

CHAPTER II

THEORY

2.1 COMPOSITES

Polymeric materials have been used widely for many purposes. However, the properties of polymers are restricted by many factors such as brittleness and hardness. To develop desirable properties for polymers, the concept of making *composite polymer* is rapidly growing in acceptance.

Composites are polymer compound that have two phases or more. The main phase is known as the *matrix* and the other phase is called the *dispersed phase*. The matrix is often the polymer that one aims to improve in properties such as strength, toughness, environmental stability and so on. When a load is applied to the composite, the matrix is the first part to receive the load which is then passed on to the dispersed phase. That is why properties can be improved in composites.

There are many types of composites. Based upon the geometry of the dispersed phase and how it is placed in the matrix, composites can be classified into three types, namely the fiber-reinforced composite, laminated composites and particulated composites.

In fiber-reinforced composite, the dispersed phase is fiber embedded in the matrix. The fiber used may be in the form of chopped

fiber, cloth or filament. The dispersed fiber generally has better mechanical properties than the matrix.

Laminated composite is one that has at least two plates of material joined together. Each plate may be differently dispersed with a second phase. The objective of making a laminate composite is to combine the good properties of each plate or each laminae.

Particulated composite is one that has filler or small particles dispersed in the matrix. The composite properties depends on the properties of both the matrix and the filler.

2.2 EPOXY RESIN

The epoxy resin in the present work acts as the matrix. The term “epoxy” refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms already united in some other way. The simplest epoxy is a three-membered ring, to which the term α -epoxy or 1,2-epoxy is applied. Ethylene oxide (Figure 2.1) is an example of this type. The term 1,3- and 1,4- epoxy are applied to trimethylene oxide (Figure 2.2) and tetrahydrofuran (Figure 2.3).

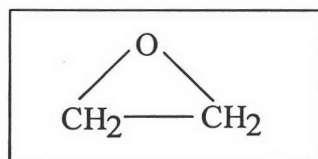


Figure 2.1: Ethylene oxide.

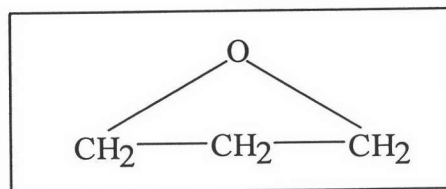


Figure 2.2: Trimethylene oxide (oxetane).

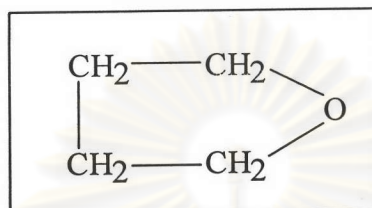


Figure 2.3: Tetrahydrofuran.

Epoxy is a monomer of a prepolymer that can react with a curing agent to yield high-performance thermosetting plastics. They are widely used in protective coating, electrical and structural applications because of their good properties such as adhesion, chemical resistance and superior electrical properties.

The most widely used epoxy resin is diglycidyl ether of bisphenol A (DGEBA) derived from bisphenol A and epichlorohydrin. Other polyols such as aliphatic glycols and novolacs can also be used instead of bisphenol A to produce specialty resins. Epoxy resins may also include aliphatic and cycloaliphatic backbones or it may include a heterocyclic hydantoin nucleus as a building block to produce epoxies with superior electrical properties and outdoor weatherability. To convert epoxy resin to thermoset, it must be cured with a curing agent

such as an anhydride, amine, polyamide, Lewis acid and other types of hardener.

Epoxy resins can be prepared commercially in three ways as follows:-

- (i) Dehydrohalogenation of the chlorohydrin prepared by the reaction of epichlorohydrin with a suitable di- or polyhydroxyl material or other active-hydrogen-containing molecule.
- (ii) The reaction of olefins with oxygen-containing compound such as peroxides or peracids.
- (iii) Dehydrohalogenation of chlorohydrins prepared by routes other than route (i).

2.2.1 History

Epoxy resins are first prepared from epichlorohydrin in 1927 in the United States. In 1936, low-melting, amber-colored resin was produced by Dr. Castan which was reacted with phthalic anhydride to produce a thermoset compound.

In the United States of America, Dr. Greenlee, early in 1939, working for Devoe-Raynolds, explored the epichlorohydrin-bisphenol A synthesis route for the production of new resins for coatings. These resins do not contain coustic-sensitive ester linkages.

In the late 1950s and early 1960s, commercialization of the epoxy resins was actively pursued by companies such as Shell, Devoe and Reynolds (now Celanese), Union Carbide, Ciba, Dow and Reichhold.

High temperature performance and other selected properties were improved in the mid 1960s by the synthesis of various multifunctional resins.

In 1976, Shell Chemical Company introduced hydrohenated bisphenol A materials as UV-weatherable to compete with aliphatic polyurethanes.

2.2.2 Types of Epoxy Resins

Epoxy resins can be classified into seven types. Each type is suitable for many purposes due to the various structure of the resins.

2.2.2.1 Epichlorohydrin and Bisphenol A Derived Resins: This type of epoxy resin can be cured with anhydrides, aliphatic amines or polyamides, depending on the desired end properties. These resins are also known as “Diglycidyl Ether of Bisphenol A (DGEBA)”.

For solvent base ambient cure systems, anhydrides are used to provide higher heat resistance systems but at the expense of the flexibility. Diluents are used to reduce the viscosity of epoxy systems

for improving the ease of application and to facilitate higher filler loading to reduce formulation cost. Figure 2.4 shows the structure of diglycidyl ether of bisphenol-A.

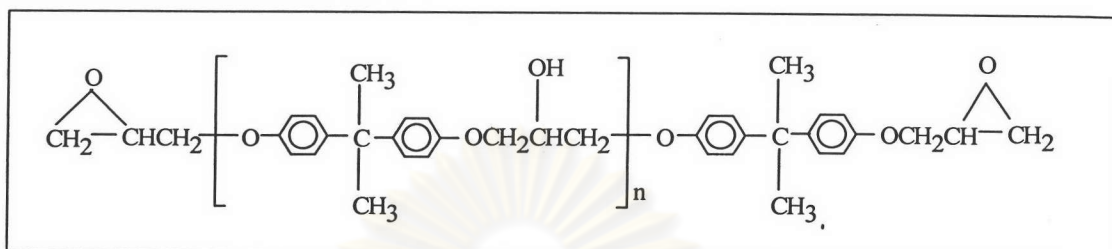


Figure 2.4: The structure of diglycidyl ether of bisphenol-A.

Other types of resins are called the *specialty epoxy resins*. There are the family of resins that contain aliphatic, cycloaliphatic, aromatic and heterocyclic backbones.

2.2.2.2 Epoxy Cresol Novolac Resins (ECN): The cresol-novolac resins are multifunctional, solid polymers whose structure are shown in Figure 2.5. The resin can hydrolyze chlorine impurities. They have high chemical resistance and good thermal performance. They are widely used in high performance electronic applications, structural moulding compounds, structural moulding powders, castings, laminating systems and powder coatings. The multifunctionality of the ECN resins lead them to possess higher reactivity and greater crosslink density. Consequently, they tend to have higher thermal resistance than the epichlorohydrin-bisphenol A systems. The melt viscosity of the ECN resins decrease sharply when temperature is elevated. Hence, excellent tool must be used to control the flow of the ECN moulding compounds.

