



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural rubber

Natural rubber (NR) is an unsaturated elastomer that can be converted to a thermoset material by vulcanization (Brydson, 1994). NR is originally derived from a milky colloidal suspension, or *latex*, found in the sap of some plants. The chemical structure of NR is identical to polyisoprene, which is synthetically produced. NR is extensively used in various applications similar to synthetic rubbers. The major commercial source of NR latex is the Para rubber tree (*Hevea Brasiliensis*) which is a member of the spurge family, *Euphorbiaceae*, due to its high latex production. Some NR sources collected from *Gutta Percha* are composed of *trans*-1,4-polyisoprene with different properties. Normally, NR used in the commercial applications mainly composed with *cis*-1,4-polyisoprene as shown in Figure 2.1 with a molecular weight of 100,000 to 1,000,000. In addition, NR consists of approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber substances. Typically, a small amount (up to 5% of dry mass) of other materials, such as proteins, fatty acids, resins and inorganic materials (salts) is found in NR.

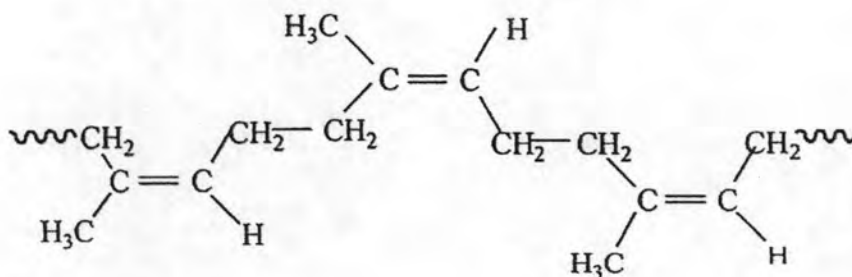


Figure 2.1 Natural rubber or *cis*-1,4-polyisoprene.

NR vulcanizates have excellent physical and mechanical properties for serving as a general purpose elastomer. It has high tensile strength, tear strengths, resilience, abrasion resistance and very low heat build-up (Holfmann, 1989). Even after vulcanization, NR still has carbon-carbon double bonds in the polymer chain. Therefore, it is susceptible to weather, oxygen and ozone resulting to chain scission. This causes the rubber to be softer and weaker (Boonlom Thavorniyutikarn, 1999). Also, NR vulcanizates have poor resistance to swell in the presence of non-polar organic solvents, oil and fuels due to the non-polarity of NR structure. For these reasons, many efforts have been applied to improve the properties of NR to be used in wider applications.

2.1.1 Properties and applications of NR latex

The unique characteristics of NR such as flexibility, resilience, high mechanical properties, and extendibility were attractive for various applications. Condoms and gloves are produced in very large numbers on highly automated production lines. This industry relies almost exclusively on NR latex since its ability to form smooth, continuous films on drying is outstanding and its vulcanizates have high strength and elasticity. In contrast, special medical products are produced on a much smaller and only semi-automated scale. Thin-walled articles are produced by straight dipping. For the thick-walled products (balloons, ultrasound transducer covers, catheters), coagulant dipping or heat sensitive dipping processes is used. NR latex tubes are produced in lengths of 10 meters, which requires a very special dipping line. To minimize the risks of latex-allergy, an intensive washing of all the products for medical applications is very important. In this aspect, producers of medical articles are working on alternative materials to meet the upcoming demand for non-latex products. However, there is no synthetic material with having comparable characteristics to NR latex. The NR latex is not only useful for producing medical gloves, it is also applied for several medical devices such as membranes, diaphragms, blood pressure cuff coils, seals, covers and tubes (Pendle, 1997).

2.2 Properties improvement methods for NR

There are two important methods to improve or modify properties of NR: blending NR with other polymers including both plastics and rubbers (Boonlom Thavornyutikarn, 1999) and chemical modification of NR structure.

2.2.1 Blending method (Orathai Sroysom, 1999)

NR is normally blended with other synthetic rubber (SR) having some properties which cannot be found in NR. For example, NR is blended with ethylene-propylene-diene rubber (EPDM) to improve weathering resistance, or with butadiene rubber (BR) to increase abrasion resistance. NR is also blended with nitrile rubber (NBR) to improve oil and fuel resistance of NR phase with better mechanical properties of NBR phase in the blend. This method is more favorable and economical than the development of new rubber. However, successful blend technology requires a sound scientific basic.

2.2.2 Chemical modification method (Orathai Sroysom, 1999)

The properties of NR can be improved via chemical modification of its molecular structure due to the presence of carbon-carbon double bonds in its repeating unit. The chemical modification of NR can be achieved by one of the following methods:

- Changing the structure or geometry of NR molecules with introducing some new materials.
- Attaching to the NR structure with some functional chemical groups having specific physical characteristics or chemical reactivities.
- Grafting short or long chains of different polymer types onto the NR backbone.

2.3 Chemical modification of NR

Chemical modification method of NR can be categorized into three main categories:

2.3.1 Modification by bond rearrangement without introducing new molecules

Examples of this method are carbon-carbon cross-linking, cyclization, *cis-trans* isomerization and depolymerization:

2.3.1.1 Cross-linking (Engels et al., 2004)

Uncured NR is sticky, easy to be deformed when it is warm and brittle when it is cold. In this state, it cannot be used to make articles with a good level of elasticity. Long polymer chains in NR structure can independently move resulting to change its shape. Thus, crosslinking is introduced by vulcanization to prevent the independent movement of NR. Vulcanization is a chemical process to convert NR into more durable materials via the addition of sulfur or other equivalent "curatives". These additives modify NR via forming crosslinks (bridges) between individual NR chains. The vulcanized NR is less sticky and has superior mechanical properties. Vulcanization is generally irreversible which is similar to other thermosets. The cross-linking is usually done with sulfur including peroxide-based systems. The reactive sites (cure sites) are allylic hydrogen atoms. These C-H bonds are adjacent to C-C double bonds. During vulcanization, some of these C-H bonds are replaced by chains of sulfur atoms to link with a cure site of other NR chains as shown in Figure 2.2. These bridges contain between one and eight sulfur atoms. The number of sulfur atoms in the crosslink strongly influences on the physical properties of the final NR products. Short chains of sulfur crosslink provide NR having better heat resistance; whereas, the crosslinks containing higher sulfur atoms give NR with superior dynamic properties, but lesser heat resistance.

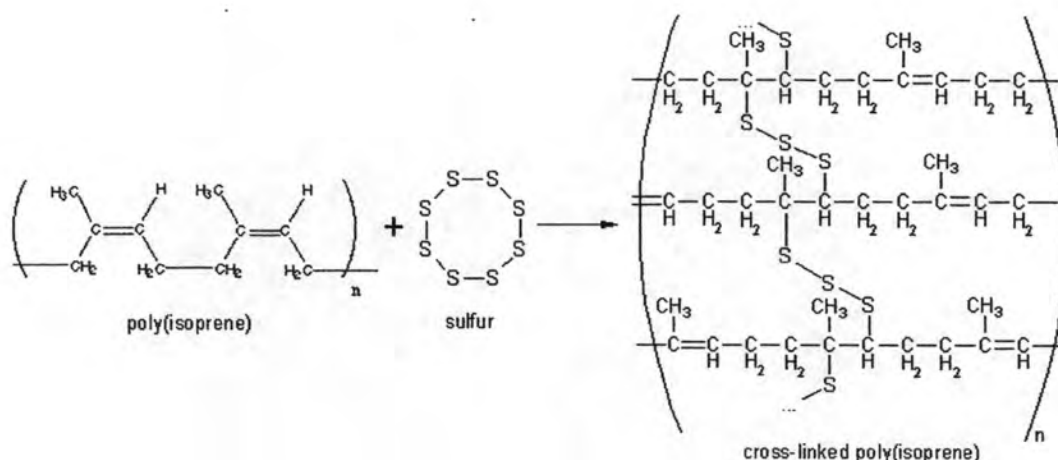


Figure 2.2 Scheme of cross-linking of NR (Engels et al., 2004).

2.3.1.2 Cyclization (Subramaniam, 1988: 762-86 cited in Boonlom Thavornytikarn, 1999)

Cyclized rubber is obtained by treating the rubber with strong protonic acid or Lewis acids. Cyclization is believed to proceed via the carbanium ion mechanism as shown in Figure 2.3 (Boonlom Thavornytikarn, 1999). Cyclized NR is a brittle resin, powder, hand sheet or crepe. It has higher density (sp. gr. = 0.96-0.99) with softening point (90-130°C) and lower solution viscosity than those of NR (sp. gr. = 0.91, $T_g = -68^\circ\text{C}$). Actual properties values are depended on the degree of cyclization. Cyclized and partially cyclized NR have been used for shoes soles, hard moulding, corrosion-resistant surface and printing ink. However, they have been mostly replaced by copolymers, e.g., cyclized synthetic *cis*-1,4-polyisoprene.

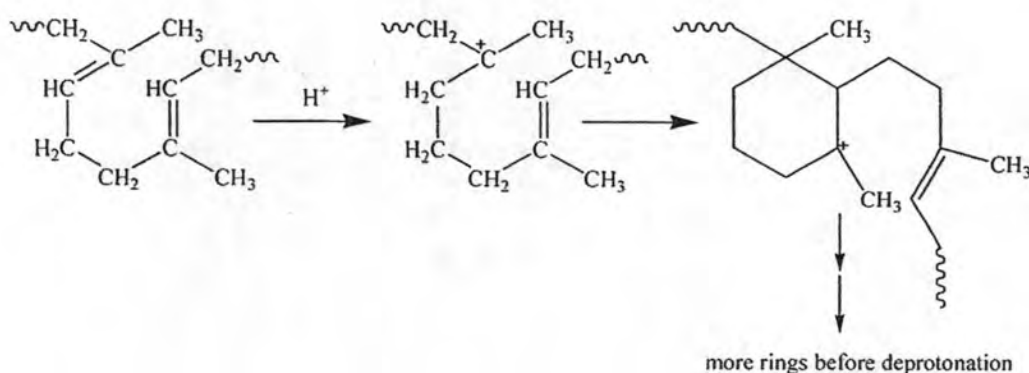


Figure 2.3 Scheme of cyclization of NR (Subramaniam, 1988: 762-86 cited in Boonlom Thavornytikarn, 1999).

