

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Waste Tires

2.1.1 Sources of waste tires

In the 21st century, tires are used in several transportation, for example aeroplanes, cars, trucks and two-wheelers. The consumption of tires has high quantity and upward tendency. After a long run, these tires are not serviceable and discarded. The discarded tires are categorized in waste tires that was difficult to be recycled. In 2010, European Union have the amount of waste tires risen to 4,000 kilo tons [16]. Table 2.1 [12] shows the general materials of tire production in tire manufacturing (in Europe and USA). These materials are the important components of tires. Natural rubber or NR has excellent flexibility to receive the impact and tensile strength. It is suitable for using at low temperature, around -40 to 70 °C. Unfortunately, NR is unable to resist the oil swelling. Synthetic rubber or IR is the artificial elastomer mainly synthesized from petroleum by-products. IR is developed to compensate some properties of NR. IR is categorized into 2 groups, high thermal stability IR and high oil resistance IR. The high thermal stability IR has the high temperature resistance but its flexibility is very low. These IR are styrene-butadiene rubber (SBR) and polybutadiene rubber (BR). The high oil resistance IR can resist the corrosive from oil and ozone. These common IR are chloroprene neoprene rubber (CR), acrylonitrile butadiene rubber (NBR). Carbon black is produced by the incomplete combustion of heavy petroleum. It use to increase the hardness of tire for the abrasion resistance. Steel is used as the hard framework in tires building process. The last material is additives which added to increase the efficiency of tires, for example fillers are used for cost reducing, Plasticizer are used for softening the compound, etc.

Unfortunately, most of waste tires have already vulcanized by vulcanization process. This process is an irreversible reaction between the elastomer, sulfur, and other chemicals. It generates the crosslinked structure between the elastomer molecular chains, leading to the formation of a three-dimensional chemical networks. The crosslinked structure modifies the property of tires such as elasticity, aging, solubility and abrasion to apply in many application. Figure 2.1 shows the crosslinked structure of NR by sulfur vulcanization process. The crosslinked tires are solid and insoluble. Moreover, waste tires become to the infusible thermoset materials



which had high resistance to the biodegradation, photochemical decomposition and chemical degradation. Consequently, the waste tires recycling is a difficult possibility.

Table 2.1 The general materials of tire production in the tire manufacturing (in Europe and USA)

Materials	In USA		In European Union	
	Passenger tire	Truck tire	Passenger tire	Truck tire
Natural rubber (%)	14	27	22	30
Synthetic rubber (%)	27	14	23	15
Carbon black (%)	28	28	28	20
Steel (%)	14-15	14-15	13	25
Additives ¹ (%)	16-17	16-17	14	10
Average weight	New 11 kg, Scrap 9 kg	New 54 kg, Scrap 45 kg	New 8,5 kg, Scrap 7 kg	New 65 kg, Scrap 56 kg

¹ Additives are fabric, fillers, accelerators, antiozonants, etc.

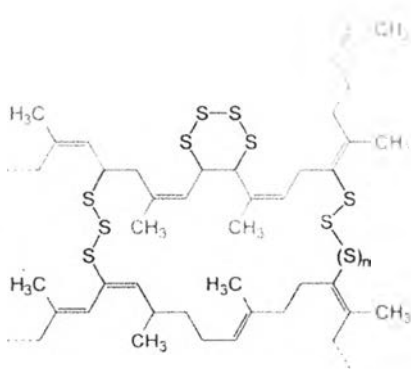


Figure 2.1 The crosslink structure of natural rubber by sulfur vulcanization process [2].

The most of waste tires are made from the crosslinked rubbers, representing a specific property of raw materials for the rubber industry. Consequently, the recycling or reclaiming process are hard possible. Moreover, the low scale of reusing and recycling waste tires is from main reasons include this following:

- The recycling process has to have specific equipment and special technology for high quality and quantity process to receive recycled tires.
- The substitution agents or additives for the tire compounds are hardly eliminated from waste tires.
- The cost of waste tires recovery process was high due to the more stringent regulations for environmental protection.
- A large amount of labor unit was required to input into the recycling or reclaiming process.

Because of these main reasons, the major requirements of waste tires recycling consist of the specific equipment, advanced technology, labor unit and high cost. Generally, using tires are naturally degraded by heat, sunlight and rain during the wearing out in use. The damage for degradation depends on the worked hour and the severity of weather. In case of waste tires, they are left as the disposal which needed a very long time for natural degradation. These waste are a serious threat to both the natural environment and human health because of the risk of fire and their being used as a suitable habitat by rodents, snakes and mosquitoes [17]. Accordingly, the increasing amount of waste tires has become a serious environmental concern.

2.1.2 Recycling and application of waste tires

Waste tires drive two main problems, the loss of valuable rubber and environmental pollution. To decrease the environmental concern, recycling waste tires is provided to solve the problem. Moreover, reusing is developed to manage the application from waste rubber. However, these methods are well known as the reclaiming process which gave the reclaimed tires.

Generally, the solid materials in tires, such as fabric and steel, are eliminated easily by the separation manufacturing. The separated solid compounds are reused and recycled in many industries. The most disposal compounds are used rubber which was the main composition of tires. Due to the complex structure from crosslink and the presence of stabilizers and other additives, waste rubber were hardly decomposed by the natural decomposition. Fortunately, waste rubber is recycled as filler in many application [18].



