in which the black is made by burning petroleum or coal tar residues in shallow pans. The "*smoke*" is then conducted to settling chambers in which the carbon flocculates.

1.1.2.b: Non-Black Fillers:(2)

Non–black fillers which are used to reduce cost, to improve processing by reducing "nerve", and to reinforce the polymer by increasing hardness, tensile strength, tear resistance, abrasion resistance, and other properties in the production of white compounds.

They are usually classified as:

1. Fillers used mainly to reduce cost such as calcium carbonates and oxide and barytes (barium sulphate).
2. Semi–reinforcing fillers such as antimony trioxide.

3. Reinforcing fillers used to achieve high performance in non-black products as aluminium bydroxide, aluminium silicates, china clay, magnesium carbonate and titanium dioxide.

Also there are a larg number of heat resistance fillers: the powdered graphitic form of carbon, magnesium oxide, silica and Talc.

Some workers(8) added *barium titanates* to polymeric materials to improve the mechanical and dielectric properties.

Another efforts made to incorporate TiO_2 into polymeric materials to reach a good dielectric and electronic properties in the electronic instruments.

Zinc oxide used as an activator, accelerator and also as a reinforcing filler.

1.2: ELECTRICAL CONDUCTION IN POLYMERS : (9)

The range of elecrtrical conductivity observed in materials covers range of 25 orders-of-magnitude. This is one of the largest variations in any materials property.

The disordered molecular material or polymers may not have a band stucture; there may be an array of molecular states and

molecular ion states, as well as many localized dipole states associated with the disordered molecular materials.
Such properties are complicated by the existence of molecular ion states and regions of differing polarity or polarizability. The free charges may prefer to exist as molecular ions, they may be trapped in polar regions, or they may be trapped as a result of polarization of the surrounding medium.

There are three levels of stucture to be considered. The first level is the basic chemical composition. The nature of the monomer unit(s) will determine the behaviour of the polymer, particularly where photoconduction is involved. The second level of stucture involves the spatial arrangement of the basic polymer units within the individual polymer molecules *[the microstructure].* This is determined to a great extent by the polymerization reaction and the precise reaction conditions. The third level of structure is the spatial arrangement of the polymer chains in the solid state *[the macrosturcture].*

We should note, in addition, that where insulators are concerned the origin of the charge carriers is by no means clear. A polymer with a molecular weight of 10^{6} has about 12×10^{18} end groups per cubic centimetre. An insulator with a conductivity of 10^{-17} Ω^{-1} cm^{-1} and a hypothetical

mobility of 10^{-5} cm^2/v sec requires only about 10^8 mobile charge carriers by cubic centimetre. Most polymers, particulary condensation polymers, can easily contain such a level of ionic impurity. The extent to which extrinsic charge carriers [impurities, electrons, or holes injected from electrodes] control the conductivity of the insulating polymers is seldom unambiguous.
Thus, many discussions of electrial conduction in insulating polymers are open to criticism on the grounds of suspect purity and spurious electrod effects, unless it is clear where the charge carriers originate.

The specific electrical conductivity of a solid , σ Ω^{-1} cm^{-1}, is defined as the current, in amps, flowing through a centimetre cube of the materials under unit electrical potential and it is related to two basic parameters, the charge carriers density n (cm^{-3}) and the charge carrier mobility μ cm^2/V sec ;i.e.

$$\sigma = \sum_i q_i \, n_i \, \mu_i \, ,$$

where q_i is the charge on the ith species. With polymeric materials , such parameters n_i or μ_i may be ambient-sensitive, and may be influenced by the precise conditions of fabrication.

The type of electrical conductivity measurement reported in the literature usually involves a simple measurement of current as a function of time, temperature, ambient atmosphere, and potential. Attempts are then made to relate the conductivity of physical processes through to be occuring in the polymer. Until recent years, there have been few attempts to study, for example, charge—carrier mobility as an independent variable.

Frequently, it is found that electrical conductivity varies *exponentially* with temperature, is a function of time, and may vary with electrical field i.e.,

$$\sigma = \sigma_o \exp [- E\sigma/KT] = f (time) = A f(E) \quad (1.1)$$

changes in $E\sigma$, the activation energy of conduction, are often observed in the neighborhood of glass-transition temperature. Since the conductivity is made up of terms relating to both the number and the mobility of the charge carriers, any prediction regarding the conduction process that does not recognize these dependences is meaningless. As more mobility measurements have been carried out, it has become recognized that the motion of charge carrier is an activated process. Thus, the simple assumption that polymers can be described in terms similar to those used for crystalline, covalent semiconductors has been seriously questioned. Much has been learned from the study of disordered inorganic materials and by the extention of experimental techniques to polymers.