2.3.1.3 *Cis-trans* isomerization (Blackley, 1997)

The most attractive way to decrease the crystallization tendency of the NR macromolecules is to isomerize a proportion of the olefinic double bonds to the *trans* configuration. Cunneen and Shipley (1997) have reported that one way of satisfactorily achieving partial *cis-trans* isomerization of NR is to heat the NR latex with a small amount of an alkane or arylencarbothiolic acid (R-CO-SH), together with a free-radical generator such as cumene hydroperoxide, tert-butyl hydroperoxide. The product of such reaction is a rubber with much less prone to irreversible low-temperature hardening than unmodified NR. The change is believed to be a consequence of partial *cis-trans* isomerization.

2.3.1.4 Depolymerization

Liquid NR (LNR) is produced from the depolymerization of NR to have shorter polymeric chains. It is tacky but has excellent crosslinking reactivity with lower molecular weight (M_w) less than 10^5 . The properties of LNR are depended on the production techniques: peptization, thermal methods, mechanical methods, photolysis and redox methods. For photolysis methods, a source of light such as solar radiation, ultraviolet light or visible light is used together with 'chain breaker compounds' like nitrobenzene, hydrogen peroxide or photosensitizers. Figure 2.4 shows the depolymerization process of NR in the presence of ultraviolet and nitrobenzene (Turro, 1988).

From the redox methods, reducing agents (*p*-methyl-benzene sulfinic acid, phenylhydrazine, sodium chlorite, sodium nitrite and sodium hypochlorite) and oxidizing agents (hydrogen peroxide or its derivatives) are used (Gan et al., 1990). The mechanism of the depolymerization using a phenylhydrazine/oxygen system is shown in Figure 2.5. LNR can be used as viscosity modifier, adhesive, tackifier, sealing agent, and plasticizer to improve the processability of rubbers used in tire compounds (Kawasaki, Miyamoto and Tanaka, 1998).

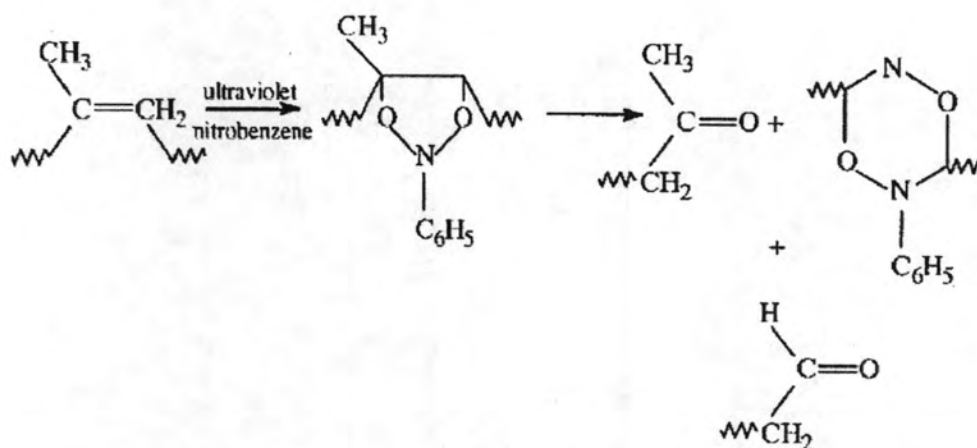
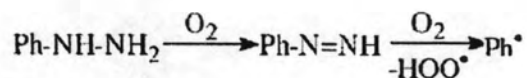


Figure 2.4 Scheme of depolymerization of NR by ultraviolet and nitrobenzene (Turro, 1988).

Oxidation of phenylhydrazine:



Depolymerization by Ph[•] radicals:

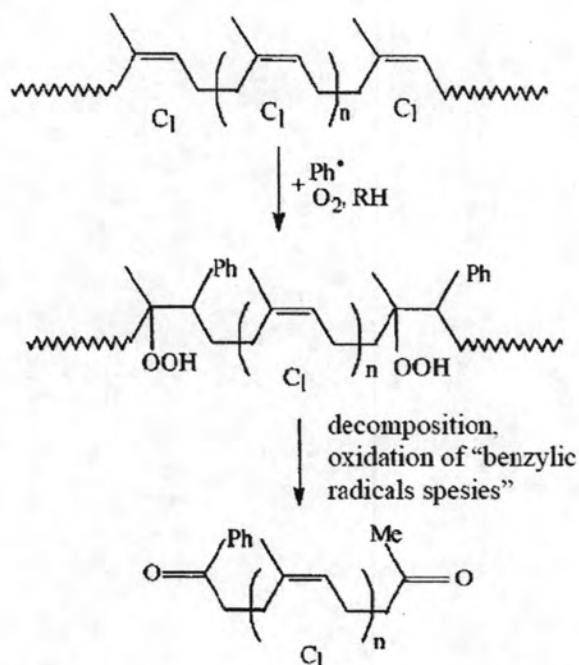


Figure 2.5 Scheme of preparation of LNR using phenylhydrazine/oxygen system (Kawasaki, Miyamoto and Tanaka, 1998).

2.3.2 Modification by attachment of new chemical groups at olefinic carbon carbon double bonds

Examples of this method are hydrogenation, halogenation, hydrohalogenation, epoxidization and ene reaction.

2.3.2.1 Hydrogenation (Bhowmick and Stephens, 2001)

Complete hydrogenation of NR gives an alternating copolymer of ethylene and propylene. Scheme of NR hydrogenation is presented in Figure 2.6. NR hydrogenation can be performed by using catalysts and hydrogen gas passed through NR dissolved in organic solvents. Catalyst systems may be conveniently classified into four groups: metal and supported metal catalysts, noble metal catalysts, organometallic systems and diimide generators. Hydrogenated NR (HNR) is more crystalline and has a slightly higher glass transition temperature than that of NR. The HNR vulcanizates with high hydrogenation degree show higher thermal and ozone resistance.

2.3.2.2 Halogenation (Subramaniam, 1988: 762-86 cited in Boonlom Thavornnyutikarn, 1999)

Chlorination, one of halogenated rubber types, has been extensively studied. The reaction is complex and may include addition, substitution, cyclization, crosslink and degradation. Chlorination can be carried out in the solid rubber state or in the solution state or by letting the latex react with gaseous chlorine. However, traditionally chlorinated NR (CNR) is prepared by dissolving NR in a solvent before chlorination. CNR is used as raw material for paint because of its resistance to wear, acids and alkalis, ageing and corrosion from sea water.

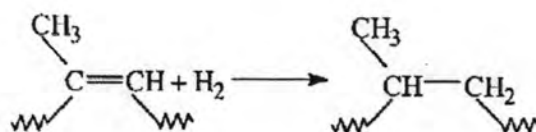


Figure 2.6 Scheme of hydrogenation of NR (Kroschwitz, 1987).

2.3.2.3 Hydrohalogenation (Bhowmick and Stephens, 2001)

Hydrogen chloride is added into NR to give a hydrochloride rubber. The addition follows the Markonikov's rule, but it is also accompanied by some cyclization. The scheme of hydrohalogenation of NR is shown in Figure 2.7. The hydrochloride rubber has high crystallinity and it is also a tough semi-elastic material which can be used as a packaging film and a rubber-to-metal adhesive. This kind of hydrochloride rubber is normally produced in a powder form which is unstable. For the hydrochloride rubber with low degree of crystallinity, it shows the elastic properties with higher stability to heat and bases. However, this hydrochloride rubber with low crystalline content becomes more brittle material at room temperature. Consequently, it has not been commercially produced.

2.3.2.4 Epoxidization (Gelling and Porter, 1988)

Epoxidation can be carried out in solution or latex form, but the latex form is commercially produced. Peracid is usually used in the epoxidation of NR in latex form because of its compatibility with the aqueous system. The mechanism of NR epoxidation is shown in Figure 2.8. The degree of epoxidation is depended on the reaction conditions. The epoxidized NR (ENR) is an elastic material with higher density than NR.

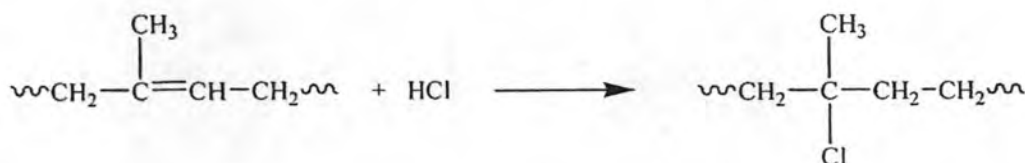


Figure 2.7 Scheme of hydrohalogenation of NR (Bhowmick and Stephens, 2001).

After epoxidation, the glass transition temperature (T_g) of ENR linearly increased by 1°C for every mole percentage of epoxidation resulting the reduction of resilience and air permeability with higher hysteresis. Due to the higher T_g , some mechanical properties of ENR such as tensile and fatigue behavior, damping properties, bonding to metal and wet grip are expected to be better than those of NR. However, the wet traction of ENR is better. The epoxy groups also increase the polarity to enhance the hydrocarbon oil resistance. ENR can be potentially applied in engineering components such as inner liners of tubeless tyres, oil seals and tire treads.