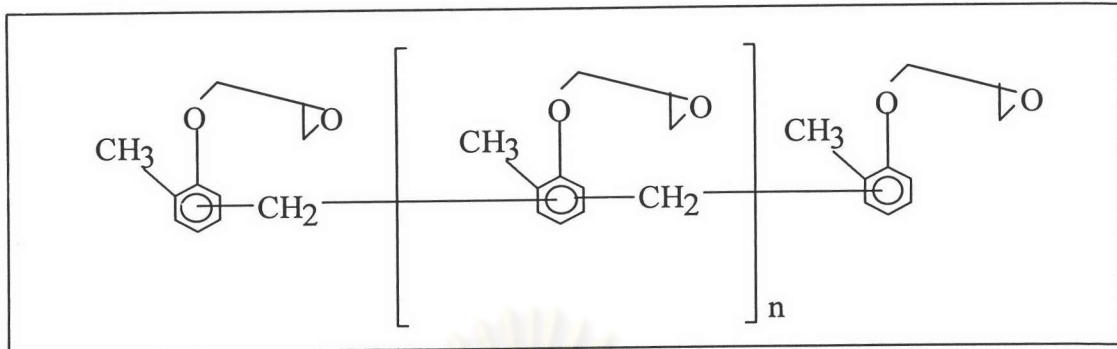


Figure 2.5: The structure of epoxy cresol novolac ECN resins.

2.2.2.3 Epoxy Phenol Novolac Resins: The structure of epoxy phenol novolac resins is shown in Figure 2.6. The epoxy phenol novolac resins produce more tightly crosslinked cured systems than other type of epoxy resin. As a result, their elevated temperature performance is improved and their chemical resistance tends to be greater than that of the epichlorohydrin-bisphenol A resins.

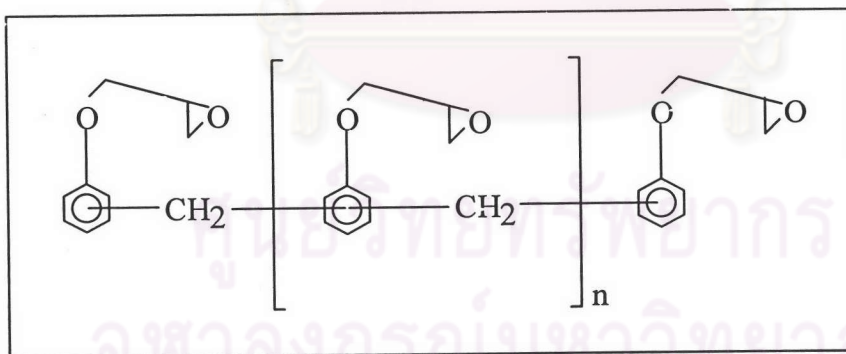


Figure 2.6: The structure of epoxy phenol novolac resins.

Epoxy phenol novolac resins can be used in adhesives, structural and electrical laminates, filament-wound pipes, storage tanks, liners for pumps and corrosion-resistant coatings. Appropriate curing

agents for epoxy phenol novolac resins include aromatic amines, catalytic curing agents, phenolics and some anhydrides.

2.2.2.4 Bisphenol F Resins: Bisphenol F Epoxy resins generally have lower viscosity. This implies that a higher amount of filler can be filled. Faster bubble release is also achieved. Bisphenol F resins are used in high-solids-high-build systems such as tank and pipe lining, industrial floors, road and bridge deck toppings.

2.2.2.5 Polynuclear Phenol-Glycidyl Ether-Derived Resins: This type of resins have polyfunctionality that result in good thermal stability, high chemical resistance, electrical and mechanical properties. They are used in adhesives and moulding compounds. In addition, they have also been applied as an upgrader in laminated systems.

2.2.2.6 Cycloaliphatic Epoxy Resins: Cycloaliphatic epoxy resins have low viscosity. They consist of two components, cycloolefins epoxidized with peracetic acid and diglycidyl esters of cyclic dicarboxylic acids. Their good properties are high UV resistance and high arc-track resistance. Curing agents that can best react with cycloaliphatic epoxy resins are the anhydride and the phenolic types of curing agents. The cyclohexane ring structure and the short side chains of cured cycloaliphatic epoxy resins means that they have high deflection temperatures. However, cured cycloaliphatic epoxy resins are quite brittle when they are crosslinked. They are used to form parts of transformers, insulators, bushings, wire, cable, generators and motors.

2.2.2.7 Aromatic and Heterocyclic Glycidyl Amine

Resins: The four significant aromatic types of epoxy resins are tetraglycidylmethylenedianiline-derived resins, triglycidyl-p-aminophenol-derived resins, triazine-based resin and hydantoin epoxy resins.

This chapter will focus on the theory of DGEBA type of epoxy resins only as it is the type selected in the present study.

2.2.3 Preparation of Epoxy Resins

Epoxy resins which are widely used in commercial industries are diglycidyl ether of bisphenol A. They are synthesized by the reaction of bisphenol A react with epichlorohydrin in the presence of an alkaline catalyst.

Bisphenol A can be prepared from the reaction of two molecules of phenol and one molecule of acetone at a temperature range of 50-60 °C. Hydrochloric acid is used as a catalyst. The reaction is shown in Figure 2.7.

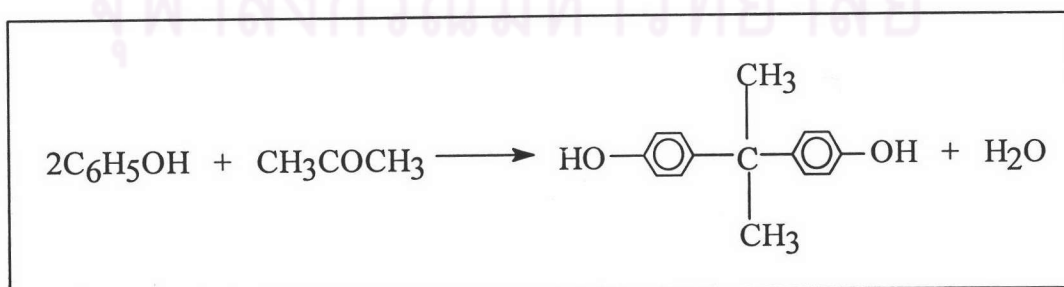


Figure 2.7: Formation of Bisphenol A from phenol and acetone.

The preparation of epichlorohydrin can start from chlorination reaction of propylene at 500 °C to form allyl chloride. Then, hypochlorous acid gas is passed at a temperature of about 30 °C to form dichlorohydrin. Finally, a base such as calcium hydroxide is applied to form dehydrochlorination reaction and yields epichlorohydrin as the reaction product.

