CHAPTER II

LITERATURE SURVEY

2.1 Ethylene-vinyl acetate copolymer (EVA)

The first ethylene copolymer, including EVA, were synthesized and patented in the 1930s at ICI in Great Britain in the same laboratories where polyethylene was discovered. The chemical structure of EVA is show in this figure
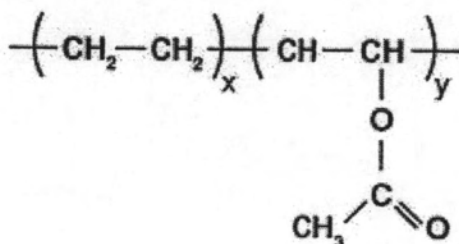

Figure 2.1 Ethylene vinyl acetate copolymer structure

Initially only low levels of vinyl acetate(VA) comonomer were used to produce "modified polyethylene". During the late 1950s and continuing to the present day, the range of EVA copolymers has widened considerably, reflecting an appreciation for the versatility of the material. Today the term "EVA copolymer" covers the diverse family of materials, which for the purposes of this article will be largely confined to copolymers containing about 2-50% by weight (wt%) of vinyl acetate.

It should now be evident that the properties of solid thermoplastic EVA copolymers vary markedly over the range of vinyl acetate content (2-50%) being considered here. This section is separated into three parts: chemical properties, physical properties and electrical properties.

2.1.1 Physical properties

Physical properties of EVA copolymer vary in there appearance in thick sections from some what opaque plastic resembling LDPE at 5 wt% vinyl acetate to a crystal clear, some what tacky, rubbery material at higher vinyl acetate contents. Even at low vinyl acetate contents the copolymer surfaces is relatively soft and can be abraded by fingernail. Although the low vinyl acetate content materials are opaque in thick sections, in thin film form they can be completely transparent, showing higher clearity than similar films produced from LDPE. This is due to there lower degree of crystallinity.

The surface hardness of EVA copolymers is related to both molecular weight and the degree of crystallinity. As would be expected, hardness reduces with an increase in vinyl acetate content (lower crystallinity) and an increase in melt flow index. EVA copolymers, being semi-crystalline, soften gradually as the temperature is increased until, at a certain point that varies with vinyl acetate content and chain branching, the crystalline regions start to melt. At this point the copolymer viscosity begins to decrease rapidly with further increase in temperature until all the crystalline have completely melted. The softening point, as measured by either Vicat (ASTM D1526) or Ring and Ball (ASTM E28) methods varies significantly with molecular weight and the degree of crystallinity However the peak melting temperature as measured by Differential Scanning Calorimetry (DSC), is determined solely by the degree of crystallinity and is un affected by molecular weight. These relationships are shown in table 2.1. Increasing the vinyl acetate content lowers the softening and the DSC crystalline melting points of the EVA copolymers dramatically.

Table 2.1 Variation of softening and melting point of EVA copolymers with molecular weight, VA content and chain branching

VA content	MI	Hydrocarbon branches (methyl group) per 100 carbon atom	Softening Point (°C)		DSC Peak melting Temperature (°C)
			Vicat	Ring & Ball	
7.5	2	9	81	-	103
12.5	2	8	69	-	97
18	2	8.5	59	185	88
18	150	8.5	-	100	88
28	5	5	-	150	70
28	25	7	-	115	70
28	400	9	-	85	70
28	400	19	-	80	63

All EVA copolymers can be describes as tough, comparatively low modulus materials. Stiffness, or flexural modulus, is mainly determined by crystallinity and to a lesser extent by chain branching. Table 2.2 lists typical flexural modulus values (1% strain) as a function of vinyl acetate content in EVA copolymer. This modulus values decrease dramatically with increasing vinyl acetate content.

Table 2.2 Flexural modulus of several EVA copolymers

%VA	Tensile modulus (MPa)
2%	170
7%	160
9%	110
12%	105
17%	60
28%	20

The effect of vinyl acetate content on other mechanical properties is illustrated with a set of stress-strain curves shown figure 2.2. At low vinyl acetate concentration (2-5 wt%), the EVA stress-strain curve shows a yield region disappears and high strength at high elongation is developed. This behavior can be characterized as rubbery in nature. Unlike true rubbers, however, EVA copolymers do not fully recover if elongated beyond 100%.
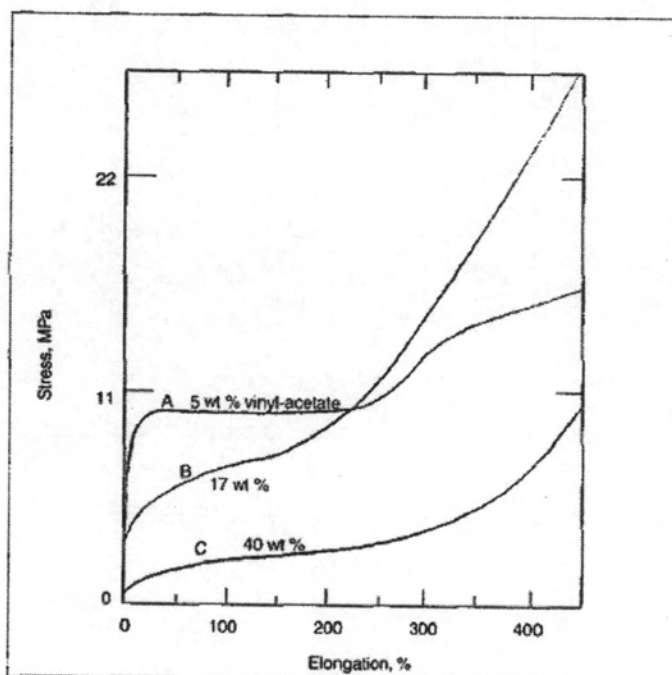

Figure 2.2 Stress-strain curves for ethylene-vinyl acetate copolymers of various composition.