2.3.2.5 Ene reaction (Bhowmick and Stephens, 2001)

The general ene reaction with NR represented in Figure 2.9. This reaction is not related to active species such as ions and free radicals which act as intermediates. The ene reaction applied to NR leads the concept of rubber-bound

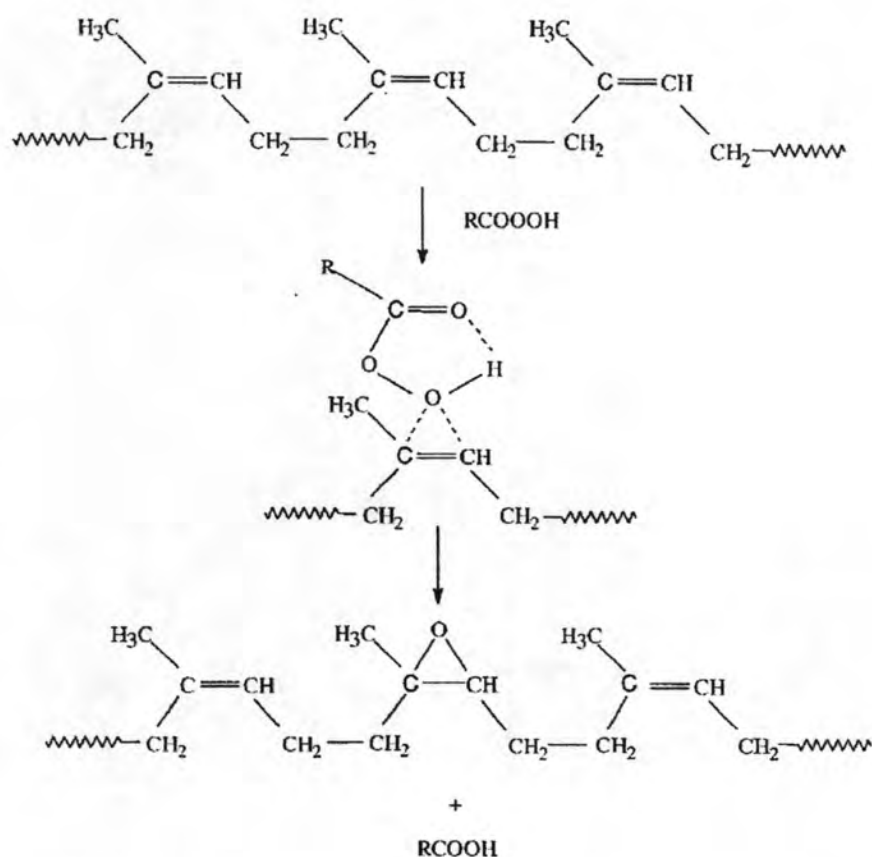


Figure 2.8 Scheme of mechanism of NR epoxidation with a peracid (Gelling and Porter, 1988).

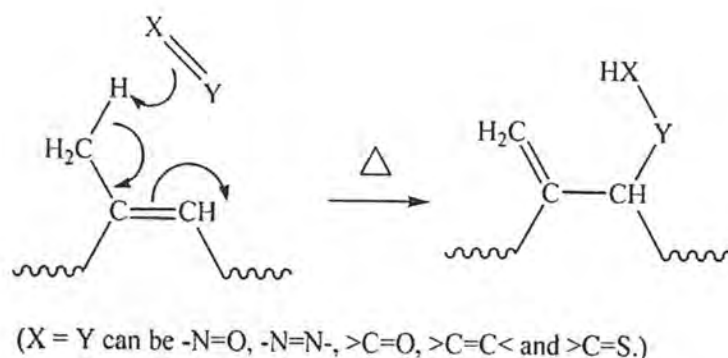


Figure 2.9 Scheme of ene reaction of NR (Bhowmick and Stephens, 2001).

antioxidants. The initial stage of the ene reaction involves the reaction between the rubber and a nitroso compound. Nitrosoarenes give a hydroxylamine as a main product. Such antioxidants are not leached during washing or solvent treatment. Thus, it may be useful for a rubber tread for garments. However, this process has not been exploited because of the formation of coloured by-products.

2.3.3 Grafting a second polymer onto NR backbone

Graft polymerization of NR can be carried out in solution, solid rubber, and latex phases; however, the latter is the most economical and practical method. Studies on the preparation, characterization and properties of graft copolymer of NR with acrylonitrile (ACN), methyl methacrylate (MMA), methyl vinyl ketone, styrene, caprolactone and polyethylene using various initiator systems have been reported (Brandrup, 1989 and Krause, 1978). However, Hammer et al. (1957) found that MMA and styrene were the most suitable monomers for graft copolymerization onto NR to yield high grafting levels. Graft copolymerization of NR and vinyl polymers is prepared by polymerization of a monomer initiated by free radicals or attachment of a polymer to the rubber backbone. The backbone and the branches polymers may be homopolymer or copolymers with different chemical nature or composition. The simplest case of graft copolymer can be represented by the following structure as shown in Figure 2.10, where A and B are two different monomers. The properties of graft copolymer are different from a random copolymer (ABABABAB) or a physical mixture consisting of two homopolymers from $(A)_n$ and $(B)_n$ (Odián, 2004).

The mechanism of grafting copolymerization onto NR chains consists of 3 steps: initiation, propagation and termination. Cumene hydroperoxide (CHPO)

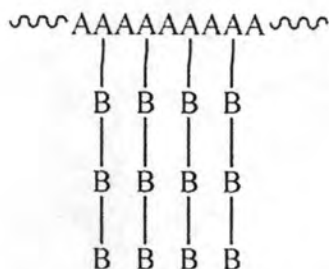
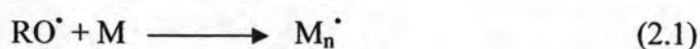


Figure 2.10 Scheme of model of graft copolymer (Odian, 2004).

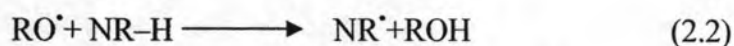
in the dilute aqueous solution induced by Fe^{2+} used as an initiator will decompose to alkoxy radicals (RO^\bullet). For initiation step, alkoxy radicals might attack either the monomer (M) (Eq. 2.1) or the rubber molecule (Eq. 2.2) to produce monomer radicals (M_n^\bullet) and polyisoprene radicals (NR^\bullet), respectively as grafting sites. During formation of the graft copolymers, the surfaces of latex particles become the loci of polymerization. α -Methylene hydrogen atoms (H) of NR (NR-H) can also become the site of graft copolymerization due to its more active. The alkoxy radical can attack α - methylenic hydrogen atoms to form polyisoprene radicals (NR^\bullet) to initiate monomers for producing graft copolymer radicals (NR-M_n^\bullet) (Eq. 2.3). For propagation step, NR-M_n^\bullet attacks M to form graft copolymers (NR-M_{n+1}) (Eq. 2.4) or M_n^\bullet attacks M to form free copolymer radicals (M_{n+1}^\bullet) (Eq. 2.5). Then, the M and NR-M_n^\bullet will either combine with NR^\bullet to terminate the process or transfer to NR via chain transfer agent (A) to form NR-M_n^\bullet (Eq. 2.6-2.10). Finally, the NR-M_n^\bullet can also terminate the process by reacting with free copolymers (Eq. 2.10-2.13) on the surfaces of latex particles (Wanvimon Arayapranee et al., 2002).

Initiation:

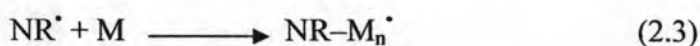
Attacking monomer:



Attacking rubber:

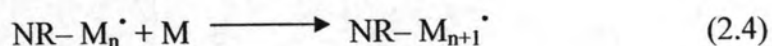


Reinitiation:

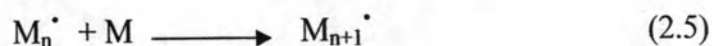


Propagation:

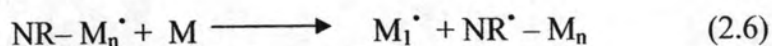
Propagation of graft polymerization:



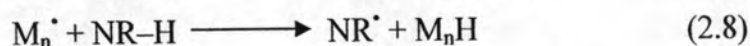
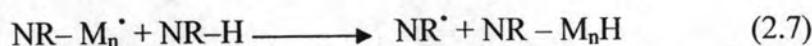
Propagation of free polymerization:

**Chain transfer to macromolecules:**

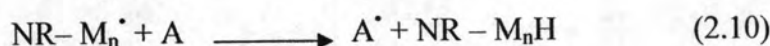
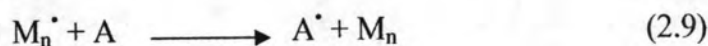
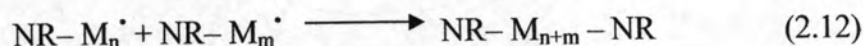
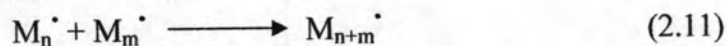
Transfer to monomer:



Transfer to rubber:



Transfer to chain-transfer agent:

**Termination by combination:**

Normally, there are two methods to synthesize graft copolymers. (Narawadee Chansook, 2001):

1. The side chain polymer can be directly linked by a suitable chemical reaction to the backbone polymer.
2. The backbone polymer can be initiated to occur active sites such as free radicals or ions to be used for polymerization of suitable monomers resulting the side chain polymer.

2.3.3.1 Radical graft polymerization

The radical graft polymerization can be carried out by various methods such as chain transfer and copolymerization, ionizing radiation, redox initiation and living radical polymerization.