Waste tires are able to be a renewable source as valuable raw materials. This source is applied to use in many process for the recovery method. The effective conversion of waste tires is reusing to receive the new materials production or recycling as energy consumption. Although the recycling and reusing of waste tires are the good way to decrease the environment problems, recycling and reusing require the specific equipment and the methodology to support the complex process. These requirements base from the recovery of thermosetting materials which referred to waste tires. Because of the three dimensional crosslinked network in waste tires, they are unable to be softened or remolded by heating again like thermoplastic rubber [19]. The crosslinked network of thermosetting materials can be broken down by cleavage of the crosslinked chain or the carbon backbone of the main rubber chain. This severe reaction generated the fragmented products which are cleaved from the crosslinked rubber. All products are different from the raw thermosetting materials. Typically, the technology for thermosetting recycling is complex, high cost and less viable in the commerce.

Commonly, the recycled or reclaimed thermoplastics are used concurrently with virgin rubber and fresh additives to receive the desired formulation products. Each the formulation has a specific requirement. To obtain the desired properties, the amount of virgin rubber, additives and reclaimed thermoplastics are controlled by the suitable fraction. In case of the thermosetting materials, the reprocessing to the new polymer formulation is still difficult because the thermosetting reclamation has some trouble on flow and characteristic deformation during the process. These reasons support the low scale of waste tires recycling. Currently, the recycling and reusing waste tires can be sorted in 5 categories as follow [7, 10, 12, 20-23];

- Retreading

Retreading or recapping or remolding is a procedure that replace the tread on used tires. This method is useful to recover the used tires by extending the lifetime of tires. Moreover, retreading is able to reduce amount of new tires by replacing new tread on used tires. In the transportation system, this method preserves 90% of new tires and 20% of the material cost. This preservation is compared to the manufacturing of a new one. Retreading is the primary process to regenerate used tires before it become to waste tires. The basic procedure is performed in 2 steps. First, used tires with old tires tread is inspected to ensure that the tires carcass had no



damage. Then, the certified tires is retreaded by stripping old tire tread and apply a new one. Generally, retreading can classified in 2 types, cold process and hot process. The cold process is carried out at low temperature around 100 °C by coating the appropriate prepared carcass with a layer of a binder from rubber mixture. The mixture is prepared from a proper pattern and size of primarily vulcanized tread. All components are pressed onto the carcass which used special rubber. Then, it is enveloped and vulcanized in an autoclave at the commented temperature for 4-5 h. On the other hand, the hot or high temperature process is started by laying on the carcass with the fresh rubber mixture. The mixture is controlled by necessary composition and volume. Then, all of the mixture is vulcanized in mold to generate the tread pattern on the carcass around 200 °C and elevated pressure.

Retreading is useful in the economic system by reducing the energy requirement and the amount of raw materials used for new tires production. Moreover, it is a waste free process because the by-product from retreading process is pulp rubber which can be reused in the polymer composite manufacturing or in the construction industry. Generally, the most of used tires are regenerated by retreading. Although retreading in some cases had to spend high cost, it is helpful to reduce the purchase of new tires and decreased the amounts of rubber waste. Truck and aircraft tires are rarely regenerated by retreading for reasons of economy. The quality to price ratio for large size retreaded tires is much higher than in the case of new tires. Car tires is not retreaded because of their nearby cost of new tires, poor quality and safety.



Figure 2.2 The retreading of used tires [10].

- Energy recovery

The energy recovery is the basic way to generate an energy from the raw materials, recycling from waste tires. The energy which is recovered from waste tire is known as fuel and is denoted as tire derived fuel or TDF in the international classification [24]. In the cement industry, waste tires are selected to use as alternative fuel because their calorific value was 32 MJ/kg which make them competitive with other types of fuel. Moreover, a calorific value of used tires is higher than coal. For this reason, used tires are able to be used as co-combustion with coal. The co-combustion can be desired the quantity of power from the energy recovery process. Furthermore, the cement kilns in the cement plants have to be operated at high temperatures, above 1200 °C, which are able to be the waste-free process from the complete combustion of all waste tires components. The advantage of cement kilns provides the environmental safe by the lower emission of dusts, carbon dioxide, nitrogen oxides and heavy metals when compared to the coal combustion. The co-combustion of coal with waste tires improves the thermal efficiency of steam boilers and furnace, generating the fuel which is used as energy in the production of steam, electrical energy, paper, lime and steel. Moreover, the co-combustion can control the permission limit of the exhaust gases and dusts.