Due to their modulus. Low softening points, and rubbery nature when their vinyl acetate content exceeds 5 wt%, articles fabricated from EVA rarely fail in service due to impact forces. In all but exceptional circumstances EVA copolymers give satisfactory service down to -40 °C.

2.1.2 Chemical properties

Chemical properties of EVA is effected of increasing vinyl acetate content that increase the polarity of the molecules. This allows better incorporation of inorganic fillers or fillers such as carbon black with active surface, give greater tackiness and adhesion

to most substrates, and reduces resistance to chemicals. EVA copolymers are attacked by most organic solvents and by high concentrations of oxidizing acids (e.g. >30% nitric and >50% chromic). This effect increase with increasing vinyl acetate content. As with LDPE, halogens attack EVA and lead to embrittlement, although dilute solutions of chlorine and bleach have little effect. Aqueous salt solutions do not effect EVA copolymers.

Due to their more polar nature, EVA copolymers are more permeable to gases and moisture vapor than LDPE. Typical gas permeabilities and water vapor transmission rate are given in table 2.3.

Table 2.3 Gas and Moisture Permeability of Films Produced from EVA Copolymer

Polymer	Oxygen	Nitrogen	Carbon dioxide	Water Vapor Transmission at 90% RH
	Unit cm^2 / sec-mm-Hg (at NTP)			(Units: $g.mm^2$-24h)(film 25 μm thick
LDPE	2.7×10^{-9}	-	18×10^{-9}	24
18% vinyl acetate, 2 MI EVA	6.5×10^{-9}	2.2×10^{-9}	23×10^{-9}	70

EVA copolymers are less thermally stable than LDPE. Degradation occurs primarily by two mechanisms: oxidation and elimination of acetic acid. Oxidation can be minimized by use of antioxidants, but elimination of acetic acid cannot be prevented. Fortunately, this problem is minimal at processing temperature up to 210°C, acetic acid elimination increases rapidly.

Thermal properties of EVA was investigated by thermogravimetric analysis in many research, all of them reported that EVA thermal degradation occurs in two consecutive step both air and inert atmosphere [4]. The first step (300-380 °C) correspond to the deacrylation of vinyl acetate group of copolymer with elimination of

acetic acid and formation of double bond. The second step (380-450°C) may be assigned to the further degradation of polyethylene chain formed in the first step accompanied with the degradation of main chain. The thermal degradation of EVA was show in figure 2.3
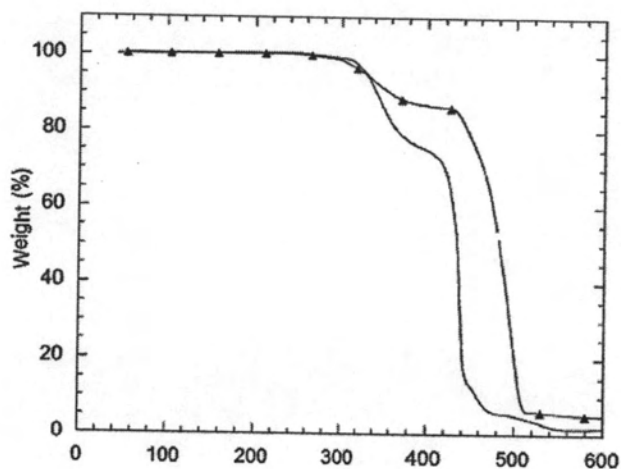

Figure 2.3 Weight loss curve of EVA/LDPE blend (-)

UV light cause photo-oxidation of EVA copolymers. This can be minimized by incorporating 2-3% carbon black or UV stabilizers.

2.1.3 Electrical properties

EVA copolymers do not share the excellent dielectric properties of polyethylene due to the polarity of the vinyl acetate group. This mean the EVA is not suitable for use in, for example, telephone cable insulation applications where high frequencies are encounted. On the other hand, this does able to the use of radio frequency sealing techniques to be used with films made from EVA copolymers containing more than about 15% vinyl acetate. In addition, the dielectric strength and volumn resistivity of EVA are such that they can be used in low to medium voltage, low frequency applications, EVA's polar nature allows incorporation of high levels of carbon black and flame retardant actives. Table 2.4 gives typical value of electrical properties for EVA copolymer containing 7.5, 18 and 28 wt% vinyl acetate.