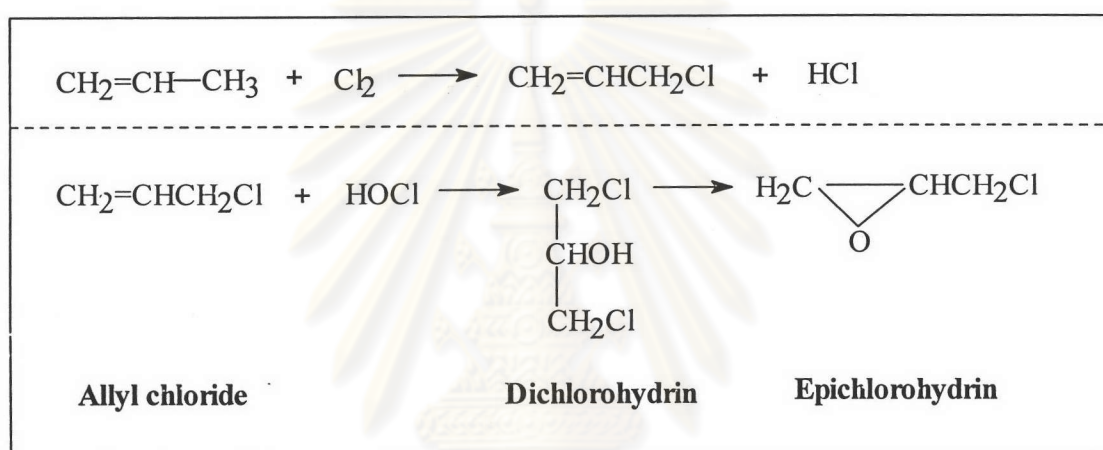


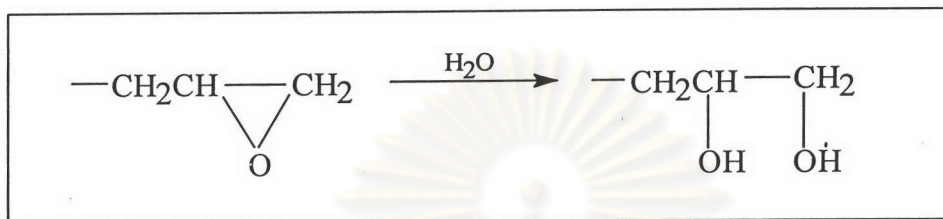
Figure 2.8: The formation of epichlorohydrin.

The reaction to form epoxy resins can be achieved by use 1 mole of bisphenol A reacting with 4 moles of epichlorohydrin at a temperature range of 105-110 °C under nitrogen atmospheric condition with a stoichiometric quantity of alkali such as sodium hydroxide. The product of the reaction is diglycidyl ether of bisphenol A. The structure of which is shown in Figure 2.4.

From the structure in Figure 2.4, it can be seen that the molecular weight of epoxy resins depends on the value of “n” which is the functionality of the epoxy resin. The use of a large excess amount of

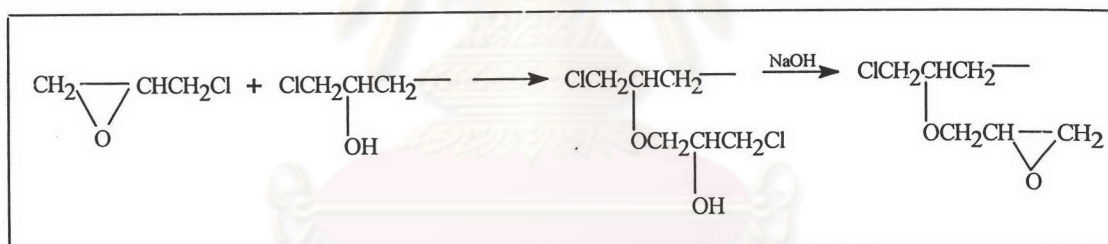
epichlorohydrin can minimize the formation of higher molecular weight species. Moreover, side reactions can also reduce the theoretical epoxide functionality. These side reactions are listed as follows:-

(i) Hydrolysis



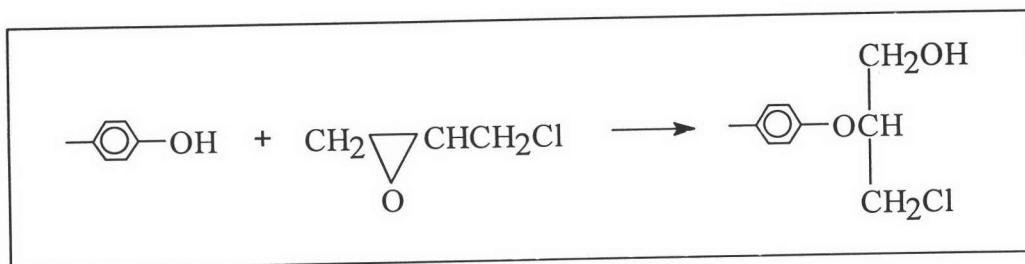
α -glycol formation

(ii) Formation of bound chlorine by the reaction of epichlorohydrin with alcohol OH groups.



3) Incomplete dehydrohalogenation resulting in a residual amount of saponifiable chlorine (hydrolyzable chlorine).

4) Abnormal addition of epichlorohydrin, i.e., an addition to the more substituted carbon atom.



The pure diglycidyl ether of bisphenol A is a crystalline solid with a melting temperature of about 43 °C. The weight per epoxide (WPE) or the epoxide equipment weight is 170. The typical commercial unmodified liquid resins are viscous liquid with a viscosity of 11-16 Pa.s (110-160 Poise) at 25 °C.

2.2.4 Basic Characteristics of Epoxy Resins

Many good properties of epoxy resin have led them to a rapid growth and they are used in a wide range of industries.

Epoxy resin is generally a liquid resin which readily converts to the thermoset phase upon the admixture of a proper curing agent. Other liquid resins such as phenolics, polyesters, acrylics and others are cured in a similar fashion. Epoxy resin tends to possess a rather unique combination of properties as following:

Low viscosity: The liquid resins and their curing agents can form low-viscosity, easy-to-process (or modify) systems.

Easy cure: Epoxy resin cure quickly and easily at practically any temperature ranging from 5 to 150 °C, depending on the selection of the curing agent.

Low shrinkage: One of the most advantageous properties of the epoxy resins is their low shrinkage during cure. Phenolic casting resins which evolve water, reveal high shrinkage, as do the acrylic and polyester resins which must rearrange and reorient considerably in the liquid and semigel phase. Epoxy resins react with very little rearrangement and with no volatile by-products being evolved.

High adhesive strengths: Because of the chemical makeup, chiefly the presence of polar hydroxyl and ether groups, the epoxy resins are excellent adhesives. The resins cure with low shrinkage, so that the various surface contacts set up between the liquid epoxy-resin formulation and the adherents are not disturbed during cure. Adhesive strengths, without the need for either open time or high pressures, are perhaps the best obtainable in the contemporary plastics technology.

High mechanical properties: The strength of properly formulated epoxy resins usually surpasses that of other types of casting resins. This is probably in part a result of their low shrinkage, which minimizes stresses that otherwise would weaken the mechanical structure.

High electrical insulation: Epoxy resins are excellent electrical insulators.

Good chemical resistance: The chemical resistance of the cured epoxy resin depends considerably on the curing agent used. Outstanding chemical resistance can be obtained by selecting appropriate specification of the curing agent. Most epoxy resins possess extremely high resistance to caustics and good to excellent resistance to acids.

Versatility: Epoxy resins are probably the most versatile of the contemporary plastics. The basic properties may be modified in many ways: by blending of resin types, by selection of curing agents and by using modifiers and fillers.