- Pyrolysis

Pyrolysis is the recycling of waste tires by using high temperature of 400-700 °C in the absence of oxygen to decompose the elastomers containing in the waste tire. This method is the way to reprocess waste tire by generating new products such as fuel gas, oils and a solid residue or char. All products from pyrolysis contain mineral matter and low grade carbon black. The pyrolysis is performed in the special pyrolytic furnaces to operate in the specific conditions of normal or low pressure in the atmosphere of an inert gas, especially nitrogen gas. The pyrolysis production are solid, liquid and gaseous form. The solid products consist of soot, fly ash, silica, steel and char. The liquid products contain aromatic hydrocarbons and oils. The gaseous products are rich in hydrogen, carbon monoxide, carbon dioxide, aliphatic hydrocarbons and hydrogen sulfide. The pyrolysis products of waste tires are the series of chemical compounds which is useful in the petrochemical industry. For example, the high calorific value liquid products from the pyrolysis process which is already removed the contaminating sulfur compounds can be mixed with diesel oils and other petroleum products to use as fuel in the industry. Unfortunately, the pyrolysis of waste



tires is rarely performed on an industrial scale because this process has high cost for the installation of equipment and the maintenance of process. Moreover, the price of products from pyrolysis is uncompetitive in the large scale. Figure 2.3 shows the pyrolysis products from waste tires by burning scrap tires. The scrap tires are the separated rubber from the waste tires. This process had 2 main steps. The first step is the pyrolysis of scrap tires at 500-900 °C to generate the primary products such as pyro-gas, oil and char. The next step is the transformation of the primary products to more valuable products by secondary thermal processes.

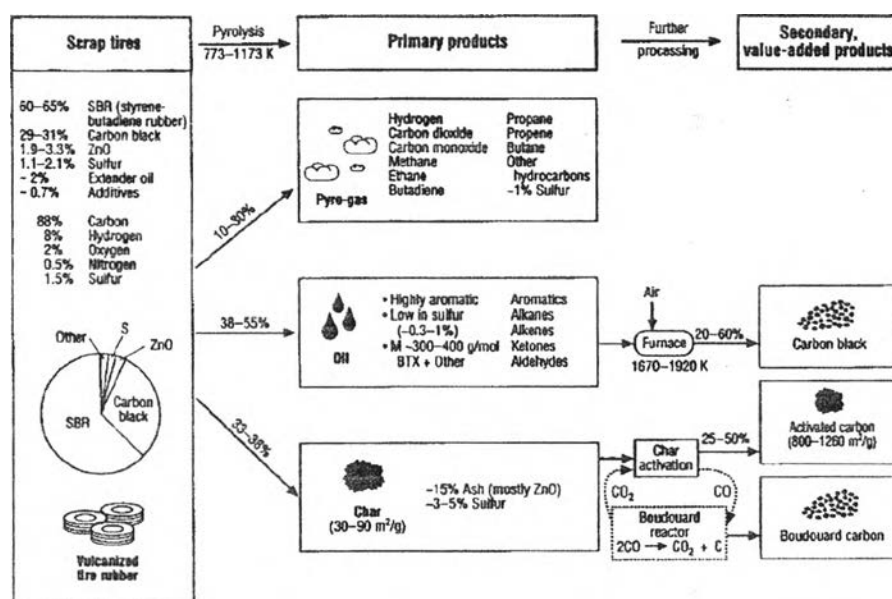


Figure 2.3 Industrial example of pyrolysis products derived from scrap tires [4].

Product recycling

The product recycling is a method in which the waste tires are changed to new products without any physical or chemical treatment. The method that is applied to recycling is based on the properties of the waste tires. Generally, the waste tires are cheap material and easy to apply in many applications. Because of their size, shape, high elasticity and good resistance to vibrations, noise and shocks, the waste tires are used to form the protective barriers along roads and highway to protect the car bumping from the accidents. Moreover, the waste tires are applied as bumpers around the pontoon to protect the bumping between a boat and the border of pontoon during the transportation. In the habitation, the waste tires are recycled to

the furniture or equipment such as table, chair, pot, etc. Furthermore, the ornament business transforms the waste tires to goods by cutting, reshaping and decorating. Earrings, necklace and bracelet are the favored goods of the decoration market. Figure 2.4 shows the new products which are obtained from the product recycling of used tire. However, the product recycling can reduce the small amount of waste tires.

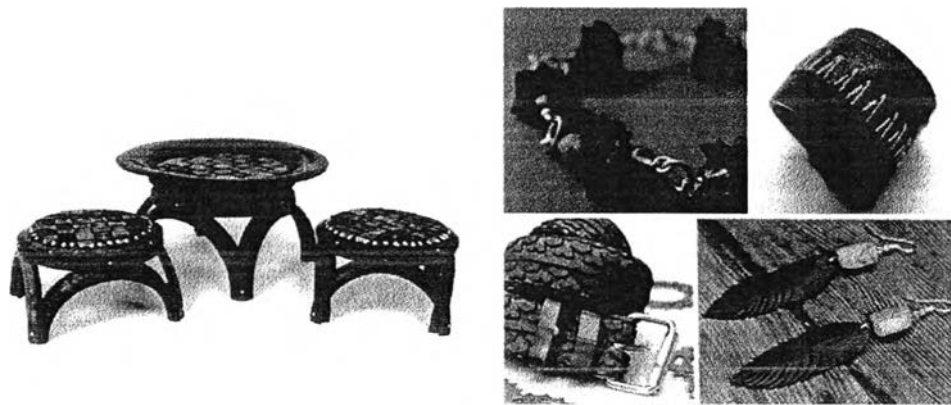


Figure 2.4 Examples of new products obtained from the recycling of waste tires.