(a) Chain transfer and copolymerization (Odian, 2004)

The chain transfer reaction is the most well recognized and extensively studied for free radical polymerization. For the graft polymerization of polystyrene (PS) onto polybutadiene (PB) (Figure 2.11), the radicals on PB (1) are formed through chain transfer from PS radicals to PB. The resulting product (2) consists of polystyrene grafted on the backbone of 1,4-poly-1,3-butadiene. Polymer radicals are also formed by attacking on a polymer chain by primary radicals from an initiator. In addition, the C-C double bonds in 1,4-poly-1,3-butadiene are also grafted by the PS radicals initiated via chain transfer as shown in a product (3).

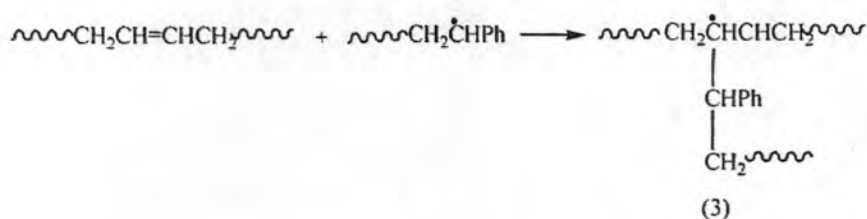
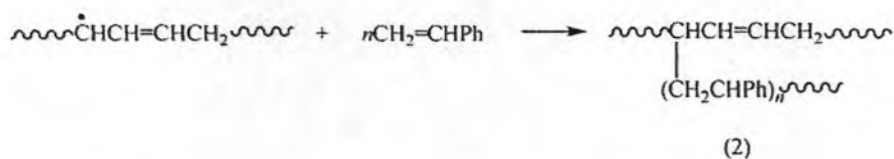
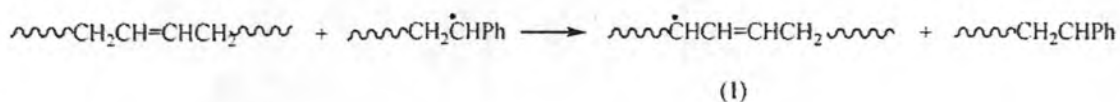


Figure 2.11 Scheme of chain transfer reaction (Odian, 2004).

(b) Ionizing radiation

The ionizing radiation has been widely used to produce chemically active polymers for adsorption and separation processes. The irradiation of NR in the presence of vinyl monomers primarily leads to a synthesis of graft copolymers, but some block copolymers are always occurred. The ionizing radiation can be carried out in solution, emulsion or suspension. The monomers used in this process can be applied as liquid with or without a diluent or as vapor. The rubber may be pre-irradiated in the absence of air to produce free radicals for later monomer addition. However, the life time of these radicals is short. Irradiation at very low temperature makes a possibility to use the trapped radicals technique for a variety of natural and synthetic rubbers. The graft polymer in the latex form is generally favored due to its simplicity. Thus, it can be seen that the graft copolymerization of vinyl monomers such as MMA, styrene (ST), acrylonitrile (ACN) and vinyl chloride (VC) onto NR has been done in this way (Lee, Bondar and Han, 2008).

(c) Redox initiation

Redox initiator is an efficient method for graft polymerization. The redox reaction relates to both inorganic and organic components. An advantage of redox initiation is that radical production occurs at reasonable rate for wider range of temperature (273-323 K), which is depended on the particular redox system (Odiان, 2004). For example, Wanvimon Arayapranee et al. (2002) studied the graft copolymerization of ST/MMA monomer mixture at 50/50 (%W/W) onto NR latex using cumene hydroperoxide (CHPO)/sodium formaldehyde sulfoxylate dehydrate/ethylenediamine teraacetic acid (EDTA)-chelated Fe^{2+} as a redox initiator. The effects of the process factors such as the amount of initiator, emulsifier, and chain-transfer agent, monomer-to-rubber ratio (M/R) and temperature on the grafting efficiency (GE) and grafting level (GL) were reported. It was found that the formation of graft copolymers occurred on the surface of latex particles. It was implied that the graft copolymerization was a surface-controlled process.

(d) Living radical polymerization (Boonlom Thavornnyutikarn, 1999)

Free radical polymerization is a chain-growth addition of a vinyl monomer involving four reaction steps: initiation, propagation, chain transfer and termination. In the last step, it is related to chain-breaking process which a growing polymeric chain becomes a dead chain. Free radical polymerization has innate side reactions such as intermolecular radical coupling reactions, disproportionation reactions and chain transfer reactions yielding a polymer with uncontrolled molecular weight and ill-defined structure. Such a less controlled reaction is overcome by a rapid progress in living radical polymerization that can control molecular weights and molecular weight distributions of resulting polymers. The living free radical polymerization typically consists of initiation and propagation steps, while the chain-breaking processes are absent. The common feature of this polymerization relates to reversible and rapid equilibrium between activated and dormant species as illustrated in Figure 2.12. The terminal covalent bonds in the dormant species can be dissociated by heat, radiation or transition metals to produce active growing radical species.

2.3.3.2 Initiation system

The different initiator systems have been extensively used to prepare graft copolymerization of vinyl monomers onto NR in recent years as follows:

(a) Thermal decomposition of initiators (Odian, 2004)

The thermal or hemolytic dissociations are widely used to generate radicals to initiate polymerization for both commercial process and theoretical study.

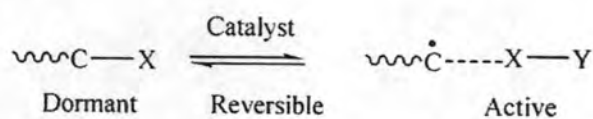


Figure 2.12 Scheme of living radical polymerization (Subramaniam, 1988: 762-86 cited in Boonlom Thavornnyutikarn, 1999).

The number of different chemicals used as thermal initiators is rather limited. Normally, the thermal initiators should have bond dissociation energies in the range of 100-170 kJ mol⁻¹. Several different types of peroxy compounds are widely used. There are acyl peroxides such as acetyl and benzoyl peroxides, alkyl peroxides such as cumyl and tert-butyl peroxides, hydroperoxides such as tert-butyl and cumyl hydroperoxides and peresters such as tert-butyl perbenzoate. Aside from the various peroxy compounds, the main other class of compound extensively used as initiators is the azo compounds. 2,2'-Azobisisobutyronitrile (AIBN) is the most important member of this class of initiators. For example, Qu et al. (2002) studied the graft copolymerization of ST and ACN onto EPDM via free radical polymerization. The graft NR was prepared by solution polymerization in n-hexane/benzene using benzoyl peroxide (BPO) as an initiator.

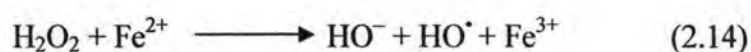
(b) Persulphate initiator system (Narawadee Chansook, 2001)

In aqueous solutions, the persulphate ion is known as a strong oxidizing agent, which can be used either alone or with activators. The reaction proceeds via a free radical mechanism involving the decomposition of persulphate by using heat or reducing agents to produce sulphate radical.

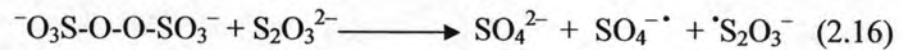
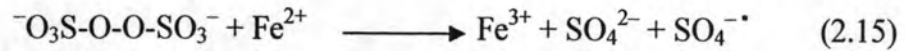
(c) Redox initiator system (O dian, 2004)

The redox initiations are normally used for graft copolymerization such as:

- Peroxide with combination of a reducing agent is a common source of radicals. For example, the reaction of hydrogen peroxide with ferrous ion generates HO[•] as illustrated in Eq. 2.14.



- The combination of various inorganic reductants and inorganic oxidizing agents to promote the radical polymerization as shown in Eq. 2.15-2.16.



(d) Ionizing radiation (Narawadee Chansook, 2001)

The irradiation of organic macromolecules predominantly leads the formation of free radicals. The two available radiation sources are Co-60, which is commonly used in the radiation plants, and Cs-137. The Co-60 source is relatively cheaper with 5.25 years of useful half life.

2.4 Graft copolymerization induced by microwave irradiation

2.4.1 Microwave radiation

Microwaves are electromagnetic waves with wavelengths in the range of one meter to one millimeter, or equivalently, and frequencies between 300 MHz (0.3 GHz) and 300 GHz (Figure 2.13). Microwaves are similar to sound since they travel in waves. However, microwaves are different from sound because they can travel through space, whether air is present or not. Rather than creating slight pressure differences, microwaves create electromagnetic waves which are commonly applied for our everyday life such as light, AM and FM radio and cell phones including wireless home networks (Pojar, 1998).

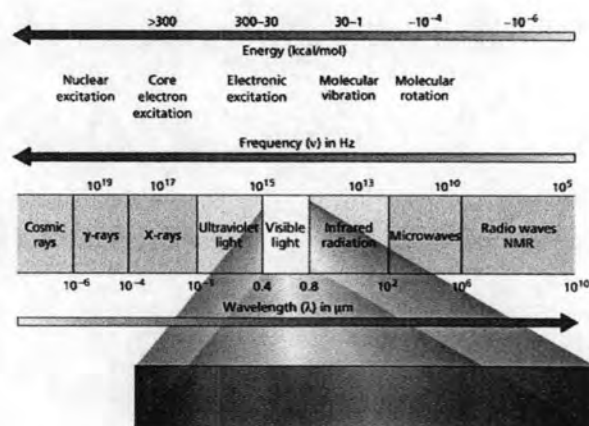


Figure 2.13 Frequency range of electromagnetic spectrum (Walters, 2006).

Microwaves are largely reflected from metallic conductors, but well interact with dipoles (asymmetrically charged molecules), such as water. Microwaves are an efficient method for heating of non-conductive materials having dielectric properties, which they cannot be efficiently heated by conventional convective methods. Microwaves rapidly change electric fields resulting to the change of orientation of dipole. If the field change is near the natural frequency at which reorientation occurs, then a maximum utilization of energy is realized and optimum heating occurs. The material is then said to be 'well coupled' with the microwaves (Pozar, 1998).