Table 2.4 Typical Electrical properties of EVA copolymers

Propertiy	Vinyl acetate of EVA copolymer		
	7.5%	18%	28%
Power factor at 50 Hz	0.0016	0.0012	0.0008
Power factor at 10(6)Hz	0.014	0.035	0.043
Permittivity at 10(6)Hz	2.46	2.7	2.95
Apparent Volumn Resistivity 1 mm value (ohm-cm)	2×10^{17}	2.5×10^{16}	3×10^{14}
Dielectric strength (Kv-mm^{-1})	20	20	20

2.2 Natural Rubber

Natural rubber is a solid product obtained through coagulating the latex produced by certain plants, particularly the Brazilian rubber-tree (Hevea Brasiliensis). This raw material is usually tapped from the rubber tree, which is native to Amazonia. Although there a large number of species that exude secretions similar to latex when the bark is cut, only a few produce sufficient quantities of a quality adequate for exploitation on economic bases.

Natural rubber is a polymer whose repeating unit is cis-1,4-isoprene that show in figure 2.4. This material, obtained from the bark of the rubber tree, has been used by humans for many centuries. It was not until 1823, however, that rubber became the valuable material we know today. In that year, Charles Goodyear succeeded in "vulcanizing" natural rubber by heating it with sulfur. In this process, sulfur chain fragments attack the polymer chains and lead to cross-linking. The term vulcanization is often used now to describe the cross-linking of all elastomers. The vulcanization process was shown below in figure 2.5
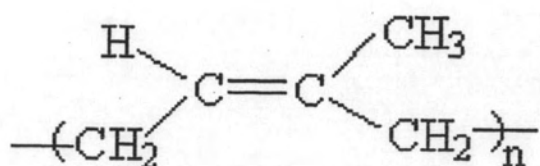
Figure 2.4 Natural rubber chemical structure poly(*cis*-1,4-isoprene)
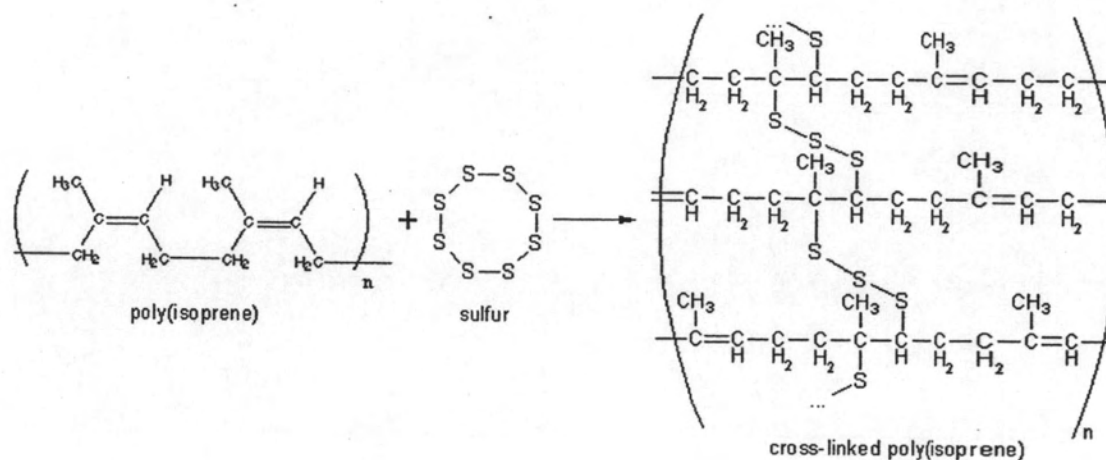

Figure 2.5 Vulcanization process of natural rubber by sulfur

Vulcanization is generally considered to irreversible process [5]. The irreversible cure reaction defines cured rubber compounds as thermoset materials, which do not melt or heating. Usually the actual chemical crosslinking is done with sulfur, because on polyisoprene molecule there are a number of sites reactive to sulfur atom, but there are other technology to use peroxide based system to vulcanization. During vulcanization the eight-member ring of sulfur break down to smaller size with varying number of sulfur atoms. These parts are quite reactive. At each active site on rubber molecule, one or more sulfur atoms can attach in three dimensions, and from there the sulfur can grow, until it eventually reach a cure site on another rubber molecule. These sulfur bridges are typically from two to ten atoms which usually call "crosslink". These crosslink must be sufficiently frequent to prevent polymer chain from sliding over each other but not frequent enough to destroy their flexibility; in practice about 1 % of repeating units take part in the vulcanization process [6]. The number of sulfur atoms in a crosslink chain has

strong influence on the physical and chemical properties of the rubber product. Short sulfur crosslink, which just one or two sulfur atom on crosslink section give rubber have a good heat resistance. Crosslink with higher sulfur atom, up to six or seven, give the rubber have very good dynamic properties but poor in heat resistance. Dynamic properties are important for molecular movements of rubber

Since Goodyear was so successful and correct in his comments about vulcanized rubber, he also created one of the most difficult materials to recycle, as it will mot melt, dissolve or lend it self to the usual methods of chemical decomposition. Interestingly, Goodyear recognized the need for methods of reuse of his spent rubber articles and in 1853 he patented the ideal of adding vulcanized rubber powders to virgin material, a process know as regrind blending today [6].

Recently, the importance of recycling waste materials has been increasing for all industries worldwide. Rubber waste is usually generated during the manufacturing process of products for these industries and by disposal of post.
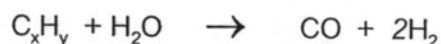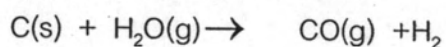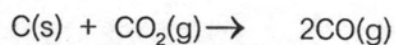
2.3 Thermochemical process

2.3.1 Combustion

Combustion of the generation of electric power is familiar to the utility industry, although fossil resource, especially coal, have been more commonly employed than other materials.