- Material recycling

Material recycling is the process in which the waste tires was recycled to the new products or raw materials by physical or chemical treatment. This process transforms the waste tires into new species or back to the original one which can be used as raw materials in many applications. The major application of the recycled tires is additive. It is used to mix with virgin rubber to form the rubber compound which is prepared for feeding to the vulcanization process. This is the way to reduce the consumption of virgin rubber and cost. Generally, the material recycling is the devulcanization because the main point of this process is to cleave the rubber bonding which crosslinked from the vulcanization. This process has 2 parts, grinding and devulcanization. The material recycling method is started with separating the steel and textile which are overlaid in the waste tires. These separated materials are fed into the recycling processes. The steel is recycled by smelting while the textile is cleaned and reuse in the combustion process to recover the energy. Moreover, the textile can be reused to form the thermal insulator for the construction industry. The major product from the separation is the used rubber which is the main composition of used

tires. This separation step is called the grinding process. The recovered rubber are grinded and milled to black powder, so-called crumb rubber. After that, crumb rubber is applied to use in many application by the transformation or treatment processes. This step is a specific management which called devulcanization process. Figure 2.5 shows crumb rubber obtained from the grinding process before the devulcanization process. The details of the devulcanization process will be explained in the next topic (2.2).

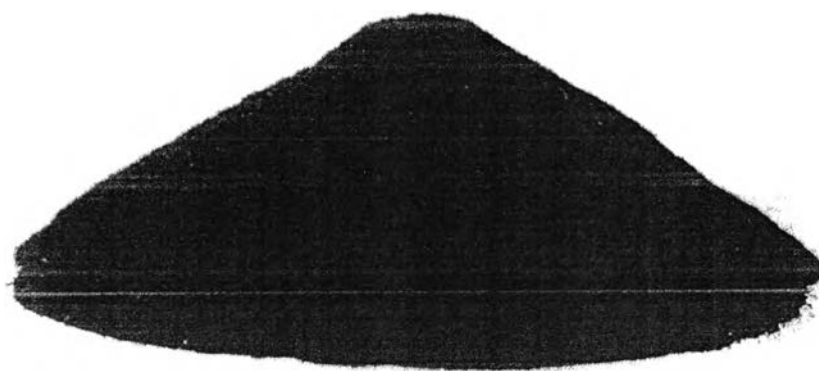


Figure 2.5 Crumb rubber from the grinding of used rubber [7].

2.1.3 Advantages of waste tires recycling

Currently, waste tires are often recycled in 2 parts, waste rubber and solid waste. The solid waste are steel and textile which are easily recycled. Waste rubber are reclaimed as crumb rubber which are important for the rubber industry. Because of the saving cost and energy, crumb rubber is used as additive in various rubber formulation. Moreover, amounts of crumb rubber affect to the mechanical properties of fresh rubber formulation. Furthermore, the mechanical properties of fresh rubber formulation can be adjusted by the ratio of crumb rubber and fresh rubber.

Crumb rubber are function of plasticizer when it was mixed in the rubber formulation on the large size of the reclaiming process. In the rubber formulation, crumb rubber as the additive are helpful to consume less time and power than the pure fresh rubber formulation. Moreover, crumb rubber are useful to reduce the heat generation in the mixing process. These are particular advantage with compounds containing high carbon black loading.



The virgin rubber can be processed at lower temperature when they are mixed with the crumb rubber. Because the crumb rubber are function as plasticizer, they provide the faster processing, especially the extruding and calendering. The mixing of crumb rubber and virgin rubber are called the reclaimed rubber. After the vulcanization process, the reclaimed rubber are more thermosetting than the new compounds. So, they can hold their shape better when they are extruded and cured. The shrinkage of calender and the swell of the extruder die are reduced by the proper ratio of reclaimed rubber. Moreover, reclaimed rubber permit the high speed using of calender in the tires carcass stocks production which obtained the smooth uniform coating products. For tires carcass compound, reclaimed rubber give the better penetration in the fabric and chord.

After calendering, the tack of reclaimed rubber compound tend to maintain longer than the fresh rubber compound. Generally, the fresh rubber compounds become more tacky in hot weather and dry in cold weather. In contrast, the hot and cold weather are less influenced to the tack of reclaimed rubber compound. This characteristic of reclaim rubber compound is properly applied as the pressure sensitive tape.

Reclaimed rubber compound is curing faster than the virgin compound because reclaimed rubber has proper active sites. It can help the compounds to retard and reduce sulfur bloom form uncured and cured stocks. Thus, it use less energy in the process that is useful in the commercial purpose. Vulcanization of reclaim rubber containing stocks shows less tendency to revert indicating better aging resistance.

Conclusion, use of reclaimed rubber to produce the rubber compound can reduce the cost and the feed stock. It helps to save the energy consumption with less energy to gain more products. Moreover, crumb rubber can use as additives to comfort the process and become to the important material which reduce amount of new rubber. However, many research studied about the use of reclaimed rubber. They are developed to apply in many application. Although, the devulcanization process is the method which can regenerate the used tire back to the virgin rubber, it requires many condition for perform the process. Moreover, devulcanization is hard to control for the industrial scale.