2.2.5 Applications of Epoxy Resins

Because of their versatility, epoxy resins are used in many industrial applications. The largest single use of epoxy resins is for protective coatings because of their high chemical resistance and adhesion. Epoxy resins are used in the automotive area, in container coatings such as two-piece cans, beer and beverage containers. They are also used in pipeline project during the worldwide energy problems. The greatest progress in the last several years has been in the laminates-composites segment. Epoxy resins also find extensive applications in electronics industry, particularly in computers parts, communication equipments, military and automobile parts, printed circuit boards and molding-casting systems. Figure 2.10 shows the marketshare of epoxy resins in each application.⁽¹⁶⁾

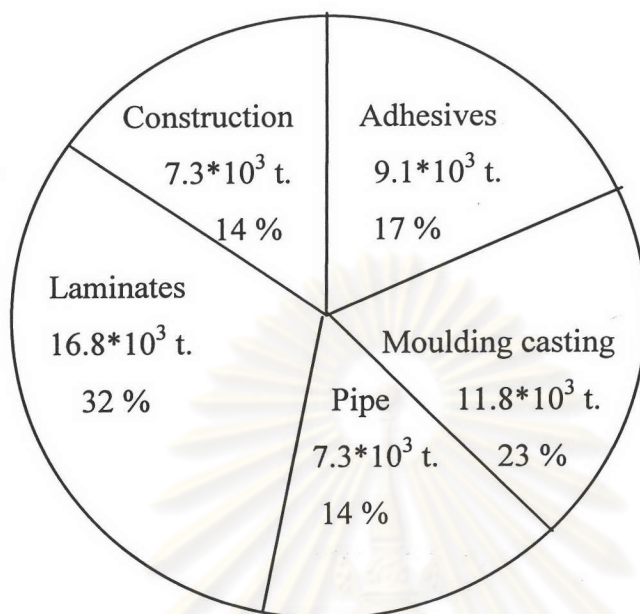


Figure 2.9: The use of epoxy resins in electrical and structural market in USA.⁽¹⁶⁾

The epoxy resins are also applied as additives for a variety of other plastic materials, such as vinyl, acrylic resins, natural and synthetic rubbers. They have also been used in decorative floor applications; as chemically resistant mortars and floor topping compounds, in printing inks, in fabric-treating applications, in dental surgical and prosthetic applications, for breaking petroleum emulsions and for lightweight chemically resistant foams.

The growth of epoxy resin in adhesives segment has been slower than other segments because of increasing competition from other materials such as polyurethanes and acrylics. Anyway, epoxy resins are

still introduced as specialty-packaged adhesives into the consumer market and some epoxy-based paints have since gained some acceptance.

2.3 CURING AGENTS

Epoxy resins must be crosslinked before application. The compound used to crosslink epoxy resins are called “curing agents” or “hardeners”. The crosslink reaction occurs at both ends of the epoxy molecules. The properties resulted from the crosslinking tend to vary, depending on the type of the curing agent. The classification of curing agent can be divided into 4 types, namely the aliphatic amines, aromatic amines, catalytic, and anhydrides.

2.3.1 Aliphatic Amines

One excellent curing agent for epoxy resin is aliphatic amine, it is highly reactive due to the number of active hydrogen atoms with aliphatic amines structure. The curing reaction, which is exothermic, can occur at room temperature. As a result, the temperature of the epoxy system during curing may rise to as high as 250 °C. Aliphatic amine cured epoxy tends to exhibit low mechanical and electrical properties when it is used at high temperature. Examples of aliphatic amines are diethylene-triamine (DETA) and triethylene-tetramine (TETA).

2.3.2 Aromatic Amines

Aromatic amines are amine curing agent with benzene ring in their structure. This is the reason why aromatic amine cured-epoxy can withstand a temperature of 150 °C and has greater thermal stability than those cured with aliphatic amine. The curing reaction may take place about 5 hours at room temperature. For good compatibility, every substrate must be heated before cure. Examples of aromatic amines are methylenedianiline (MDA) and diamino diphenyl sulfone (DDS or DADS).

2.3.3 Catalytic

Catalytic curing agent takes longer cure time than that by the aliphatic amine type, but it takes as much curing time as that by the aromatic amine. The exothermic curing reaction is capable of raising the temperature of the epoxy system to as high as 100 °C. Epoxy cured with catalytic curing agents have high temperature resistance and good chemical resistance. Examples of catalytic curing agents are tridimethylamino methylphenol (DMP-30), dicyanodimide (DICY) and benzyldimethylamine (BDMA).

2.3.4 Anhydrides

The reaction for anhydride-cured epoxy involves less thermal energy than that for the amine cured. Moreover, anhydride curing agents have lower toxicity than that from amine curing agent.

Epoxy crosslinked with anhydride have good chemical resistance, good mechanical and electrical properties. Anhydride curing agent must be stored in dry condition because it is highly sensitive to moisture. Examples of anhydrides curing agents are hexahydrophthalic anhydride (HHPA), phthalic anhydride and alkendic anhydride.

2.4 CURING MECHANISM

The most valuable single property of the epoxy resins is their ability to transform readily from the liquid (or thermoplastic) state to brittle and hard thermoset solids. The conversion normally occurs without the evolution of by-products.

The conversion is generally accomplished by the addition of a chemically active curing agent. Some curing agents promote curing by catalytic action, others participate directly in the reaction and are chemically bound into the epoxy resin chain. Depending on the particular agent, curing may be accomplished at room temperature with heat produced by exothermic reaction, or it may require an application of external heat.

The epoxy ring will differ in reactivity, depending on whether it is terminal, internal, or ring-situated. Suitably located, and under proper conditions, it has been found to react with well over 50 different chemical groupings.

Basically the cured structure may be a homopolymer, a heteropolymer or a mixture of both. A homopolymer is one that composes essentially of epoxy resin molecules linked together through their own reactive sites while a heteropolymer is one that composes of epoxy resin molecules linked together through the reactive sites of the curing agent.

The epoxy group may react in one of the two different ways: anionically and cationically. Both types of reaction are of importance in epoxy resin technology. In the anionic mechanism, the epoxy group may be opened in various fashions to produce an anion, as shown in Figure 2.10. The anion is an activated species capable of further reaction.

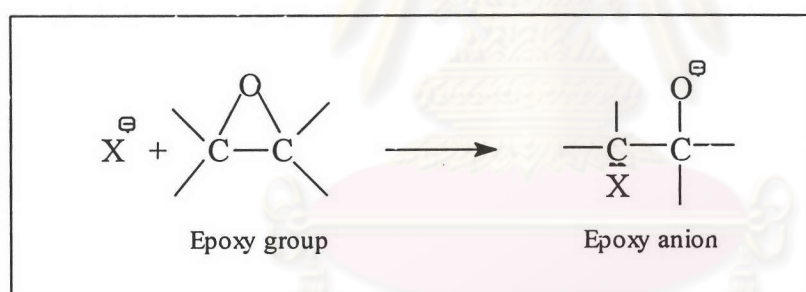


Figure 2.10: Anionic mechanism of epoxy group to produce an anion.

In the cationic mechanism, the epoxy group may be opened by an active hydrogen, i. e., hydrogen atoms which are replaceable by a metal, such as metallic sodium, to produce a new chemical bond and a hydroxyl group. The cationic mechanism may proceed in a number of ways, as shown in Figure 2.11.