2.4.2 Microwave heating

Microwave heating is a process within a family of electro-heat techniques such as induction, radio frequency, direct resistance or infra-red heating, all of which utilizes specific parts of the electromagnetic spectrum. These processes supplement or replace the conventional heating or drying process used in industry. This is because some conventional systems are very bulky and not easy to operate. It can also produce pollutants to environment resulting from harmful omissions. Above all, the conventional heating is inefficient process. The major advantages to apply microwaves for industrial processing are rapid heat transfer, volumetric and selective heating, compactness of equipment and speed of switching on and off including pollution-free environment due to no products releasing from combustion. Microwave leakage can certainly be kept well below recommended levels (Metaxas, 1996).

2.4.2.1 Microwave vs. conventional heating (Jørgensen, 2008)

Normally, the heat source to promote the organic reaction comes from the traditional heat transfer equipment such as oil baths, sand baths or heating mantles. This technique is slow and create a temperature gradient within the sample. Moreover, the hot surface of the reaction vessel may result in localized overheating leading decomposition of product, substrate and reagent when they are heated for prolonged periods. In contrast, when using microwave heating, the energy is remotely introduced into the chemical reactor and there is no direct contact between

the energy source and the reaction mixture. Microwave radiation passes through walls of the vessel or container to directly heat the substance inside. This takes an advantage of the ability of some liquids and solids to transform electromagnetic radiation into heat. The profile of surface temperature of materials under microwave irradiation compared to the conventional heating process is represented in Figure 2.14. A properly designed vessel will not be heated under microwave irradiation. Thus, the energy will be directly deposited in the reaction mixture resulting to rapidly increase temperature throughout the sample. This is possible to lead the less by-products and/or decomposition of products. Furthermore, the lack of direct contact between the energy source and sample facilitates the optimization of reaction by immediately changing the reaction conditions without the induction period for recalibrating the heat source.

2.4.2.2 Fundamentals of microwave heating

Every material has a unique set of electrical characteristics depended on its dielectric properties. More recent applications in the area of industrial microwave processing of food, rubber, plastic and ceramics have been found to benefit from knowledge of dielectric properties. Agilent Technologies Inc. offers a variety of instruments to measure the dielectric properties of materials such as

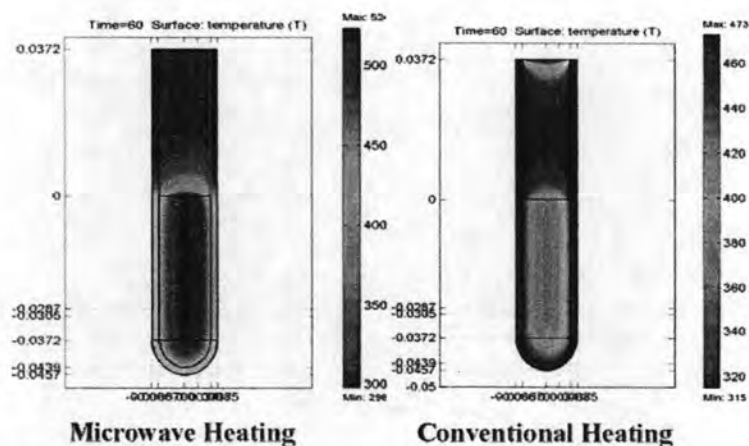


Figure 2.14 Surface temperature of microwave heating and conventional heating (Jørgensen, 2008).

network analyzers and impedance analyzers range in frequency up to 325 GHz (Altschuler, 1963).

(a) Dielectric constant (Altschuler, 1963 and Hippel, 1961)

A material is classified as “dielectric” if it has the ability to store energy when an external electric field is applied. The complex dielectric constant (κ) consists of a real part (κ') which represents the storage and an imaginary part (κ'') which represents the loss factor. The following notations are used for the complex dielectric constant interchangeably (Eq. 2.17).

$$\kappa = \kappa^* = \epsilon_r = \epsilon_r^* \quad (2.17)$$

From the electromagnetic theory, the definition of electric displacement (electric flux density, D) is shown in Eq. 2.18:

$$D_f = \epsilon E \quad (2.18)$$

where $\epsilon = \epsilon^* = \epsilon_0 \epsilon_r$ is the absolute permittivity (or permittivity), ϵ_r is the relative permittivity, $\epsilon_0 \approx (1/36\pi) \times 10^{-9}$ F/m is the free space permittivity and E is the electric field. Permittivity describes the interaction of a material with an electric field E and is a complex quantity. Dielectric constant (κ) is equivalent to relative permittivity (ϵ_r) or the absolute permittivity (ϵ) which is related to the permittivity of free space (ϵ_0) (Eq. 2.19).

$$\kappa = (\epsilon/\epsilon_0) = \epsilon_r = \epsilon_r - j\epsilon_r'' \quad (2.19)$$

The real part of permittivity (ϵ_r') is a measurement of the energy quantity from an external electric field stored in a material. The imaginary part of permittivity (ϵ_r'') is called the loss factor and is a measure of how dissipative or lossy a material is to an external electric field. The imaginary part of permittivity (ϵ_r'') is always greater than zero and is usually much smaller than ϵ_r' . The loss factor includes the effects of both dielectric loss and conductivity. When complex permittivity is drawn as a simple vector diagram (Figure 2.15), the real and

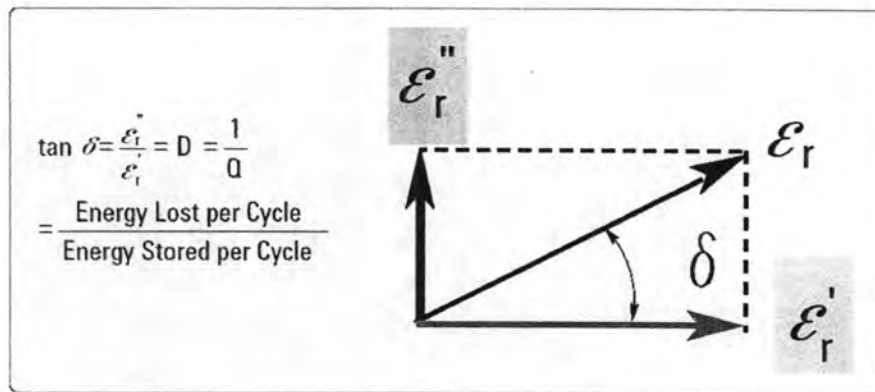


Figure 2.15 Loss tangent vector diagram (Altschuler, 1963).

imaginary components are 90° out of phase. The vector sum forms an angle δ with the real axis (ϵ_r'). The relative “lossiness” of a material is the ratio of the energy lost to the energy stored.

The loss tangent or $\tan \delta$ is defined as the ratio of the imaginary part of the dielectric constant to the real part. D denotes dissipation factor and Q is quality factor. The loss tangent $\tan \delta$ is called tan delta, tangent loss or dissipation factor. Sometimes the term “quality factor or Q -factor” is used with respect to an electronic microwave material, which is the reciprocal of the loss tangent. For very low loss materials, since $\tan \delta \approx \delta$, the loss tangent can be expressed in angle units, milliradians or microradians.

(b) Dielectric mechanisms (Altschuler, 1963 and Hippel, 1961)

A material may have several dielectric mechanisms or polarization effects that contribute to its overall permittivity (Figure 2.16). A dielectric material has an arrangement of electric charge carriers that can be displaced by an electric field. The charges become polarized to compensate for the electric field such that the positive and negative charges move in opposite directions. At the microscopic level, several dielectric mechanisms can contribute to dielectric behavior.

Dipole orientation and ionic conduction strongly interact at microwave frequencies. Water molecules, for example, are permanent dipoles, which rotate to follow an alternating electric field. These mechanisms are quite lossy which explains why food heats in a microwave oven. Atomic and electronic mechanisms

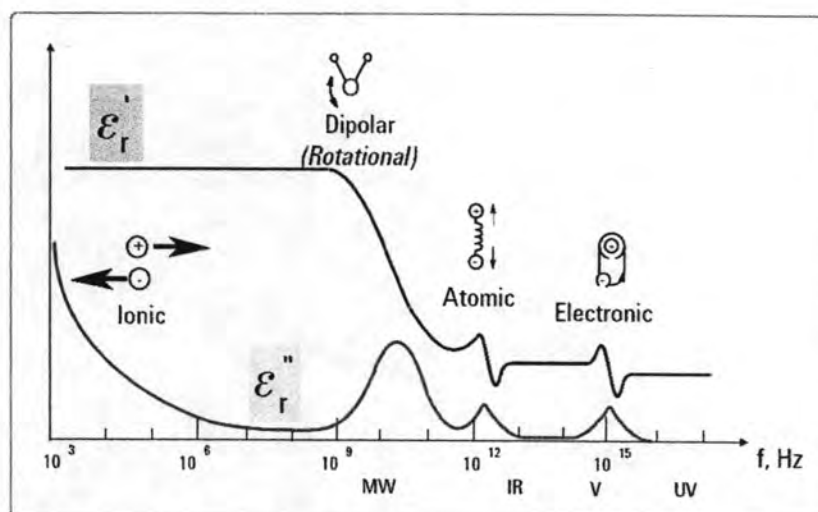


Figure 2.16 Frequency response of dielectric mechanisms (Altschuler, 1963).

are relatively weak, and usually constant over the microwave region. Each dielectric mechanism has a characteristic “cut-off frequency.”

As frequency increases, the slow mechanisms drop out in turn, leaving the faster ones to contribute to ϵ' . The loss factor (ϵ'') will correspondingly peak at each critical frequency. The magnitude and “cut-off frequency” of each mechanism is unique for different materials. Water has a strong dipolar effect at low frequencies but its dielectric constant rolls off dramatically around 22 GHz. Teflon, on the other hand, has no dipolar mechanisms and its permittivity is remarkably constant well into the millimeter-wave region.