2.2 Devulcanization Process

Devulcanization is the second step in the material recycling after the grinding process. Waste rubber are sent to the devulcanization process. This process is aimed to decompose the crosslinked structure of the vulcanized rubber. It is the partial or complete breaking of mono-, di- and polysulfidic bonds. However, the main chains of rubber polymer is also degraded by devulcanization. The product obtained from the devulcanization no longer possesses the properties of the original material (natural rubber). Sincerely, the devulcanization process involves breakdown of rubber polymer materials by selective oxidation decoupling of C–C, C–S and S–S bonds which using the cleavage method with suitable condition.

Devulcanization is the reclaiming process of scrap tires which was the most desirable approach to manage and solve the disposal problem. Reclaiming of scrap rubber products, e.g. used automobile tires and tubes, hoses, conveyor belts etc. by devulcanization process is the conversion of a three dimensionally interlinked, insoluble and infusible strong thermoset polymer to a two dimensional, soft, plastic, more tacky, low modulus, processable and vulcanizable essentially thermoplastic product simulating many of the properties of virgin rubber. This is the main objective of the devulcanization. Recovery and recycling of rubber from scrap rubber products can save some precious material resources for solution and reduction waste rubber disposal. Generally, reclaiming with devulcanization process may be broadly classified into three groups: the mechanical devulcanization, the chemical devulcanization and the biological devulcanization. Each process is described in the paragraphs below [5, 22, 25-28];

2.2.1 The mechanical devulcanization

The mechanical devulcanization is a physical reclaiming process of scrap tires recycling which used the external energy to drive the process. In this physical devulcanization, three-dimensional network of crosslinked rubber breaks down in presence of the different energy source. It is a non-selectivity process giving the small molecular weight fragments product which obtained from the transformation of the breaking down in the network structure macromolecular rubber chain. This product can be easily miscible with the virgin rubber during compounding. So the reclaim rubber produced by physical reclaiming with the devulcanization process may be used as a non-reinforcing filler. It is the important advantage to save cost and



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material for new tire production. The requirement of external energy is depended on the efficiency to cleave the specific crosslink bonds in the rubber. In this process, a specific amount of external energy and suitable condition are used to desire the capability of the process to cleave only the crosslink bonds then after reclaiming a good quality of reclaim rubber will be obtained which will be thermoplastic in nature and compare well with virgin rubber properties. Different types of physical reclaiming processes for devulcanization are described below:

- Mechanical reclaiming process

In this part, the devulcanization of scrap tires in the mechanical reclaiming process is performed by placing crumb rubber which obtained from the grinding process of scrap tire, in an open two-roll mixing mill. Then, the milling is heated to high temperature for support the process. The process is initiated by cleaving the polymer chain due to mechanical shearing at high temperature. The molecular weight is drastically breaking down. From the patent by Maxwell [29], he explained about the physical reclaiming and refining process of vulcanized rubber. The vulcanized rubber in form of ground tire is reclaimed by passing the rubber with the reclaiming agents through between an essentially smooth stator and an essentially cylindrical rotor arranged to provide an axial shear zone in which the rubber is frictionally propelled by the rotor action. This action is assisted by mixing proper amount of previously reclaimed rubber or new vulcanized rubber with the ground tire which had the supplemental heating to support this process. Moreover, the invention previously reclaimed and vulcanized rubber are able to feed and act upon as substitute for conventional refining operation. In case of vulcanized natural rubber, the mechanical reclaiming process of vulcanized natural rubber is prepared by milling vulcanized sheet of natural rubber at 80 °C. After that, it formed a band on the two roll milling which transformed from the vulcanized rubber to the reclaimed rubber. Then, various rubber additives mixed with the reclaimed rubber on the milling. For the properties controlling of the mixing, the proportion of them was specially adjusted to the proper quantities. In another case, reclaimed rubber from the mechanical devulcanization was mixed with fresh rubber in various proportions. Their curing characteristics and mechanical properties are studied which found the higher value of Mooney viscosity in the reclaimed rubber due to the low plasticity of rubber from the presence of higher percentage of crosslinked rubber. However, the extent of reclaiming, i.e. percentage of sol/gel fraction, molecular weight of the sol fraction, and



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the influence of milling parameters on the Mooney viscosity have never studied before.

The blends of fresh rubber with reclaimed rubber have the specific curing characteristics depended on the content of reclaimed rubber. The increasing in the reclaimed rubber content is affected to the increasing in the cure rate. In contrast, the scorch time, optimum cure time and reversion resistance decreased. Sincerely, the proportion of reclaimed rubber in the blends is extremely affect to the properties of the blends. As the proportion of reclaimed rubber increases modulus, abrasion loss, compression set and hardness increase while tensile strength, elongation at break, tear strength, resilience and flex resistance decrease. These results refer that the increase in the proportion of reclaimed rubber increase the crosslink density in the rubber structure. The blend ratio of natural rubber to reclaimed rubber which had high crosslink density is 25/75 giving high modulus, low tensile strength and flex properties. Thus, reclaimed rubber appeared to perform the blend as a non-reinforcing filler.