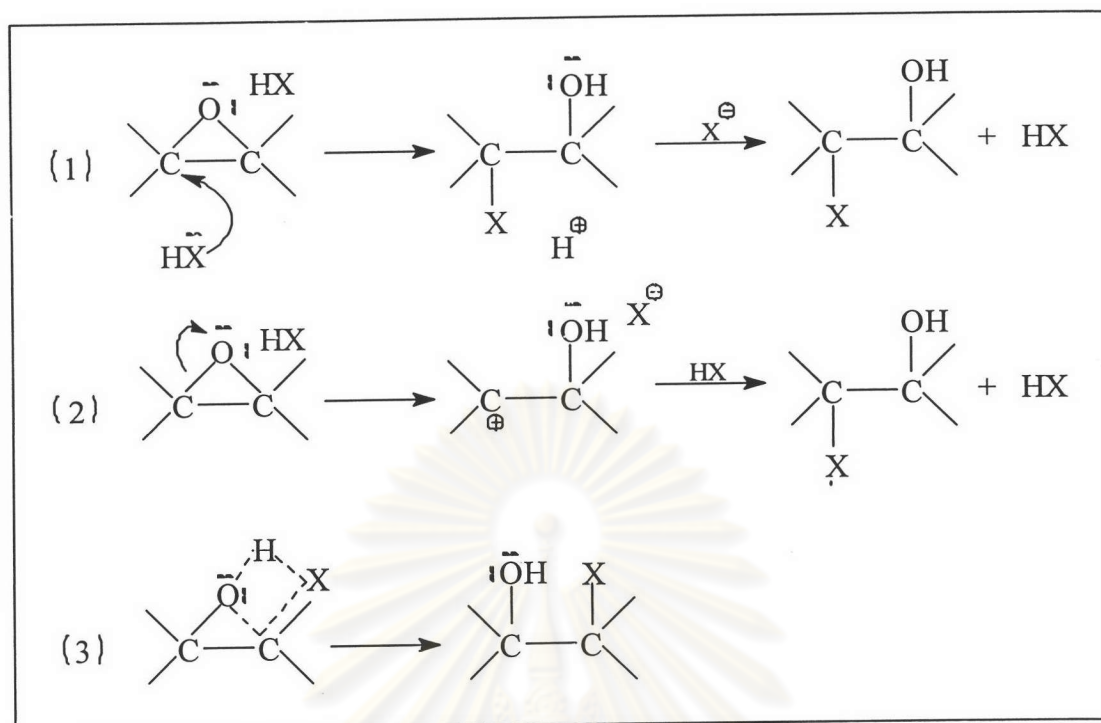
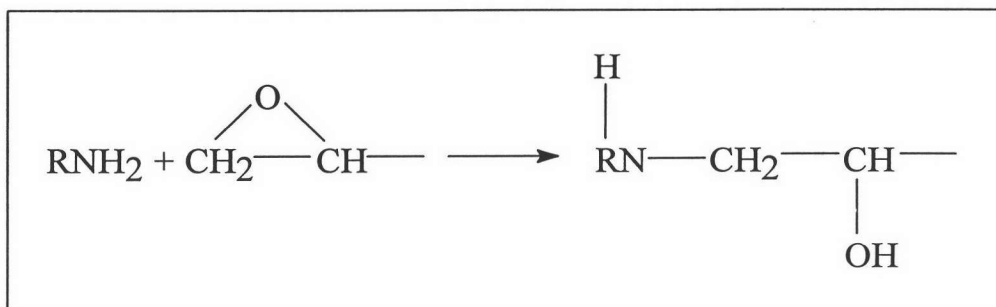


Figure 2.11: The cationic mechanism of epoxy resin that proceed in a number of ways.

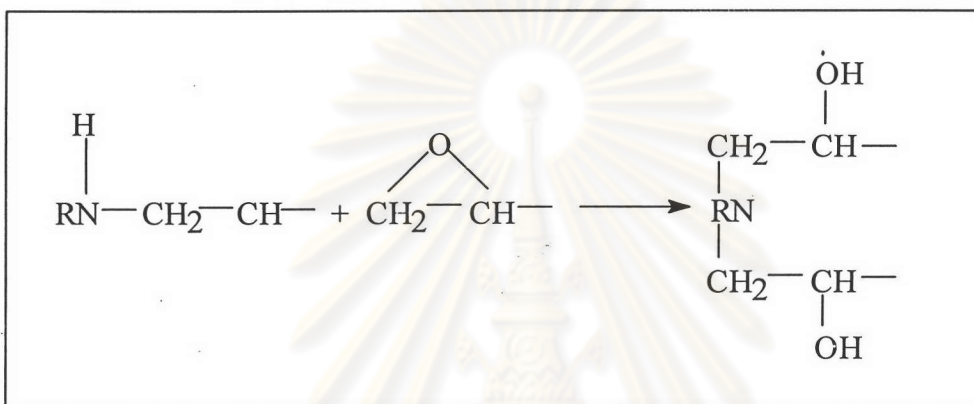
In fact, the mechanisms for the formation of epoxy anions and cations are rather more complex than indicated by the above simplified descriptions.

2.4.1 Crosslinking Epoxy Resins with Amine Curing Agents

The reaction to form network crosslinking between the epoxide group in the epoxy resin and the primary amine in the amine curing agents is shown in Figure 2.12 (a). The reaction between epoxy resins and the secondary amine group is shown in Figure 2.12 (b).



(a) Reaction with primary amine curing agent.



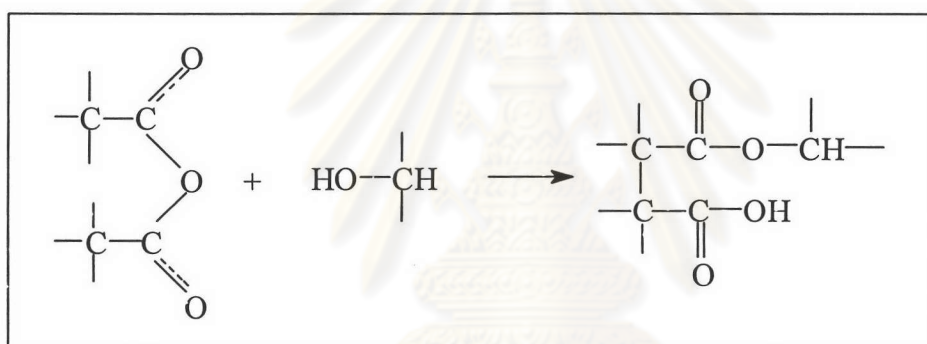
(b) Reaction with secondary amine curing agent.

Figure 2.12: Reaction of epoxy resin and amine curing agent to form network crosslinking.

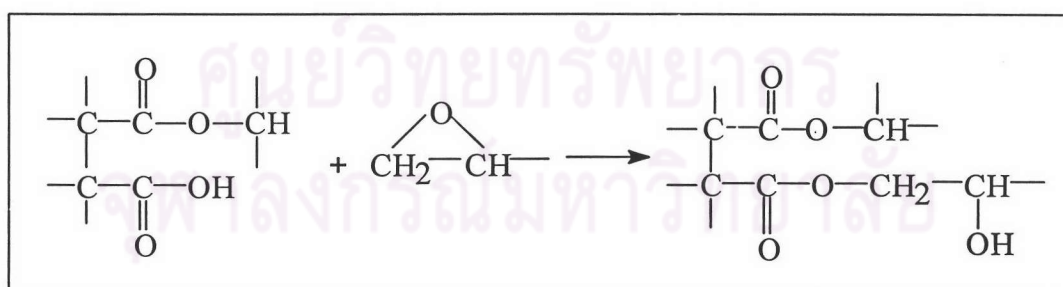
As shown in Figure 2.13, the epoxide group is reduced by the anion of the oxygen atom and epoxide ring will be opened. Crosslinking still occurs when the epoxide group and the anion of the oxygen atom still remain. For epoxy resins, there is an epoxide group at both sides of the molecule. Hence, crosslinking reaction can occur at both sides of the epoxy molecule.