1.3.1: ELECTRICAL PROPERTIES OF CONDUCTING POLYMERIC COMPOSITES:(6,10)

Probably, the simplest conducting composites consistes of a fine metal powder dispersed uniformly throughout an insulating polymeric matrix. The main drawback of this system, apart from the obvious dilution by the polymer of the conductivity of the metal, is then the metal particles remains isolated from each other, and therefore contribute no throughgoing conductivity to the composite at all, unless they are present in very high concentration. However, high concentration tend to destroy desirable mechanical properties of the polymer, the material typically becoming stiff and brittle.

The art of making a good conductivity composite is to be to able to use the minimum quantity of conductive component to acheive the required degree of electrical performance, and in this context it is important to know more about the factors which control the formation of conductive networks for a given concentration of conductive component. There are two main factors :

[a] Quality of interparticle contacts. Conductive network in a 2-phase system depend on the particles of the conductive phase being able to make good electrical contact when they touch or come close to each other. Since a colossal number of interparticle contacts are involved, any changes in contact properties will be highly significant to the conductivity that may be realized.

[b] Shape and size of conductive particles. The resistivity of compaction of carbon powder has been successfully explained on a simple model where the constrictions at interparticle contacts are assumed to have a dominating influence (Mrozowski, 1959). The theory uses Holm's (1946) expression $\rho\pi/a$ for the contact resistance between two spheres when the radius a of the circular area of contact between them is small with respect to the radius of the spheres, ρ being the resistivity of the material of the spheres. Thus, taking into account the way in which compressive forces cause elastic and yielding deformation, there by altring a , the dependance of the resistivity of the compaction on pressure may be predicted quantitatively.

1.3.2: ELECTRICAL PROPERTIES OF CARBON BLACK FILLED COMPOSITES:

The additive used more than any other to make conducting polymers is *carbon black*, which is prodused by incomplete combustion of hydrocarbon vapour. It should be mentioned that the addition of particulate fillers has been used for a long time in the rubber industry primarily to give mechanical reinforcement, and carbon black has generally been preferred for this, because (a) it is a compatible material, mixing in, and adhering to the matrix rather well, (b) it does not change the overall density very much, and (c) it is cheap, rather higher concentrations of special grades are necessary, however, for electrical purposes.

In the face of the complicated nature of carbon black it is not surprising that any theoretical relationship between the resistivity of a composite and its carbon black content is difficult to obtain. For one thing, the all important structure is affected by the process of mixing the black into the polymer. Nevertheless there are two theories which go some way in explaining the behaviour of the composites in certain regimes.

The first theory(11) sets out to treat those systems which show *non-Ohmic* conduction. This kind of behaviour is indeed often found at the low-conductivity end of the scale, and it implies that some kind of electron emission process control the conduction, probably a tunneling of electrons from one particle to the next across gaps of up 5 nm . It is relevant to note here that the very small particle size of carbon blacks means that Brownian motion might be responsible for momentarily bringing particles close enough together for electron tunnelling to occur.

Emission current density j is related to applied voltage **V** by an equation of the form

$$j = A\ V^{n} \exp [\ - B/V\ ] \qquad (1.2)$$

where A, B and n are constants; n usually lies between 1 and 3. A is a function of the tunnelling frequency, i.e. the attempt-to-escape frequency of the electron, and the factor exp [$-B/V$] defines the transition probability through the energy barrier of the gap. B will be proportional to the gap between particles, so that, neglecting the pre-exponential factor, the effective conductivity σ at a particular voltage will be given by

$$\ln \sigma \propto 1/L \qquad (1.3)$$

where, L is some average interparticle separation.
Now it may be shown that the interparticle separation for any array of spherical particles [radius a] on a cubic lattice [repeat distance L] where L >> a is given by :

$$L = a\,[4\pi/3f_v]^{1/3} \qquad (1.4)$$

where f_v is the volume-fraction of particles. For a random, low-density dispersion of particles we may therefor expect that

$$L \propto f_v^{-1/3} \qquad (1.5)$$

combining this with eqation (1.3) we then obtain

$$\ln \sigma \propto f_v^{-1/3} \qquad (1.6)$$

To assess the validity of this equation we can compare it with the purely empirical equation [Bulgin, 1945] which has a similar form :

$$\ln \sigma = [\ A/f_w]^{-p} \qquad (1.7)$$

where, f_w is the wieght fraction of the carbon black in the composite [for low carbon black concentrations $f_w \alpha f_v$], and A and p are constants.