Solid-fuel combustion consists of four steps: heating and drying, pyrolysis flaming combustion, and char combustion. No chemical reaction occurs during heating and drying. Water is driven off the fuel particle as the thermal front advamces into the particle. Once water is driven off, particle temperature rise high enough to initiate pyrolysis, a complicated series of thermally driven reactions that decompose organic compounds in the fuel. Pyrolysis proceeds at relatively low temperature in the range of 225-500°C to release volatile gases and form char. Oxidation of the volatile gases results in flaming combustion. The ultimate products of volatile combustion are carbon dioxide (CO_2) and water (H_2O) although intermediate products can include carbon monoxide (CO), condensable organic compounds and soot.

2.3.2 Gasification

Gasification is the partial oxidation of solid fuel at elevated temperature to produce a flammable mixture of hydrogen (H_2), CO, and CO_2 known as producer gas [7] [8].

Gasification consists of: heating and drying, pyrolysis, solid-gas reactions that adjust the final chemical composition of the producer gas. The mixture of products mainly consists of hydrogen, carbon dioxide, carbon monoxide, gaseous hydrocarbon, volatile and non-volatile substances will reform in accordance with the follow reaction [9];

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2$$

$$CO(g) + H_2O \rightarrow CO_2(g) + H_2$$

$$C_xH_y + H_2O \rightarrow CO + 2H_2$$

$$C_xH_y + CO_2 \rightarrow 2CO + 2H_2$$

2.3.3 Pyrolysis

Pyrolysis is defined as thermal decomposition of macromolecules by thermal energy in the absence of oxygen. This decomposition results in breaking of molecular bonds and fragmentation into small molecular species that related to constituents in their original materials. The degradation of molecules which occurs during pyrolysis is caused by the dissociation of chemical bonds and the production of free radicals. Pyrolysis products from organic materials contain gas, oil, and solid residue, which may be utilized as fuel, recycle materials and monomer. Pyrolysis was applied to reduce and recycle industrial wastes. For example, waste tires pyrolysis for gas production [10].

In 2003, N. Angela *et al* [11] investigated products from pyrolysis and combustion of different refuse constituents in a laboratory scale reactor at 850 °C. The

wastes selected in this work were PE, EVA, PET, cellulose, Kraft lignin, almond shells, and municipal solid waste (MSW). This research was focused on the fate of carbon dioxide, light hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs). Different burning behaviors could be distinguished between plastics and lignocellulosic materials. They found that the amount of volatiles emitted by plastics is higher than that generated by lignocellulosic degradation. The major products from degradation are light hydrocarbons, common to all the refuse decompositions are methane, ethylene, benzene, toluene, acetylene, and 1,3-butadiene. In the case of semi-volatile compounds, styrene, indene, naphthalene, methylnaphthalene and acenaphthylene represent the major yields. Two years later A. Marcilla, A. Gómez, and S. Menargues [12] studied the evolution of gas evolved during the thermal pyrolysis of three commercial ethylene-vinyl acetate copolymers (EVA) by TG/FTIR in N_2 atmosphere. They found the formation of acetic acid, CO and CO_2 in the fist decomposition step (elimination of acetoxic groups) and the formation of a complex hydrocarbon mixture (cracking of the polymer chain) including alkane, alkenes, and mononuclear aromatic compounds in the second decomposition step.

2.4 Microwave

2.4.1 Basics

Microwaves (frequencies of 0.3 GHz to 300 GHz and wave lengths of 1 to 1 mm) lie between radio wave frequencies (RF) and infrared (IR) frequencies in the electromagnetic (EM) spectrum. Microwaves can be reflected, transmitted and/or absorbed. The absorbed microwave energy is converted in to heat within the material, resulting in an increase in temperature. Gases, liquids and solids can interact with microwave and be heated. Under certain conditions gases can be excited by microwaves to form plasmas that also can be useful for processing. Figure 2.6 shows the electromagnetic spectrum and some applications performed at various frequencies along with example of electric volumetric heating.
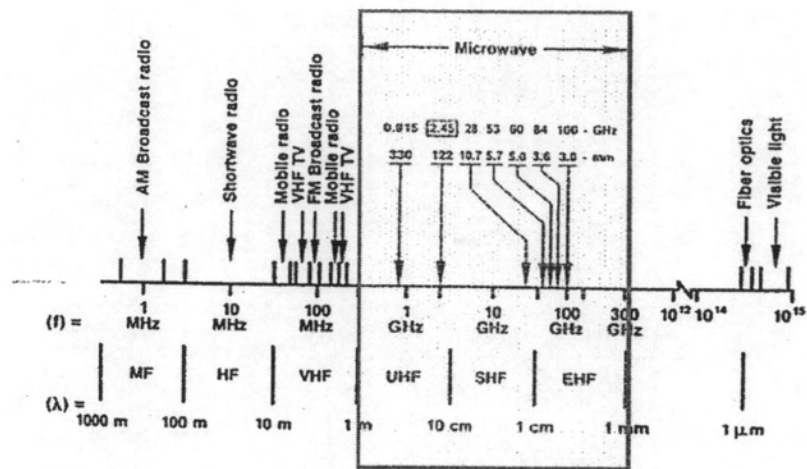
Figure 2.6 Electromagnetic spectrum in the range of microwave

2.4.2 Microwave Heating

The use of microwave radiation for practical purpose was investigated during the Second World War, in the course of intensive research on electromagnetic radiation in the frequency range from 500 MHz to 100 MHz in the development of high-definition radar. At that time the magnetron valve was invented; this is a very high-power source of microwaves with outstanding efficiency. Further development led to the introduction of microwave radiation to processing equipment by using it for heating.