2.4.2 Crosslinking Epoxy Resins with Anhydride Curing Agents

The reaction of epoxy resin with an anhydride curing agent to form a network crosslinking structure involves two steps. The first step is a reaction to open the anhydride ring with an alcohol. This is shown in Figure 2.13 (a). The second step is the crosslinking reaction between the epoxy resins and the anhydride whose ring has already been opened. The mechanism is shown in Figure 2.13 (b).



(a) Opening the ring of anhydride curing agent.

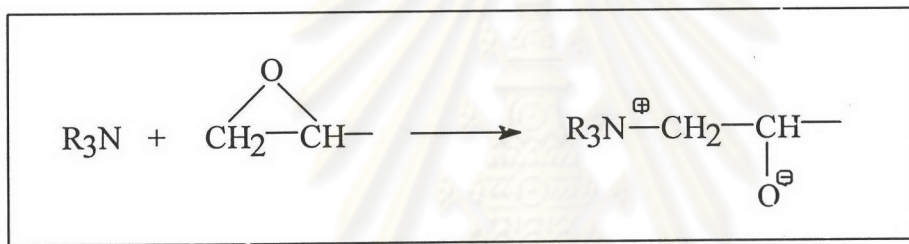


(b) Crosslinking with the opened-ring of anhydride curing agent.

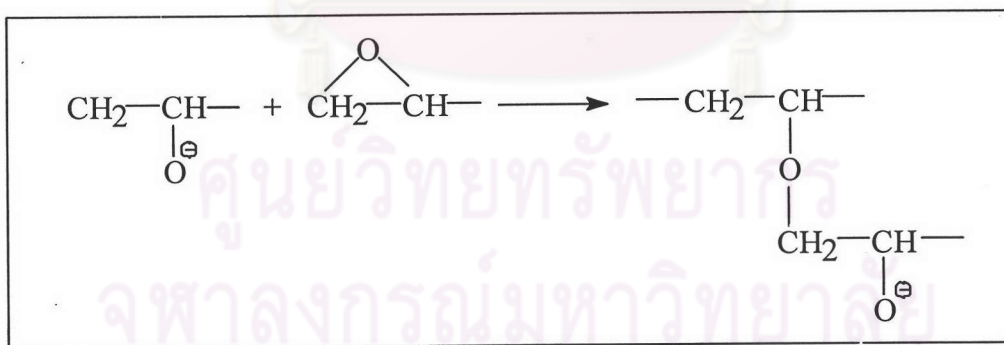
Figure 2.13: The reaction between epoxy resin and anhydride curing agent to form network crosslinking.

2.4.3 Crosslinking Epoxy Resins with Catalytic Curing Agents

Crosslinking epoxy resin with catalytic curing agents consists of two steps as shown in Figure 2.14. The first step is the reaction to open the epoxide ring with a catalytic curing agent. This is shown in Figure 2.14 (a). The second step, shown in Figure 2.14 (b), occurs when the ion from the first step opens another epoxide ring. The reaction proceeds until no more epoxide group is found.



(a) Opening epoxide ring with a catalytic curing agent.



(b) Crosslinking reaction between epoxy resin and catalytic curing agent.

Figure 2.14: The reaction between epoxy resin and catalytic curing agent to form network crosslinking.

2.5 SYNTHETIC RUBBER

As early as 1826, Faraday found an empirical formula of C_5H_8 for natural rubber. Later on in 1860, Greville Williams recognised that rubber was a polymer of isoprene type. Following works showed the straight-chain polymer structure of rubber to be hydrocarbon polymer. The elucidation of the structure of natural rubber paved the way for the development of synthetic rubbers.

Most synthetic rubbers are produced in two main stages, namely the production of a monomer or monomers and the polymerisation reaction to form rubber. From 1914 to 1918, methyl rubber was produced on a commercial scale in Germany during the World War I. It was a polymer of 2,3-dimethylbutadiene which had been discovered by Kondakoff. After an interval following the war, Germany synthesized two types of butadiene rubber which they obtained from the reaction with sodium. Hence, the German name for rubber produced from butadiene and sodium is *Buna*. In 1930, further development was made by I.G. Farben in Germany in the area of copolymer prepared from butadiene and styrene. The introduction of emulsion polymerisation brought along many advantages including greater production speed, little changes in the viscosity, and a more homogeneous polymer was obtained. Small amount of peroxide were used as catalyst. The idea arose from the fact that rubber is formed in the plant as a latex. Several patents had been taken out by Bayer Company as early as 1912.

2.5.1 Acrylonitrile-Butadiene (Nitrile) Rubbers -NBR

Nitrile rubbers were first produced in Germany in 1935. They are copolymers of butadiene and acrylonitrile. Since its first introduction in 1935, improvements have been made by the same methods as those used for styrene butadiene rubber (SBR). Nitrile rubbers are characterized by their excellent resistance to solvents. They are now available in a number of types, differing mainly in the relative proportion of the two monomers.

2.5.2 Manufacture of NBR

Basically, nitrile rubbers are manufactured by emulsion copolymerisation of butadiene with acrylonitrile in processes similar to those used for other emulsion polymer such as SBR. The main raw materials required are the monomers, butadiene and acrylonitrile. Both monomers may be synthesised from naphtha obtained from oil as shown schematically in Figure 2.15.

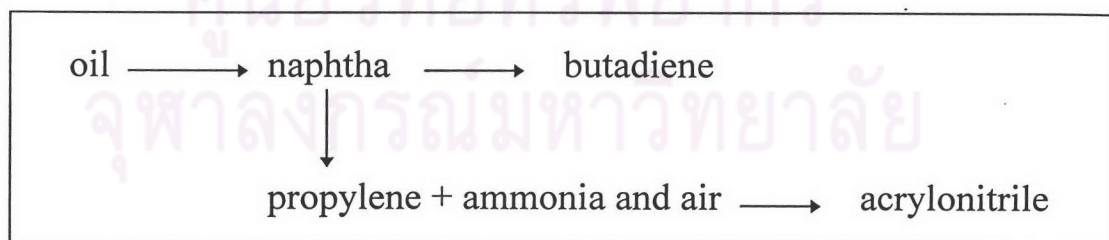


Figure 2.15: Flow chart for Butadiene and Acrylonitrile Synthesis.

At present, approximately 75% of the world production of the latter utilizes the Sohio process (Veatch *et al.*, 1962; Schmidt, 1969), in which ammonia, propylene, steam, and air are passed through a fluidised bed of finely divided catalyst at about 450-500 °C. In the theory, the polymerisation reaction can be written as that shown in Figure 2.16:

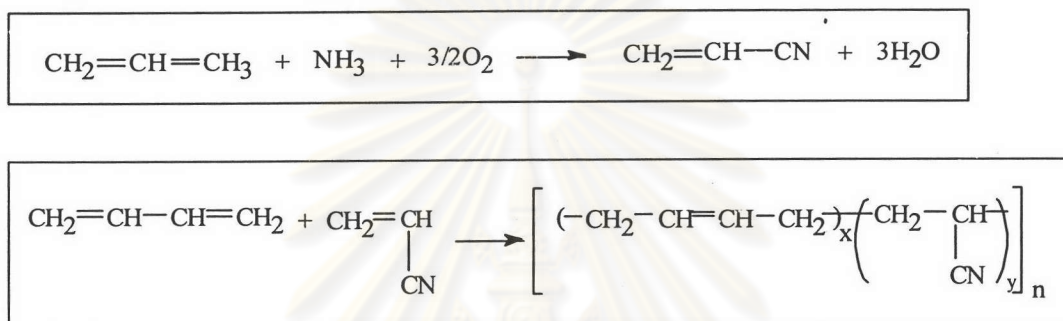


Figure 2.16 : Polymerization reaction to form nitrile rubber.