The second theory$^{(12)}$ treats the conductivity cases where *Ohmic behaviour* is encountered. It is assumed that interparticle contacts are ohmic, and going to calculate the probability of formation of conductive chains. Supposing the composite to consist of a random mixture of conducting and non-conducting elements, the probability of obtaining a sequence of n conducting elements is f_v^n. If the average conducting element is a sphere, diameter d, associated with a spherical region, diameter D, of the composite :

$$D/d = 1/f_v^{1/3} \qquad (1.8)$$

By random-walk theory, if the diameter D is taken as the mean distance between the ends of chain of n links of length d,

$$D = d\ n^{1/2} \qquad (1.9)$$

Combining eqs (1.8) and (1.9),

$$n = f_v^{-2/3} \qquad (1.10)$$

Hence the probability that the volume associated with one conductive element may be bringed by chain formation is then given by :

$$p = f_v^n$$

The ratio of the conductivity of the composite to that of the conductive component itself is the product of the proportion of conducting to non-conducting elements, the probability of chain formation and the geometrical factor, C^2, i.e.

$$\sigma / \sigma_o = f_v \times f_v^n \times C^2$$

It is found to be in fairly good agreement with experimental values obtained for a dispersion of carbon black in polyethylene.

1.4: FACTORS AFFECTING THE ELECTRICAL PROPERTIES OF CONDUCTIVE RUBBERS :

1.4.1. Effect of Carbon Black ; Type and Concentration :(13)

Electrical conductivity is important in many rubber and plastic composites including antistatic applications, wire and cable sheating, and shielding against electromagnitic interference [EMI]. Elastomers are insulators [dielectrics] to which conductivity is imparted by addition of a finely divided or colloidal filler of high intrinsic conductivity, such as carbon black. Over the years, there has developed a sizable body of information regarding measurement of conductivity, and the factors which affect it in such compounds or composites. With regarde to the physical processes involved in the conduction of electricity, various mechanisms have been proposed by various authors. It appears that many physical processes can be involved and that the dominant process depends upon the composition of the composite and the conditions of measurments.

At *low loadings* of carbon black, the conductivity of the composite is essentially that of the dielectric medium. As the loading is *increased*, a percolation threshold or critical loading is reached where the conductivity starts to *increase* rapidly as a function of loading. The entire region of conductivity increase is called the **percolation region**. In this region, conductivity is limited by barriers to passage of the charge carriers [electrons] from one carbon black aggregate to another which is close but not touching. The gap distance may be of the order of **15 - 100 °A**. The electron must surmount a potintial barrier to get out of the carbon black aggregate and across the gap.

If we add conducting particles such as carbon black aggregates to a matrix one at time, the particles will at first be isolated, then isolated clusters will be formed, and finally a through-going path will arise. The experimental evidence for **throughgoing chains at high loading** is two fold **(a)** no (or very littel) dependence of conductivity on frequency; **(b)** very littel dependence of conductivity on temperature.

The type of carbon black may affect also the electrical properties by several factors ;
(a) Particle size, (b) Porosity, (c) Number of particles per aggregates and (d) Anisometry.

1.4.2 Effect of Processing and Other Factors on the Electrical Properties of Rubber : (6)

Processing conditions, especially those involving considerable shear of the polymer/filler mixture can have a greater effect of the *resistivity* than major changes in the compound.

Satisfactory methods of preparation of specimens of **rubber/carbon black** mixings for the electron microscope has been shown that with many types of carbon black some structure does survive the mixing process.

High or low mixing temperatures are more effective than moderate temperature mixing.

Damage to the carbon structure resulting from the flow produced by moulding rubber tends to increase the resistivity and make it more variable, whereas vulcanization has the reverse effect due to the re-formation of carbon/carbon bonds during heating. The final resistivity depends slightly on mould pressure.

Neither the time of application of the voltage nor the change from dc to low frequency ac has any large effect on resistivity. Also, the effect of **ageing** on the conductivity of carbon black filled rubber is generally very small.

Due to *Norman* (1970) the effect of large strain (or stresses), time and temperature on the resistivity of conductive vulcanized rubber (carbon black filled) are very complex and depend greatly on detail of the treatments, especially on the magnitude of the maximum strain.