A resonant effect is usually associated with electronic or atomic polarization. A relaxation effect is usually associated with orientation polarization.

- Orientation (dipolar) polarization

A molecule is formed when atoms combine to share one or more of their electrons. This rearrangement of electrons may cause an imbalance in charge distribution creating a permanent dipole moment. These moments are oriented in a random manner in the absence of an electric field so that no polarization exists. The electric field E will exercise torque T on the electric dipole, and the dipole will rotate to align with the electric field causing orientation polarization to occur (Figure 2.17).

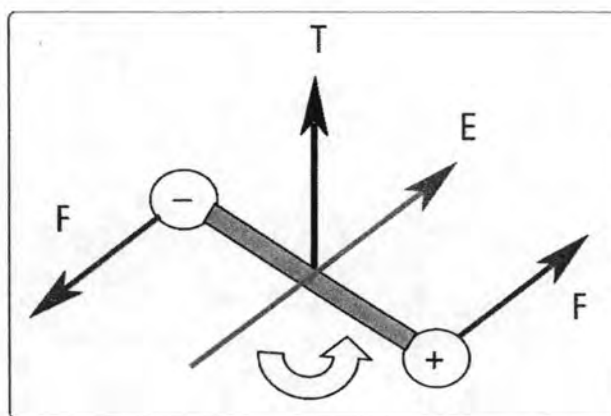


Figure 2.17 Dipole rotation in electric field (Altschuler, 1963).

If the field changes the direction, the torque will also change. The friction accompanying the orientation of the dipole will contribute to the dielectric losses. The dipole rotation causes a variation in both ϵ_r' and ϵ_r'' at the relaxation frequency which usually occurs in the microwave region. As mentioned, water is an example of a substance that exhibits a strong orientation polarization (Altschuler, 1963 and Hippel, 1961).

- Electronic and atomic polarization

Electronic polarization occurs in neutral atoms when an electric field displaces the nucleus with respect to the electrons that surround it. Atomic polarization occurs when adjacent positive and negative ions “stretch” under an applied electric field. For many dry solids, these are the dominant polarization mechanisms at microwave frequencies, although the actual resonance occurs at a much higher frequency. In the infrared and visible light regions the inertia of the orbiting electrons must be taken into account. Atoms can be modeled as oscillators with a damping effect similar to a mechanical spring and mass system (see above Figure 2.16). The amplitude of the oscillations will be small for any frequency other than the resonant frequency. Far below resonance, the electronic and atomic mechanisms contribute only a small constant amount to ϵ_r' and are almost lossless. The resonant frequency is identified by a resonant response in ϵ_r' and a peak of

maximum absorption in ϵ_r'' . Above the resonance, the contribution from these mechanisms disappears (Altschuler, 1963 and Hippel, 1961).

(c) Measurement methods of dielectric properties (Engelder and Buffler, 1991)

Several methods have been developed to measure dielectric properties of materials in the microwave frequency range. The following three methods are commonly used:

1. Open-end coaxial probe system

This system is commercially available from Agilent Technologies (Englandwood, CO). During the measurement, a coaxial probe with an open end (HP 85070B) is pressed against the sample material (Figure 2.18). The microwave signal launched by a vector network analyzer (HP 8752C, 8753, 8720 or 8510 network analyzer) is reflected by the sample. The magnitude and phase shift of the reflected waves depend upon the dielectric properties of the tested material. The analyzer receives the reflected waves, and the dielectric constant and loss factor are then calculated.

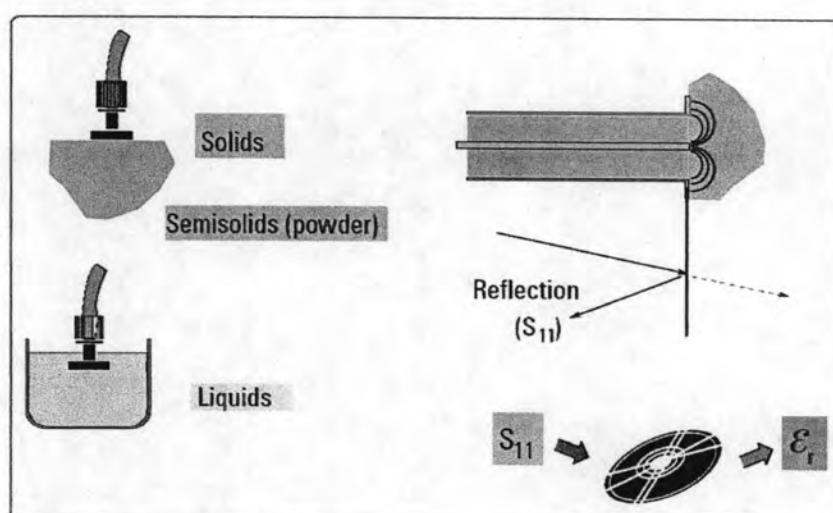


Figure 2.18 Hewlett Packard (HP) open-ended coaxial probe dielectric property measurement system (Engelder and Buffler, 1991).

A major advantage of this method is:

- It is the ease to use and it is suitable for liquids or soft solid food materials.
- The dielectric properties of the material can be measured over a large range of frequencies (from 0.2 to up to 20 GHz).
- The measurement requires little sample preparation and the system is interfaced with a personal computer.
- A sample measurement can be completed within a few minutes.
- This method is most commonly used by the food research community (Seaman and Seals, 1991; Nelson et al., 1993; Herve et al., 1998).

The accuracy ($\pm 5\%$ in best cases) of the measurement by open-end coaxial probe system is adequate for most microwave heating research. The sample thickness needs, however, to be greater than 1 cm for typical foods and the solids must have a flat surface to allow good contact between the solid and the probe surface. This method is also not suitable for measuring materials such as plastics and oil with low dielectric property.

2. Transmission line method

With the transmission line method, a sample is precisely shaped to completely fill the cross-section of a transmission line (a coaxial or a rectangular waveguide) (Goedeken et al., 1997). The change of the impedance and propagation characteristics as a result of the sample in the loaded transmission line is measured by a vector network analyzer. A personal computer interfaced with the network analyzer calculates and displays the measured value of dielectric constant and loss factor. The accuracy of this method is generally between that of the open-end coaxial probe method and that of the cavity resonance method. The transmission line method requires careful sample preparation (Figure 2.19).

In particular, the sample shape needs to precisely fit the cross-section of the transmission line for accurate measurement. Liquid foods are more difficult to measure with this method. Commercial systems are available from Agilent Technologies. However, these systems need precision transmission line fixtures (or

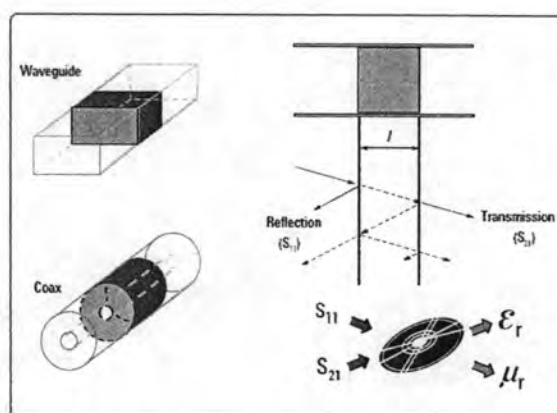


Figure 2.19 Schematic diagram for HP transmission line method: a measurement system consists of a network analyzer, a coaxial or waveguide, a computer and software for data acquisition and conversion (Engelder and Buffler, 1991).

sample holder) for narrow bands of frequencies (e.g. S-Band: 2.60–3.95 GHz; G-band: 43.95–5.85 GHz, etc.). In general, this system is more expensive for the same range of frequency than the open-end coaxial probe system, and the measurements are more difficult and time-consuming. This method also gives limited resolution when measuring low lossy foods such as oil.

3. Resonance cavity method

The resonance cavity method is based on the fact that cavities are high quality (high Q) resonance structures. A small sample material introduced inside a cavity shifts the center resonance frequency (f_c) and alters the quality factor (Q) of the cavity (ASTM, 1971). These two parameters are measured by a network analyzer (Figure 2.20). Special software calculates the dielectric properties of the material. Since the change of the f_c is small, it is essential that the network analyzer has a resolution of 1 Hz. This method gives an overall accuracy of $\pm 2\text{--}3\%$ (Ohlsson, 1989). The resonance cavity method is suited to measure the dielectric properties of low lossy materials such as oil, paper, plastics, glass or wood. This method requires precise sample shape. In addition, a resonance cavity provides dielectric properties only at a fixed frequency. The analysis may also be complex. Commercial systems from Hewlett-Packard are much more expensive than the open-end coaxial probe system.

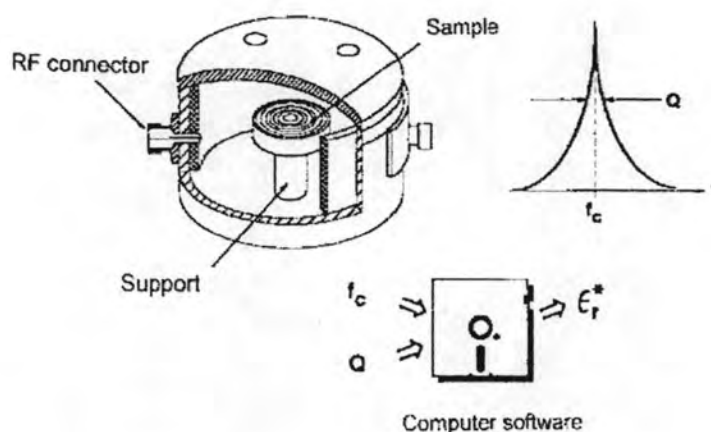


Figure 2.20 Schematic diagram for HP resonant cavity method: a measurement system consists of a network analyzer, a cavity, a computer and software (Engelder and Buffler, 1991).