According to published information, there are more than 19 producers of dry nitrile rubber, among whom manufacture about 340 separately listed grades. Table 2.1, which has been compiled from the IISRP Synthetic Rubber Manual (8th Edn 1980) lists the main producers, their trade names and available grades.

Country	Producer	Trade name	Range of acrylonitrile content	Polymerisation temperature	Special grades
UK	BP Chemicals Ltd.	Breon	28-41	H, C	Liquid NBR Polyblack masterbatch
France	Compagnie Francaise Goodyear	Chemigum	22-45	H, C	Crosslinked NBR HR grades
	Polysar France S.A.	Krynac	27-50	C	Crosslinked NBR Carboxylated NBR Isoprene-acrylonitrile
	Ugine Kuhlman(PCUK)	Butacril	22-40	H, C	Liquid NBR Crosslinked NBR
Netherlands	Ciago bv.	Hycar	29-41	C	Liquid NBR Crosslinked NBR Carboxylated NBR
W. Germany	Bayer A.G.	Perbunan N	18-39	H, C	Crosslinked NBR
Italy	Anic SPA	Europrene N	19-40	H, C	Crosslinked NBR
	Montedison SPA	Elaprim	21-38	C	Crosslinked NBR
Canada	Polysar Ltd	Krynac	27-50	C	As Polysar above
USA	B.F. Goodrich	Hycar	21-51	H, C	As Ciago
	Goodyear	Chemigum	22-45	H, C	As Goodyear above
	Uniroyal	Paracril	22-45	H, C	Crosslinked NBR

Table 2.1: Main producers of nitrile rubbers.

2.5.3 Properties

The physical properties of nitrile rubbers are good when the rubbers are compounded with carbon black of suitable type. NBR generally have good heat and oil resistance.

Nitrile rubbers have a service temperature range of -50 to +120 °C but temperatures for service nowadays rise to +140 °C. The use

of synergistic antidegradant systems and rubbers with bound antioxidants are some of the techniques employed in conjunction with a suitable cure system in achieving improved heat ageing resistance.

The commercially available nitrile rubbers differ from one another in three respects: the acrylonitrile content, the polymerisation temperature, and the Mooney viscosity. The acrylonitrile content has by far the most profound effect on the properties of a vulcanised nitrile rubber. It influences the resistance to oils and fuels.

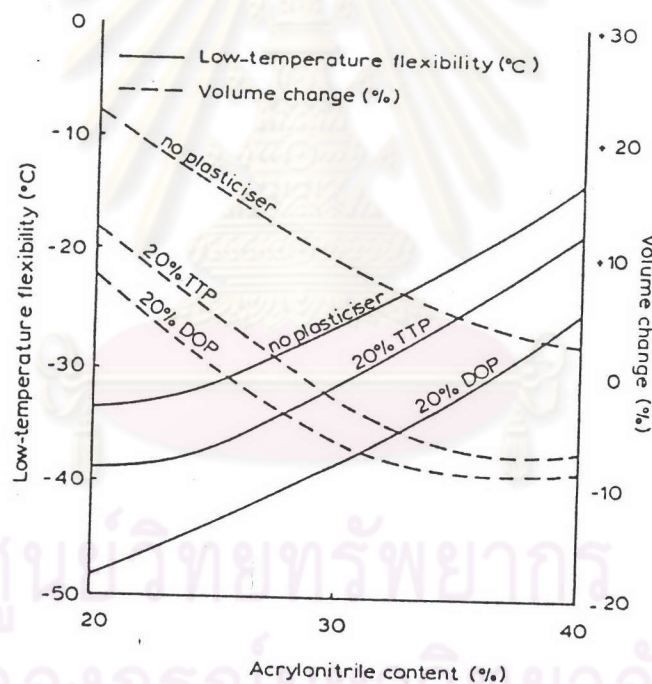


Figure 2.17 : Effect of the nitrile content on the volume change and low-temperature flexibility.

Figure 2.17 is a plot of the acrylonitrile content against the volume change upon impregnation in a mineral oil (DEF 2001) and the low-temperature flexibility. The curves show in general that the higher the acrylonitrile content, the smaller is the volume change. In any given fuel or oil, swelling may be influenced by the filler and the plasticiser content of the vulcanisate. Differences in swelling behaviour arise due to the different nature of the liquids. In benzene, toluene or xylene, a far larger volume change is observed. Much smaller volume change occurs in diisobutene or paraffin.

Rubber hose used in modern automobile engines is required to resist fuels with added alcohols. Nitrile compounds can undergo increased swelling. With suitable compounding and the use of PVC/NBR blends, satisfactory mixes can be obtained so that the PVC/NBR hoses can be used in contact with fuels and alcohols.

Polybutadiene (PBT) has very good low-temperature properties. Its glass transition temperature is in the region of -80°C . As acrylonitrile units are incorporated in the PBT chain, the low-temperature flexibility of the resultant elastomer deteriorates progressively.

2.5.4 Processing

Nitrile rubbers cannot process in the same way as natural rubber. Therefore, the viscosity of the rubber as produced (usually measured in Mooney units) has an important effect on its processing properties in addition to polymerisation temperature. 'Hot' rubbers are

usually more difficult to process than the 'cold' ones. Low Mooney rubbers absorb fillers and plasticisers more easily than high Mooney grades.⁽⁴⁴⁾ They also cause less heat build-up during mixing and faster extrusion rates can be obtained. On the other hand, when it is desired to produce soft compositions, it is preferable to use a high Mooney rubber as this will retain its strength more readily when only little filler and large amounts of plasticiser are used. The effect of acrylonitrile content on swelling, low-temperature flexibility, and other properties of nitrile rubbers can be summarised as shown in Table 2.2.⁽⁴⁴⁾

<i>High</i>	<i>Acrylonitrile</i>	<i>Low</i>
←	Resistance to fuels and oil improves	
	Low-temperature flexibility improves	→
←	Tensile strength improves	
	Resilience and elasticity increase	→
←	Abrasion resistance and hardness increase	
←	Processing improves	
←	Compatibility with plastics improves	

Table 2.2: The effect of acrylonitrile content on the properties of nitrile rubbers⁽⁴⁴⁾.

2.6 COUPLING AGENTS

Coupling agents are applied to enhance the molecular bonding at the interface between inorganic or organic fillers and polymer

matrix. The improved adhesion at the interface is believed to increase properties such as modulus of elasticity, tensile strength, abrasive resistance and compression set. Two types of commercially available coupling agents are silane and titanate coupling agents.

2.6.1 Silane Coupling Agents

The general formula of silane coupling agents is $R-Si-X_3$. R is an organofunctional and X is an alkoxy group ($-OCH_3$) which can be hydrolyzed to react with the $-OH$ bonding on the inorganic surface. In use, the silane coupling agent must first be converted to reactive silane group by hydrolysis with an alcohol before reacting with reactive inorganic surface. The mechanism of the surface treatment by silane coupling agents is shown in Figure 2.18.