Microwave heating is categorized as an electric volumetric heating method or uniform heating [3]. In figure 2.7, the wall of the oil bath was heated first there is always a temperature difference between wall and the mixture. In the case of microwave heating, only the microwave absorber materials are excited, which result the uniform heating of of the mixture.
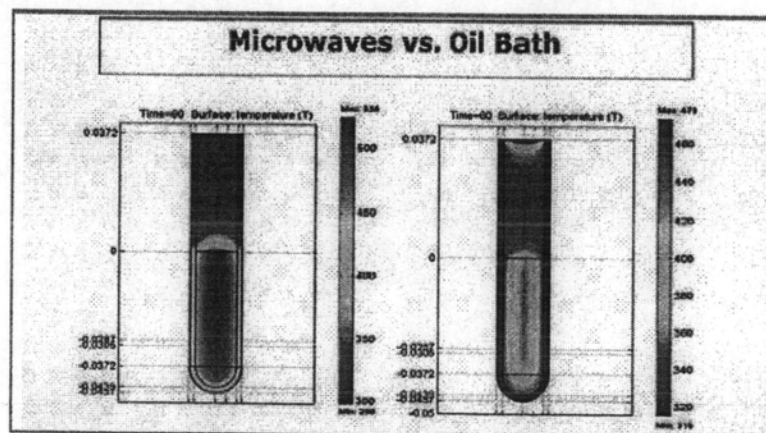

Figure 2.7 Uniform heating through microwave radiation (left) and oil bath (right)

Microwave heating is performed using frequencies close to 900 MHz (3.33 cm) and at 2.45 GHz (12.2 cm). These frequencies were chosen by international agreement to avoid interference with other bands allocated for other uses such as mobile telephony.

Microwave heating is a process tool that has a number of advantage over other, more traditional, heating method. Conventional heating is normally performed through a heated surface and is therefore governed by the temperature of that surface. Also, heating is limited by the physical properties of the material, such as density, heat capacity, and heat conductivity, i.e. the thermal diffusitivity of the material. Microwave heating on the other hand is associated with a more even distribution of heat that leads to easier control over the temperature profile in the heated material. There are basically three mechanisms are heated in a microwave field. These mechanisms arise from the displacement of charged particles in the material when they are subjected to microwave radiation and are summarized as follow [3]:

- The electron around the nuclei (electronic polarization) or the atomic nuclei themselves (atomic polarization) are displaced from there equilibrium position, giving rise to induced dipoles, which respond the applied field. In some materials (such as water) there are permanent dipoles due to the asymmetric charge distribution in each molecule. The dipoles, either induced or permanent, tend to reorient under the influence of a changing electric field.

- Another type of polarization arises from charge built-up in the contact area or interface between difference components in heterogeneous systems. This phenomenon is also known as interfacial polarization and is due to the difference in the conductivities and dielectric constants of the materials at interfaces. The accumulation of space charge is responsible for field distortions and dielectric loss and is commonly termed "Maxwell-Wagner polarization"

- Ionic conduction: some materials produce electric currents within themselves when subject to electric fields. When this electric currents flow within the structure of the materials, which in most cases have a relatively high resistivity, the materials is heated
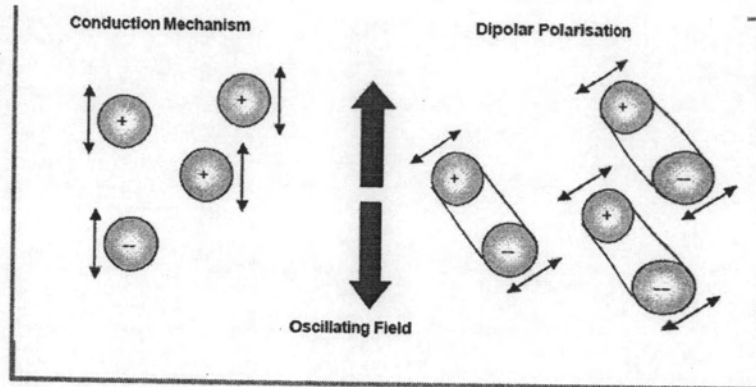
Figure 2.8 Method of heating by microwave radiation

Although most existing microwave heating process are used to heat up materials, mainly water, that have permanent dipoles, some processes use the other two mechanisms. Microwave heating unique and offers a number of advantage over conventional heating such as [13].