- Thermo-mechanical reclaiming process

This process is started by swelling crumb rubber in a suitable solvent. After that, the swollen vulcanizate is subjected to shear in the specific equipment such as open mills, twin-screw extruders etc. The equipment, especially milling and extrusion, are usually carried out at high temperatures which was higher than 80 °C [30] and not over the decomposition temperature of vulcanizate rubber. The objectives of this path are scission the crosslink bonding in the rubber to transform into the original rubber. This results are a prominent decrease in the molecular mass. The obtained rubber characteristics strongly depend on the processing equipment, its characteristics (e.g. local shear rate) and processing parameters (e.g. residence time). This process involves the thermo-mechanical degradation of the rubber vulcanizate network. On the end of process, this powder rubber is revulcanized with curing ingredients. The products thus obtained show slightly inferior properties to those of the original vulcanizates.

- Cryo-mechanical reclaiming process [30]

In 1960s, the cryo-mechanical process was developed for grinding and devulcanization scrap tire. This method is involved by placing small pieces of vulcanized rubber into liquid nitrogen. For this step, the low temperature of liquid



nitrogen, nearly 200 °C, cooled the vulcanized rubber to hard and brittle. Then, the rubber is transferred to a ball mill and ground in presence of liquid nitrogen to form a fine powder. Generally, the cryo process reduces the particle size of the rubber varied from 30 to 100 mesh which suited for the most products. The particle size is controlled by the immersion time in the liquid nitrogen and by the mesh size of screens used in the grinding chamber of the mill.

In the processing, the cryogenically rubber certain particle sizes are more suitable in specific applications. For extrusion, 80–100 mesh cryogenically rubber is needed to avoid fracturing and rough edges. In extrusion of thick section, 50–60 mesh cryogenically rubber can be used depending on the surface smoothness of the final product. The optimum ratio of cryogenically rubber to fresh rubber is 5%. For calendering, 80-100 mesh cryogenically rubber is suitable for surface smoothness of thick product. The optimum ratio of cryogenically rubber to fresh rubber in calendering is 10%. For Molding, the cryogenically rubber in all mesh sizes are allowed because all mesh sizes help to remove the trapped air during the process. The cured rubber particles provide a path for the air to escape by bleeding air from the part.

The cryo-mechanical process has many advantages. The equipment cost is less, operating costs are lower, productivity is increased, and the product has better flow characteristics than ambient ground rubber. The nature of the surface morphology on the cryogenically rubber is unique which facilitated ventilation of trapped air in unvulcanized rubber laminate products, particularly tires, thus reducing tendency for cure blistering. Moreover, the large particle size of cryogically rubber when compared to the other method helps to prevent the surface oxidation.

- Microwave reclaiming process [31]

The microwave energy is controlled at the specific frequency and energy level for the efficiency to cleave C-C bonds in rubber. Thus, used rubber is reclaimed by depolymerization to the initial material having the properties equivalent to the original vulcanizate which abled to recompound and revulcanize again. This method is useful because it provides an economical, ecologically sound method of reusing elastomeric waste to return it to the same process and products. The product from this process was originally generated with equivalent physical properties to the original materials. Moreover, the degradation of rubber in this process is missing which normally takes place in the usual commercial processes currently being practiced. The



microwave devulcanization is a method which controlled the pollution by reclaiming of sulfur vulcanized elastomer containing polar groups. The microwave energy devulcanization device generates heat at a temperature in excess of 260 °C to yield a mass which is fed to an extruder. After that, the rubber is extruded at a temperature of 90–125 °C. Moreover, the cost of devulcanized hose and inner tube material by microwave method is only a fraction of the cost of the original compound. The transformation from waste rubber to devulcanized rubber ready for remixing takes place in only five minutes with usually 90–95% recovery of the rubber. Therefore, it appears that this microwave technique is a unique method of reclaiming in terms of properties and fastness of the process.

• Ultrasonic reclaiming process [32]

In 1973, ultrasonic devulcanization was reported in patent [33]. In this process solid rubber materials such as tires are immersed into a liquid and then it was put with a source of ultrasonic energy whereby the bulk rubber effectively disintegrated upon contact and dissolved into liquid. It uses the ultrasonic irradiation with the range 20 kHz and the power intensity greater than 100W. After that, this process was developed in 1987 [34]. They subjected the NR vulcanizate to 50 kHz ultrasonic energy for 20 min to achieve devulcanization followed by redevulcanization and obtained reclaimed rubber with similar properties to those of original rubber. However, there is a possibility of rubber degradation and devulcanization by ultrasonic energy.

The devulcanization process requires a high energy level to break carbon–sulfur and sulfur–sulfur bonds. An ultrasonic field creates high frequency extension–contraction stresses in various media. These energy percolate in the network of rubber to degradation during ultrasound devulcanization. A possible mechanism of devulcanization was also discussed by the measurement of crosslink density and gel fraction of the devulcanized rubber. It was reported that both crosslink density and the gel fraction decrease in the devulcanization process. For original tire, the gel fraction is 83% and crosslink density of gel is 0.21 kmol/m³. After ultrasound treatment at 1218 °C, it reduces the gel fraction to 64–65% with crosslink density of 0.02 kmol/m³. This result is concluded that the crosslink density also decreases with higher residence time in the treatment zone and with higher specific ultrasonic energy. Moreover, it is found that the molecular weight of sol fraction decreases during



ultrasound devulcanization. This occur may be understood that ultrasound treatment attacks not only C–S or S–S bonds but also C–C bonds. Accordingly, some of the devulcanized rubber contain a large amount of sulfur which are able to response for the revulcanization.