In theory, dielectric materials can include solids, liquids, and gases. However, solid and liquid states of matter have practical significance. The dielectric constant values of some materials in solid and liquid states are presented in Table 2.1.

2.4.3 Component of microwave heating system

Typical microwave heating system is shown in Figure 2.21. Basically, there are three major components:

- Power unit where microwaves are generated at the required frequency band.
- Applicator (cavity) where the material is subjected to intense microwave fields, and to which any additional ancillary process equipment such as pumps for operation under moderate vacuum conditions, steam or hot air injection, must be connected.
- Control circuitry to optimize and regulate the overall performance of the microwave heater. Magnetron tubes are used to generate the microwave power. A ferrite iso-circulator protector is applied between the magnetron source and the applicator (Metaxas, 1993).

Table 2.1 Dielectric constants of materials at 20°C (Frederikse, 1973 and Kienitz, 1981)

Material	Dielectric constant (Approx.)	Material	Dielectric constant (Approx.)
Air	1.0	Paper (dry)	1.5-3.0
Acetone	20.7	Paper (coated)	2.5-4.0
Barium titanate	100.0-1250.0	Parafin oil (medicinal)	2.2
Beeswax	2.4-2.8	Polycarbonate	2.9-3.2
Benzene	2.3	Polyethylene	2.3
Borosilicate	4.0-5.3	Polyimide	3.4-3.5
Carbon tetrachloride	2.2	Poly(methyl methacrylate)	3.4
Cellulose acetate	2.9-4.5	Polystyrene	2.4-3.0
Diamond	5.5-5.7	Polytetrafluoroethylene (PTFE; teflon)	2.1
Diethyl ether	4.3	Polyvinylchloride (unplasticized)	3.2
Epoxy resin	3.4-3.7	Propanol	20.5
Ethanol	24.5	Quartz	4.4
Fiber	5.0	Rubber (hard)	2.0-4.0
Glass	3.8-14.5	Ruby mica	5.4
Gutta percha	2.4-2.6	Silicone oil	2.2
n-Hexane	1.9	Titanium dioxide	100.0
Hydrogen	1.2	Toulene	2.4
Methanol	32.7	Vaseline	2.2
Neoprene	4.0-6.7	Water (distilled)	34.0-78.0
Nylon	3.4-22.4	Wood (dry)	1.4-2.9

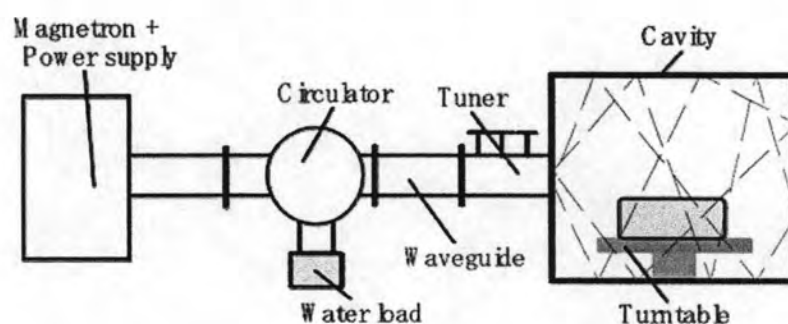


Figure 2.21 Typical microwave heating set-up (Phadungsak Ratanadecho, 2002).

2.4.3.1 Microwave applicators (Metaxas and Meredith, 1993)

The most common form of an applicator, comprising well over 50% of industrial systems, is the multimode type. In principle, it is an extension of the domestic microwave oven but built for large scale material processing.

(a) Single-mode resonant applicators

In single (fundamental or higher order) mode, resonant cavities the superposition of the incident. The reflected waves give a standing wave pattern which is very well defined in space. This enables the dielectric material to be placed in the position of maximum electric field for optimum transfer of the electromagnetic energy. A most versatile single mode resonant applicator is shown in Figure 2.22, which operates in the TE_{10n} (Transverse Electric; TE) mode. It consists of a rectangular waveguide, into which a co-sinusoidal electric field distribution of n half-wavelengths is established, connected to a flange with a coupling iris on one side and a non-contacting short-circuit plunger on the other side.

The dielectric material is inserted into the applicator through a slot in the broad dimension of the waveguide. The dielectric experiences the maximum electric field of the standing wave set up within the applicator, which is in the range $1 < E < 2$ kV/cm with moderate output power from the source, say a few kW. Larger electric fields, say up to 10 kV/cm, can also be achieved resulting in a very high heating rate, typically exceeding 30°C/s. For optimum performance of such an applicator, both the position of the plunger, which determines the operating frequency, and size of the iris, which establishes how much of the energy is in fact transferred to the applicator, are dependent upon the dielectric properties of the material under consideration. Optimization procedures are carried out at low power using a network analyzer which measures the reflection coefficient, VSWR (Voltage Standing Wave Ratio; VSWR - a measure of reflections) and the cavity impedance (Metaxas and Meredith, 1993).

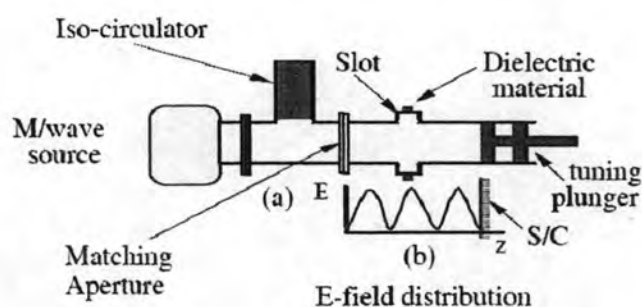


Figure 2.22 TE_{10n} single mode resonant applicator (Metaxas and Meredith, 1993).

(b) Coupling systems of TE_{10n} rectangular cavity with TM_{01n} cylindrical cavity

Similarly to the TE_{10n} cavity, the cavity operation in the TM modes should be very useful since the electric field is along the direction of propagation and the dielectric material placed along its axis. Of all possible TM modes that can develop in a cylindrical waveguide most attention has been paid to the cylindrical cavity operating in the TE_{01n} mode. This obvious preference is best explained upon considering the distribution of the electric and magnetic field within such a cavity, the most important aspect being the existence of an axial electric field. This renders such a cavity very suitable for treating filamentary materials such as textiles, fibers and liquids placed along its axis. Furthermore, coupling of the microwave energy into such a cavity is facilitated by the existence of a circumferential magnetic field. Thus, it is able to transfer the power from the generator to the cavity via a rectangular waveguide operating in its dominant TE_{10} mode. Such $H-H$ coupling can be obtained by connecting the waveguide and TM_{010} cavity, as shown in Figure 2.23, via an appropriate matching aperture (Metaxas and Meredith, 1993).

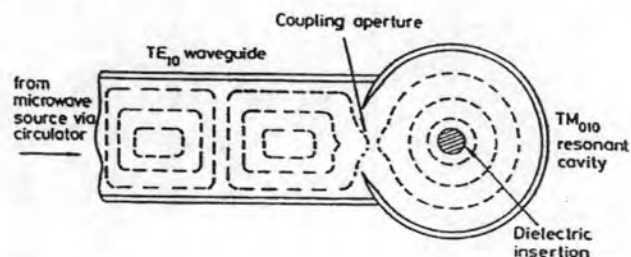


Figure 2.23 $H-H$ coupling of a cylindrical cavity to the connecting rectangular waveguide (Metaxas and Meredith, 1993).

2.4.3.2 Waveguides (Kuphaldt et al., 2007)

A waveguide is a special form of transmission line consisting of a hollow metal tube. The tube wall provides distributed inductance, while the empty space between the tube wall provides distributed capacitance. Types of waveguide are shown in Figure 2.24. Waveguides conduct microwave energy at lower loss than coaxial cables. Waveguides are practical only for signals of extremely high frequency, where the wavelength approaches the cross-sectional dimensions of the waveguide. Below such frequencies, waveguides are useless as electrical transmission lines. The waveguides are considerably simpler than two-conductor cables (especially coaxial cables) in their manufacture and maintenance. With only a single conductor (the waveguide's "shell"), there are no concerns with proper conductor-to-conductor spacing, or of the consistency of the dielectric material, since the only dielectric in a waveguide is air. Moisture is not as severe a problem in waveguides as it is within coaxial cables, either, and so waveguides are often spared the necessity of gas "filling."

All electromagnetic waves consist of electric and magnetic fields propagating in the same direction of travel, but perpendicular to each other. Along the length of a normal transmission line, both electric and magnetic fields are perpendicular (transverse) to the direction of wave travel. This is known as the *principal mode*, or *TEM* (Transverse Electric and Magnetic) mode. This mode of wave propagation can exist only where there are two conductors. It is the dominant mode of wave propagation where the cross-sectional dimensions of the transmission line are small compared to the wavelength of the signal (Figure 2.25).

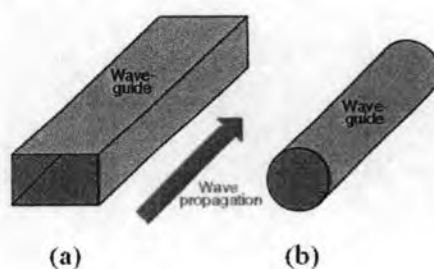


Figure 2.24 Scheme of (a) rectangular waveguide (b) coaxial cables (Kuphaldt et al., 2007).