- non-contact heating
- energy transfer, not heat transfer
- rapid heating
- material selective heating
- volumetric hating
- quick start-up and stoping
- heating start from interior of the material body
- highly level of safety and automation

The extent to which a materials is heated when subjected to microwave radiation depends on two parameters: the dielectric constant ε' and the dielectric loss factor ε''. The dielectric constant describes the ease with which a material is polarized by electric field, while the loss factor measures the efficiency with which the electromagnetic radiation is converted into heat. The ratio of these properties gives the dielectric loss tangent or dissipation factor:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \ \text{------------------------------------}(2.1)$$

Which defines the ability to absorb and convert electromagnetic energy into thermal energy at a given temperature and frequency. On the other hand a material with high 'loss' factor is easily heated by microwave energy. In fact, ionic conduction and dipolar rotation are the two important mechanisms of microwave energy loss. Since microwave heating depends mainly on the characteristics of the workload, when a material is suitable for this type of heating, the source of microwave radiation enable high temperature and high rate of heating and show excellent efficiencies of conversion of electrical energy in to heat (80-85%).

Microwave are reflected from surface and therefore do not heat metals because metals in general have high conductivity and are classed as conductors. Conductors are often used as conduits (waveguide) for microwaves. Materials which are transparent to microwave are classed as insulators. Insulator are often used in microwave oven to support material to be heated. Materials which are excellent absorbs of microwave energy are easily are class as dielectrics materials

Non-homogeneous materials (in term of electric property) may not heat uniformly, that is, some part of materials heat faster than others. This phenomenon is often referred to as thermal runaway. This condition can be minimized by keeping the sample in mixing or fluidized condition. The effectiveness of a microwave heating of semiconductor material is dependent on the initial temperature. In fact, above a certain critical temperature even insulator materials become responsive to microwave heating. The extent of microwave heating also dependent on the size of the material; for example, a metal in fine particle size can be heated by microwaves through a microarching process. In addition, low lossy or insulator materials can be heated with a microwave heat facilitator, such as, magnetic, silicon carbide or carbon. Microwave energy first heats the facilitator, which subsequently heats the insulator or low lossy material.

2.4.3 Microwave pyrolysis

For microwave pyrolysis, it was tested by Tech-En company LTD [14]. They mixed plastic wastes with microwave absorber such as carbon and found that the temperature can be reached to 1,000 °C within a short time. Nowadays, this technique is widely used to pyrolyze tire, chlorofluromethane, pentachlorophenol, wood, coal and municipal solid wastes [15].

2.4.3.1 Microwave and plastics

Thermoplastics (with exception of Nylon) normally have very low dielectric constants and low loss factor and therefore there is limited scope the use of microwave in their processing. This is further aggravated by the fact that when plastics start to heat and molecular mobility increases, the absorption of microwaves also increases and, at the gel transition or melting point, it can increase substantially. This can result in 'thermal runaway' where increasing amounts of microwave energy are absorbed as temperature rises. This effect could result in a poorly controlled pyrolytic reaction or combustion, depending on the condition. For some thermoplastics there is a 'critical temperature' for microwave heating which has been shown to correspond to molecular segments can move on a timescale similar to the exciting microwave energy. Microwave pyrolysis of plastic wastes is a relatively area that has been studied and less information in the sciencetific literature compared with other approaches to the pyrolysis of plastic, in 2001 C. Ludlow-Parafox and H. A. Chase [14] investigated the microwave-induced pyrolysis by the degradation of high-density polyethylene and aluminum/polymer laminates. They found that this process has the same general features as other, more traditional, pyrolytic processes but with the advantage that it may be applied to problematic wastes such as laminates. They reported that clean aluminium was recovered together with hydrocarbons.

2.4.3.2 Microwave pyrolysis of plastics

As mentioned in the previous section, plastics are not able to heat up efficiently or controllably to a temperature high enough for them to pyrolysis. The most efficient solution involves, mixing plastics with a microwave-absorbent material (this is what is know as microwave-induced pyrolysis). In a sense this process utilizes a 'fourth'

method for microwave heating since microwaves are used as indirect source of heat. Graphitic carbon and some inorganic oxides are materials that are used as microwave-absorbents, with carbon having a predominant role due to its low price and high abundance. When subjected an electromagnetic field at microwave frequencies, some molecular structures of carbon absorb energy, which is subsequently converted by ionic conduction and dipole rotation. This method is usually use to treat ceramic materials [3] and remediation contaminated soil [16].

Microwave is currently used to heat carbon for sintering in the ceramics industry, achieving good heating rates and high temperature. Ceramics have very low loss factors for microwave processing at low temperature, however, when the temperature reaches a certain value, the electrical conductivity of the ceramic drastically increases and sample rapidly heats. Carbon has been to accelerate the first of the heating process by applying a very thin coat (0.01mm) of the ceramic surface.

C. Ludlow-Parafox and H. A. Chase [14] investigated the relationship microwave-induced pyrolysis by the degradation of high-density polyethylene and aluminium/polymer laminates .They founded that this process has the same general features as other, more traditional, pyrolytic process but with the advantage that it is able to deal with problematic wastes such as laminates. They reported that clean aluminum was recovered together with hydrocarbons.

Another area where microwave heating is used to heat is in the regeneration of activated carbons. When spent activated carbon is subject to a microwave field, the heat generated within the particles produces rapid temperature rises and the release of other compounds absorbed on the carbon. In a similar process, carbon used as absorbent to remove NO_x and SO_x from gas stream can be regenerates with microwaves producing CO_2 and N_2 as gases and elemental sulphur.