2.2.2 The chemical devulcanizaiton

The chemical devulcanization has high selectivity in the scissions of S–S or C–S bonds. This method is always used in industries by using the chemical reclaiming agents for the manufacture of reclaimed rubber. Generally, the organic disulfides or mercaptans which are exclusively are used during mechanical working at elevated temperature. Based on these chemicals many processes have been developed and subsequently patented. Apart from these a few inorganic compounds have also been tried as reclaiming agent. Table 2.2 shows the chemical probes for devulcanization of the crosslinked structure. Each method is commonly explained below;

Table 2.2 The chemical probes for devulcanization of the crosslinked structure

The chemical probes	Attacking position
Sodium di-n-butyl phosphite	Di and polysulfide
Propane-thiol/piperidine	Polysulfide
Hexane-1-thiol	Di and polysulfide
Dithiothreitol	Disulfide bonds into two thiol groups
Lithium aluminium hydride	Di and polysulfide
Phenyl lithium in benzene	Di and polysulfide
Methyl iodide	Monosulfide

• Reclaiming by organic disulfides and mercaptans

Reclaiming scrap tires by using the organic disulfides and mercaptans was found since 1910. As a result, a large number of chemical reclaiming agents for natural and synthetic rubbers have been developed. In the present, many researches reported the chemical probes for devulcanization of the crosslinked structure which

selectively cleaved C-S and S-S bonds in mono-, di- and poly-sulfides. Moreover, they avoid to cleave C-C bonds in the main chain of polymer.

For the example, the reaction in Figure 2.6 shows the breaking of polysulfide bonds in presence of propane thiol/piperidine probe as follows;

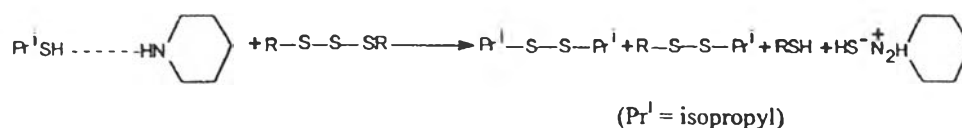


Figure 2.6 the reaction in for breaking of polysulfide bonds in presence of propane thiol/piperidine probe [5].

- Reclaiming by inorganic compounds

The crosslinked rubber is swelled in the solvent which suspended at high temperature around 300 °C in the oxygen atmosphere. Generally, the solvent is used such as toluene, naphtha, benzene and cyclohexane. After the swelling, the mono-, di- and poly-sulfidic in the crosslinked rubber are cleaved by the alkali metal. It is the specific attack on the sulfidic bonds or S-S and C-S which rarely gave the same molecular weight of main chain rubber. In contrast, the main chain or C-C bonds were cleaved in the severe condition. In the other hand, the devulcanized rubber and carbon black are recovered for reusing in the vulcanization process again without separation of the solvent by using the suitable vulcanization process. However, this process is not convenient because of the difficult controlling alkali metal in the process. The process drives the swollen vulcanized rubber in the solvent to react with alkali metal in the reactor. The temperature of reactor is controlled to cleave the sulfidic bonds in the crosslinked rubber.

For example, the reaction of etheral solvent which had the polysulfides linkages with lithium aluminium hydride (LAH) at average temperature. This reaction works with a weak acid. The production is consisted of thiol group and hydrogen sulfide. Figure 2.7 shows the scissions of lithium aluminium hydride in the reaction.



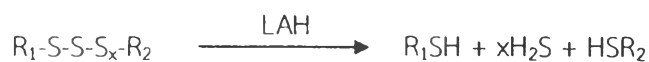


Figure 2.7 The scissions of lithium aluminium hydride (LAH) in the reaction [5].

2.2.3 The biological devulcanization

This method uses the nature to devulcanize the vulcanized rubber. Biology is able to apply as the devulcanizing agents which used the microbial attack. This method is interested to use bacterium in aqueous suspension for the biological attack on the surface of rubber powder. Then, the polymer chain is changed by the specific attack of bacterium. The treated rubber is able to vulcanize with virgin rubber again. Generally, the scrap tire is hold with the suspension of bacterium with air supply until the microbiology attacked which presented the elemental of sulfur or sulfuric acid. The microbial devulcanization is studied to increase the possibility of producing high quality rubber products containing a larger amount of recycled rubber. This studied is performed by the different species of bacterium for example Thiobacillus i.e. *T. ferrooxidans*, *T. thiooxidans*, *T. thioparus*. From this studied, the oxidation from devulcanization depends on the size of particle. However, the biological devulcanization has to develop in the future for suitable to use in many process.

Nowadays, the biological devulcanization is developed in the laboratory to study the pathway in the devulcanization. From the recently research [35], *Alicyclobacillus* sp. Is a bacterium which was studied in the devulcanization capability of waste vulcanized rubber. The increase in devulcanization time affects to the increase in swelling of rubber but the decrease in crosslink density. Moreover, the content of C-S and S-S bonds are decreased which presented of the S-O bond belonging to sulfones group. From this result, the hydrophilic properties of rubber is changed. Using *Alicyclobacillus* sp. In the devulcanization is mild and effective because it can break the crosslinked sulfur in the structure of rubber.