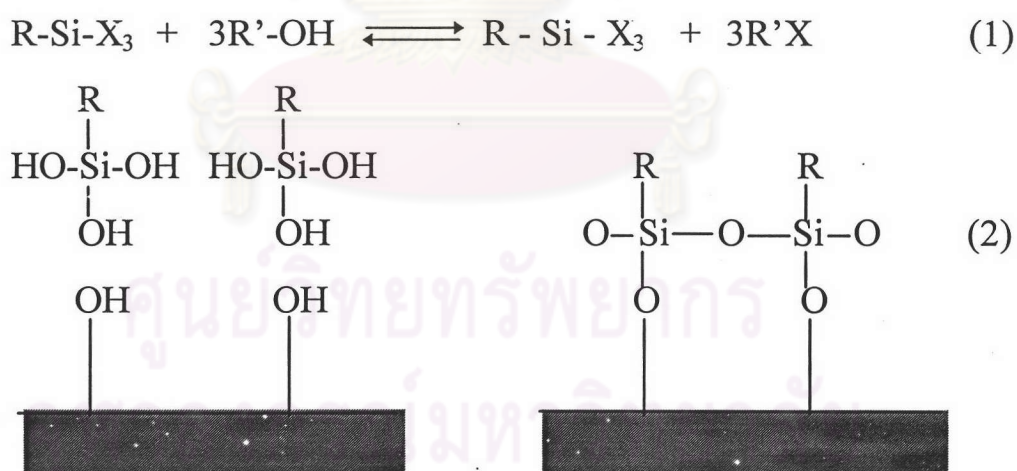


Figure 2.18 : The reaction of a silane coupling agent on an inorganic filler surface.

2.6.2. Titanate Coupling Agents

Titanate coupling agents are specially designed molecules which are more complicated than silane coupling agents. The general chemical formula is $(R-O)_m -Ti-(O-X-R^2-Y)_n$. They can form a monomolecular layer on most materials such as metals, metaloxides, carbonates, sulfates, chromates, siliceous materials, carbon black, graphite, Kevlar[®], dispersed dyes, organic pigments and so on.

The R-O group can hydrolyze to react with free proton (-H) on the inorganic/organic surface. The free proton often comes from either free water or reactive portion on the fillers. The free water is present in chemical bonding and physical bonding by absorption on the filler surface. The reaction of titanate coupling agents forms a monolayer on the inorganic surface as shown in Figure 2.19.

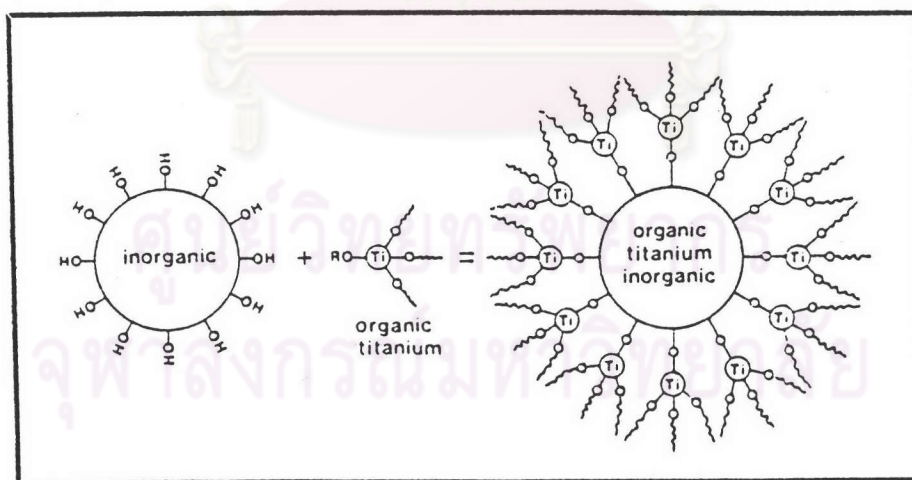


Figure 2.19 : The reaction of titanate coupling agents on an inorganic filler surface.

The hydrolysis reaction occurs at room temperature (25° C) but an accelerated rate of reaction is achieved at temperature between 60 and 80 °C.

The X group in the titanate coupling agent chemical formula may be alkylate, carboxyl, sulfonyl, phosphate or phosphite group. It improves properties such as corrosive protection, acid resistance, antioxidation or flame retardation.

The R² group are aliphatic group. They enhance the compatibility between the thermoplastic and the mineral fillers by promoting a secondary bonding of Van der Waal' s type.

The function of the Y group is to bond with thermosetting such as amino, acrylic mercapto and hydroxly group.

2.6.3. Application Methods for Titanate Coupling Agents

The methods of surface treatment are very important for fiber for reinforcement or fillers. Proper application will provide uniform distribution of a small amount (<1 % based in filler by weight) of liquid titanate coupling agents on the large filler surface area. The general methods of application are dry blending, slurry blending and in-situ surface treatment. The details for each method are as follows.

Dry blending surface treatment

In dry blending surface treatment, the filler is placed in mixing chamber of a ribbon blender or a high speed mixer. The liquid titanate coupling agent is added to a solvent to increase its volume. The coupling agent solution is fed to the filler by using a spray gun. They are then mixed thoroughly until all solvent evaporates.

Slurry blending surface treatment

The liquid titanate coupling agent is dissolved in a large quantity of solvent. It is then poured into the mixing chamber equipped with a stirrer. The filler is added while continuously stirring for complete reaction. The slurry is dried in an oven until all solvent has evaporated.

In - Situ surface treatment

All materials such as the titanate coupling agent, the polymer and the filler are pre-blended in a high speed mixer. Pre-blending is done when all materials are uniformly dispersed. Then, the pre-blend is directly used for compounding.

2.7 FRACTURE OF POLYMERS

The three general approaches to the study of fracture in polymers are continuum, molecular and statistical approaches. The main emphasis in this chapter is upon the continuum approach where a polymer is considered a continuum with particular physical properties but for which the molecular structure is mainly ignored. However, to gain a full idea of the fracture of polymers, their molecular structure must be taken into account and so the molecular approach is also discussed where it is relevant. The statistical approach sees the fracture process as being due to a series of events which can be predicted using statistical arguments. To clearly understand the fracture process, all three approaches need to be followed simultaneously.

It has generally been known that polymers tend to have rather lower fracture strengths than other materials such as metals or ceramics. When the relatively low density of polymers is taken into account, their specific strengths, which is defined as the fracture stress divided by the density, are quite comparable with other materials. Hence polymers have a high tendency to replace metallic components when weight-saving is at a premium.

A major problem of polymers is their tendency to undergo brittle/ductile transitions behaviour when modifying the polymer or changing the testing conditions. In general, this transition can be considered as being due to a competition between a brittle fracture mechanism such as *crazing* and a ductile mechanism such as *bulk shear*

yielding. The brittle mechanism tends to be favoured by reducing the test temperature, increasing the strain-rate or specimen thickness, having sharp notches or annealing the polymer.

Polymers can be toughened. Increasing the amount of plastic deformation at the crack tip will help the toughening effect. It is possible to increase the toughness of polymers by modifying the material rather than by changing the specimen geometry. For example, polycarbonate quenched from T_g is relatively tough whereas it can be embrittled by prolonged annealing. This is believed to be induced by annealing which tends to increase the yield stress but leaving the craze stress relatively unaffected. Hence the annealed polymer is brittle because it tends to undergo localised crazing rather than extensive shear yielding. Another important method of toughening polymers is by incorporating a soft rubbery phase into a brittle polymer matrix. This is a technique known as **rubber toughening**. Examples of this technique are high-impact polystyrene which is toughened by multiple crazing. Such mechanism causes extensive plastic deformation at crack tips and lead to a considerable increase in fracture energy over the unmodified polymers.

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