In microwave pyrolysis of plastics, when carbon (or other microwave absorbent) is exposed to a microwave field, it can reach temperature up to 1,000 °C in a few minutes. Evidently this depend on the amount of carbon and power of microwave field. If shredded plastics are mixed with the carbon, prior to or during heating, the energy absorbed from the microwaves is transferred to the plastics by conduction, providing a very efficient energy transfer, and if carbon is used as microwave-absorbent, a highly

reducing chemical environment. The latter avoids formation of undesired oxygenated organic compound, in case oxygen present in the system with in molecules of plastifers, additive, paint, inks or other materials such as paper and bio-waste. The basic aim of this pyrolytic method is to provide a process for the disposal of plastic wastes, making use of the high temperatures that the carbon achieves when subject to a microwave field, and has advantage over other more convention pyrolytic processes. In summary, microwave pyrolysis combines the advantage of microwave heating with the environmental benefits and commercial opportunities arising from the pyrolysis wastes.

Microwave pyrolysis has been proven to be useful process to treat some real plastic wastes. In 2001, C. Ludlow-Parafox and H. A. Chase [14] investigated the relationship microwave-induced pyrolysis by the degradation of high-density polyethylene and aluminium/polymer laminates .They founded that this process has the same general features as other, more traditional, pyrolytic process but with the advantage that it is able to deal with problematic wastes such as laminates. They reported that clean aluminum was recovered together with hydrocarbons.

2.4.3.3 Microwave pyrolysis of other materials

Examples exist of other processes, in which microwave heating of microwave-absorbents is used as away to transfer energy to a microwave-transparent material. For example, the pyrolysis of chlorodifluoromethane has been carried out in a microwave-heated fluidized bed with a performance comparable to that of tubular reactors, the best traditional equipment for the pyrolysis of this compound.

The simultaneous decomposition of pentachlorophenol and regeneration of activated carbon, using microwaves was reported, claiming that the quality of the carbon was maintained or actually increased after several adsorption/microwave-regeneration cycles. Carbon, in graphite form, has also been used as a microwave absorbent for the microwave pyrolysis of urea.

Similarly, microwave have been used for pyrolysis of coal, which is known to have very poor microwave absorption, by mixing it with inorganic oxides or with carbon. After the initial stages of pyrolysis the coal undergoes some graphitization, turning into

carbon black that further absorbs microwaves. Moreover, L. Bilali *et al* [17] studied the heating process of Moroccan rock phosphate under the microwave irradiation.

Microwave pyrolysis has also been tested with materials that, even though they are dielectric, contain some molecules responsive to microwave fields and can therefore absorb microwaves, heat up and pyrolysis. Examples are wood blocks [18], and cellulosic materials [19].

Another material that now interest to treated with microwave pyrolysis has been sewage sludge. Disposal of this material, which is a by-product in microwave treatment process, is a considerable problem and currently accounty for up to 60% of operational cost of wastewater treatment plants. Microwave pyrolysis of sludge provides a rapid and efficient process with reduced process time and energy requirements compared with conventional pyrolysis. It have many research that interest to applied microwave to pyrolysis of sewage sludges. Almost of them describe products of process in three components (liquid, gas, and solid). In 2002, J.A. Menéndez, M. Inguanzo, J.J. Pis [20] studied a new method for pyrolyzing sewage sludge with microwave heating. They found that temperature can be raised to 900 °C if sewage sludge is mixed with small amount of suitable microwave absorber such as char. When compared with conventional heating, microwave heating saves considerable time and energy for a similar degree of pyrolysis.

In the case of liquid products, in 2003 A. Domínguez *et al* [21] studied oil from pyrolysis of sewage sludge in a microwave oven using graphite as microwave absorber. The oil composition was analyzed by GC-MS. They found that the oil from the microwave oven had *n*-alkanes, 1-alkenes and aromatic compound but detected no PAHs. In contrast, PAHs were founded in the experiments with electric oven. Two years later, A. Domínguez *et al* [22] studied main component of high temperature oils obtained from the microwave pyrolysis of sewage sludge under different conditions (multimode, single mode and graphite, char microwave absorber). Although qualitative composition was the same for both microwave ovens, certain quantitative differences were observed. Microwave heating required shorter time for pyrolysis and oils obtained were more aliphatic and oxygenated and contained no environmentally harmful compounds such as heavy PAHs. They suggested that microwave radiation is a good method for drying,

pyrolyzing and gastifying sewage sludge in one single step. Recently A. Domínguez *et al* [23] studied oil product from pyrolysis of sewage sludge using microwave and electrical ovens as the source of heat. The use of conventional electric heating in the pyrolysis of sewage sludge produced oil that could be have a significant environmental and toxicological impact. Conversely, microwave pyrolysis still preserved some of the functional groups of the initial sludge such as aliphatic and oxygenated compounds. Furthermore, the condensables from microwave pyrolysis contain less carcinogenic compounds than those produced in conventional pyrolysis and the noncondensables have a higher concentration of CO and H_2 (synthesis gas) after microwave pyrolysis than after conventional pyrolysis. Furthermore, almost of research have the same conclude that the condensables from microwave pyrolysis contain less polycyclic aromatic hydrocarbon (PAHs) than those produced in conventional pyrolysis. On the other word, microwave pyrolysis is environmental friendly process.