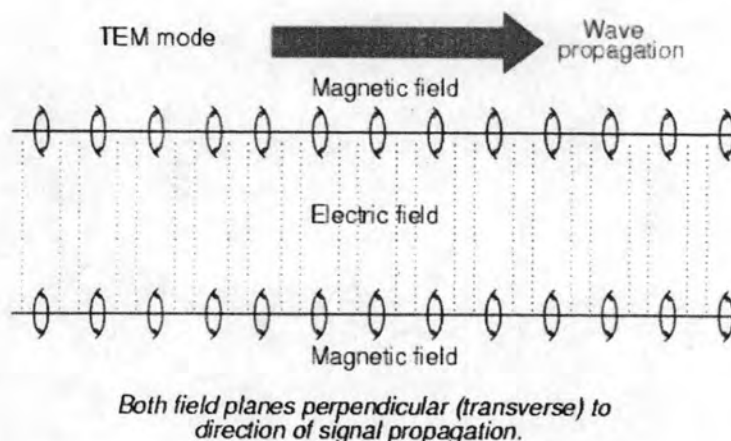


Figure 2.25 Scheme of twin lead transmission line propagation: TEM mode (Kuphaldt et al., 2007).

When an electromagnetic wave propagates down a hollow tube, only one of the fields (either electric or magnetic) will actually be transverse to the wave's direction of travel. The other field will “loop” longitudinally to the direction of travel, but still be perpendicular to the other field. Whichever field remains transverse to the direction of travel determines whether the wave propagates in *TE* mode (Transverse **E**lectric) or *TM* (Transverse **M**agnetic) mode (Figure 2.26).

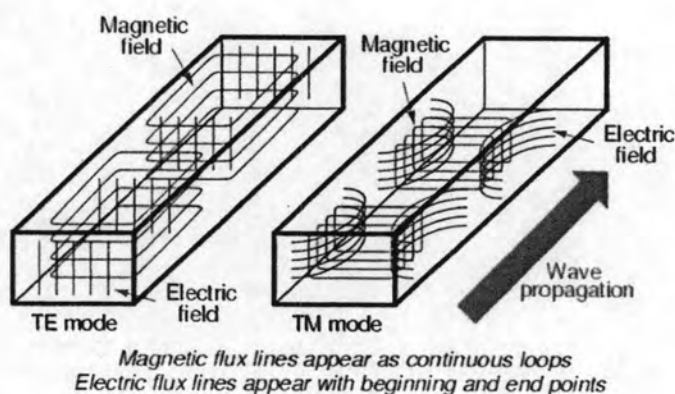


Figure 2.26 Scheme of waveguide transverse electric (TE) and transverse magnetic (TM) modes (Kuphaldt et al., 2007).

2.5 Literature reviews

Singh et al. (2006) studied chitosan (Ch)-*graft*-poly(methyl methacrylate) (Ch-g-PMMA). It was successfully synthesized using potassium persulfate ($K_2S_2O_8$)/ascorbic acid as a redox initiator. This was carried out in the presence of oxygen at 35°C. It was found that the reaction induced by microwave required shorter and gave higher yield without the use of redox initiator or catalyst. The Ch-g-PMMA with 160 % grafting was prepared from 0.17 M of methyl methacrylate (MMA) and 0.1 g of Ch in 25 ml of 5% aqueous formic acid using 80% microwave power in 2 min. At the same concentration of the MMA and the Ch, 105% grafting was observed when $K_2S_2O_8$ /ascorbic acid was used as redox initiator in the presence of Ag^+ (catalyst) and oxygen atmosphere (co-catalyst) at $35 \pm 0.2^\circ C$. The graft chitosan obtained from microwave irradiation was an efficient adsorbent for Zn^{2+} . Moreover, the solubility of chitosan is improved by grafting with MMA solubility shifted towards neutral from acidic pH.

Wang et al. (2003) studied the graft copolymerization of maleic anhydride (MAH) onto low density polyethylene (LDPE) in xylene initiated by using benzoyl peroxide (BPO) under microwave irradiation. The influence of reaction conditions such as initiator concentration, monomer concentration and irradiation time was investigated. At the weight composition of xylene/LDPE/MAH/BPO = 10/1/1/0.07, the grafting degree reached to 56.5 mmol of MAH/100 g of PE within 8 min by using 100 W microwave power at 138°C.

Singh et al. (2006) studied the preparation of chitosan (Ch)-*graft*-polyacrylamide (PAM) (Ch-g-PAM) without any radical initiator or catalyst using microwave (MW) irradiation. Under optimal conditions, 169% grafting was observed at 80% MW power and 95°C in a very short reaction time of 1.16 min. At similar condition, the conventional grafting process initiated by $K_2S_2O_8$ /ascorbic acid in the presence of Ag^+ and oxygen as catalyst and co-catalyst, respectively at $35 \pm 0.2^\circ C$ required 1 h to achieve 82% grafting. The Ch-g-PAM could be used as an adsorbent for Ca^{2+} and Zn^{2+} in the waste or natural water.

Kaith et al. (2009) studied the hybridization of the natural polymers with synthetic polymers for using as biomedical and biodegradable materials. The graft copolymers of MMA on acetylated *Saccharum spontaneum L.* fiber was synthesized by using ferrous ammonium sulphate–potassium persulphate (FAS–KPS) as a redox initiator under the influence of microwave radiation (MWR). Different reaction parameters such as time, initiator molar ratio, monomer concentration, microwave power, pH and solvent were optimized to get maximum grafting yield (72.2%). It was found that the percentage of crystallinity of graft product rapidly decreased resulting to the reduction of its stiffness and hardness. Moreover, graft copolymers had higher resistance to moisture, chemical and thermal degradation.

Liu et al. (2005) studied the graft polymerization of ϵ -caprolactone onto chitosan under microwave irradiation. This reaction was induced via a protection-graft-deprotection procedure using phthaloylchitosan as a precursor and stannous octoate as a catalyst. The result indicated the higher 100% grafting percentage was achieved in short reaction time (ca. 12.5 min).

Kalia and Kaith (2008) studied the graft copolymerization of MMA onto flax fiber under the influence of microwave radiation. 24.6% grafting was found at 210 W of microwave power under optimum reaction conditions. The graft copolymers were then used for preparation of phenol-formaldehyde (PF) composites. Modulus of rupture (MOR), modulus of elasticity (MOE) and stress at the limit of proportionality (SP) of composites were measured. It was found that the composites reinforced with flax-g-poly(MMA) showed better mechanical properties in comparison to ones reinforced with raw flax.

Huacai et al. (2006) studied the graft copolymerization of chitosan with acrylic acid under microwave irradiation and investigated its water absorbency. Acrylic acid was grafted on chitosan by using ceric ion as an initiator in the presence of *N,N'*-methylenebisacrylamide (MBA) as a crosslinker under microwave irradiation based on their modified apparatus. The effects of some grafting variables on the water absorbency were investigated by orthogonal tests. The result showed

that the microwave irradiation enhanced the reaction rate by eight times over the conventional method. It was also found that the obtained graft copolymer was an effective superabsorbent resin (SAR) for absorbing water ca. 704 times of its own dry weight.

Sen and Pal (2009) studied the microwave initiated synthesis of polyacrylamide grafted carboxymethylstarch (CMS-*g*-PAM) for sustained drug release. 'In vitro' release of a model drug (5-amino salicylic acid) from CMS-*g*-PAM matrix was investigated. The results showed that the higher percentage of grafting could promote the faster rate of drug release. Furthermore, the correlation of percentage of grafting vs. t_{50} value (i.e. time taken for release of 50% of the enclosed drug) was studied for the first time to find the possibility of a programmable drug release matrix based on grafted polysaccharide. In this matrix, the rate of release of the enclosed drug could be precisely programmed by adjustment of percentage of grafting during synthesis.

Tiwari and Singh (2008) studied the microwave-induced synthesis of electrical conducting gum acacia-*graft*-polyaniline. In the presence of catalytic amount of ammonium peroxydisulfate (APS) as oxidant/initiator, the grafting of polyaniline (PANI) onto gum acacia (GA) was performed under mild acidic condition using microwave irradiation. The synthesis could be rapidly accomplished under atmospheric conditions. The grafting condition was optimized by varying the microwave power, exposure time and concentrations of initiator, acid, monomer and gum acacia. The gum of acacia-*graft*-polyaniline (GA-*g*-PANI) exhibited that the pH switching electrical conducting behavior was depended on the grafting extent and pH of the material.

Zhang et al. (2010) studied the synthesis of polyamidoamine (PAMAM) dendrimer-grafted silica with microwave assisted protocol for reduction of reaction time. By comparing with the conventional grafting method at $246 \mu\text{mol g}^{-1}$ grafting of the PAMAM modified silica, the graft copolymerization of PAMAM onto silica induced by microwave at 40°C required short reaction time (ca. 60 min); whilst, the conventional method was carried out using longer reaction time as 24 h.

The results indicated that the number of amino groups and the percentage of nitrogen increased with increasing PAMAM content. The microwave assisted protocol was found to be effective method. Bovine serum albumin (BSA) was used as a model biologic molecule to react with the dendrimer-grafted silica by chemical bonding through glutaraldehyde. The immobilization efficiency for BSA increased with increasing PAMAM generation.

Kumar et al. (2009) studied the graft copolymerization of xanthan-g-poly(acrylamide) assisted by microwave and studied the vitro release behavior of the obtained graft product. Matrix tablets of diclofenac sodium were formulated using graft copolymer as the matrix by direct compression technique. Release behavior of the graft copolymer was evaluated using USP type-II dissolution apparatus in 900 ml of phosphate buffer (pH 6.8), maintained at 37°C with constant stirring speed at 50 rpm. Microwave-assisted grafting provided graft copolymer with higher %grafting in a shorter reaction compared to the used of time in the ceric-induced grafting. The %grafting increased with increasing the power of microwave and/or time of exposure. The matrix tablets released the drug following the zero-order kinetics. The faster drug release was observed from graft copolymer matrix than the xanthan gum matrix. Although, the graft copolymerization reduced the swelling, the enhancement of erosion of xanthan gum was observed.