In the case of gas production, J.A. Menéndez *et al* [24] studied pyrolysis of four types of sewage sludge by multimode-microwave oven and compared with those from a conventional pyrolysis employing an electrical furnace. It was found that microwave pyrolysis gave rise to gas product with high content (up to 62%) of CO and H_2 (synthesis gas) while conventional pyrolysis generated a gas with an elevated propotion (ca 25%) of hydrocarbon of high calorific value.

In the case of solid residue, Masakatsu Miura *et al* [25] investigated large-scale microwave rapid pyrolysis of cellulosic materials. Levoglucosan was obtained from a larch log as the main anhydrosugar in 2.6% yield on the basis of dry wood weight. The yield would be much higher than that obtained from conventional pyrolysis in the large-scale reaction.

2.5 Characterization of pyrolysis products

2.5.1 Gas Chromatography/Flame Ionized Detector

Gas chromatography (GC) is a dynamic method of separation and detection of volatile organic compounds and has chosen as an attractive method to analyze the complex mixture of pyrolysis products. GC involved the partitioning of gaseous solutes between an inert carrier gs as a mobile phase and a stationary liquid or solid phase.

Figure 2.9 is the major compartments of GC consist of gases, injection port, column, detector and data acquisition system.
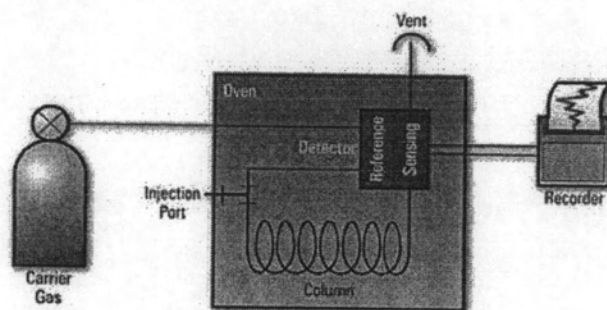

Figure 2.9 Gas chromatrography components

Helium is one of the most commonly used gases to carry the sample through the system. Increase the flow rate of carrier gas results in shortens the retention time. Injection port is the next major component to introduce the sample into the carrier gas stream. A split injection port is designed to allow only small fraction of sample volumn into the column because of a limited sample capacity of the capillary column. Many split injection port can also operate in a splitless mode. In the splitless mode most of the sample is allowed to the column. This technique is suitable for samples with trace concentration. The third major component is column for separation of the components in sample mixture. The more narrow the diameter and the length, the greater the column efficiency to separate sample. The fourth major component of GC is the detector that senses the presences of components separated from the column and convert that information to the signal. The most commonly used detector is Flame Ionizaion Detector (FID) because it responds to any type of hydrocarbon component. When hydrocarbon components burn in a flame, producing ion that are collected and converted into a current signal. As the components are separated and reach the detector, the signal increases and the detection or retention time of each peak is recorded and translated into a chromatography by data acquisition system.

Gas chromatography is a well- established method in the analysis of pyrolysis products. Identification of pyrolysis-gas chromatography (PY-GC) is based either on the

comparison with know chromatograms or the detailed analysis of pyrolysis products such as the combination with mass spectrometry.

2.5.2 Elemental analysis

Elemental analysis on carbon, hydrogen and nitrogen is performed to characterized and prove the elemental composition of an organic sample to determine the empirical formula of compound. The sample under test is weighted in tin capsule. The sample is then placed into the reactor chamber where excess oxygen is introduced before. At about 990°C the material is mineralized and carbon monoxide is formed at this temperature. The complete oxidation is reached at tungsten trioxide catalyst which is passed by the gaseous reaction products. The resulting mixture should consist of CO_2, H_2O, NO_x and some excess O_2 passes the catalyst. The product gas mixture flows through a silica tube packed with copper granules. In this zone, remaining oxygen is bound and NO_x are reduced to N_2. So the leaving gas stream consists of CO_2, H_2O and N_2. The gas mixture passed to a gas chromatographic system. The individual components are then separated and elemental mass percentage of element in the sample is measured by thermal conductivity detector (TCD). Elemental analyzer component has shown in figure 2.11.
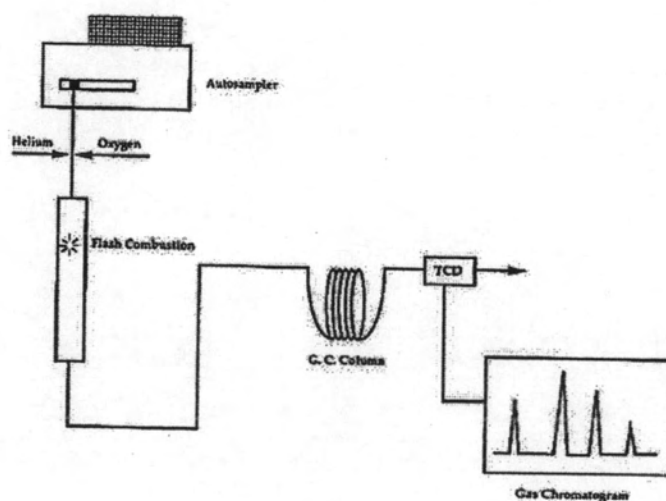

Figure 2.10 Elemental analyzer component.