2.3 Oxidation Process

Oxidation is the chemical reaction which consisted of two main reactants. One atom of reactant donates its electron to other atom of the different reactant. Generally, the oxide compound is applied to reaction with other elements. In the reaction, the oxidized compound has lose electrons during the oxidation while the

oxidizing agent has gained electrons. In contrast, the oxidizing agent is reduced by the reduction to gain electrons. Oxidation and reduction are the parallel reaction which always occurred simultaneously. Figure 2.8 shows the reaction of oxidizing agent and reducing agent.

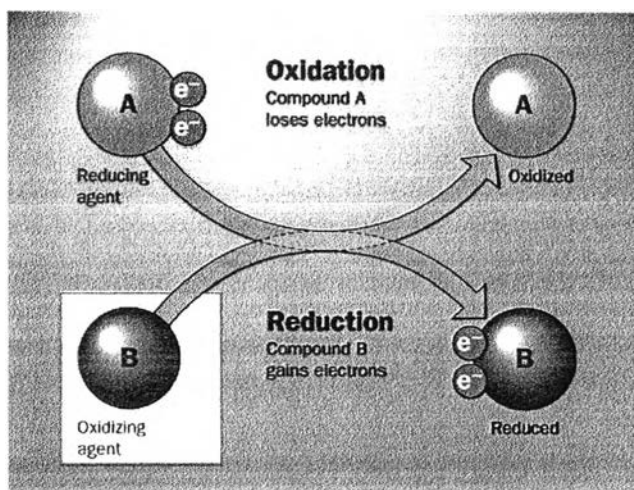


Figure 2.8 shows the reaction of oxidizing agent and reducing agent.

In the recently research, the oxidation is used to oxidize the crosslinked rubber. The common oxidizing agent are hydrogen peroxide (H_2O_2) and nitric acid (HNO_3). Oxidation is an effective route to devulcanize the crosslinked rubber due to process simplicity, low cost and high reactivity. The manner, in which the different types of sulfidic bonds are reacted and the structure of devulcanizate is formed, depends on types of oxidizing agent and reaction conditions. Moreover, the oxidation of thiol (R-SH) and disulfides (R-S-S-R) will generate sulfonic acid groups ($\text{R-SO}_3\text{H}$) which have high ion-exchange capacity. Accordingly, the sulfur crosslinked rubber are oxidized by the oxidizing agent to generate the sulfonic groups. In case of H_2O_2 , sulfonic acid groups are generated from the oxidation of thiol and disulfide with the presece of acid to catalyze the oxidation. The oxidation of thiol groups leading to sulfonic acid groups are performed in 2 steps which is showed in Figure 2.9. The first step is initiated with oxidation of thiol which leded to disulfides by a proton-coupled electron transfer or an s-oxygen. The second step is the oxygen transfer to sulfur that leading to the sulfonic groups [36, 37]. Figure 2.10 shows the oxidation of thiol and disulfides to sulfonic acid groups by using hydrogen peroxide as the oxidizing agent and methyltrioxorhenium CH_3ReO_3 as the catalyst. In case of nitric acid, the disulfides in

the crosslinked structure is oxidized to sulfonic acid groups which split gas in the reaction [1]. Figure 2.11 shows the oxidation of disulfides with nitric acid.

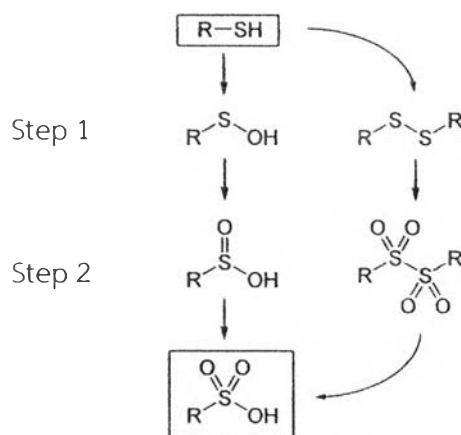


Figure 2.9 The oxidation of thiol groups leading to sulfonic acid groups.

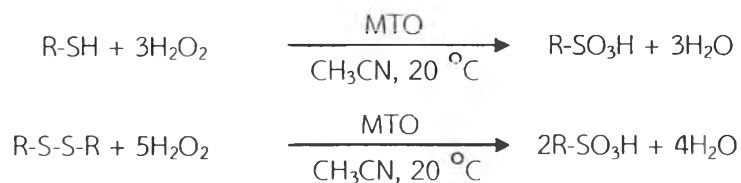


Figure 2.10 The oxidation of thiol and disulfides to sulfonic acid group.



Figure 2.11 The oxidation of disulfides with nitric acid.

2.4 Heterogeneous Catalysis System

The catalysis system is referred to the chemical reaction which used catalyst. This system increases the reaction rate, resulting the equilibrium of reaction is reached faster. Moreover, heterogeneous catalyst is not permanently consumed in the reaction. A catalyst repeatedly takes part in the intermediate chemical interaction of the

reactants. The function of catalyst is increasing the reaction rate by bonding with the substance [38].

The heterogeneous catalysis is a sequence of reaction that the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid, and gas but also immiscible liquids, e.g. oil and water. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids. The heterogeneous catalytic conditions has several advantages compared to the homogeneous and biological catalytic processes;

- Avoids formation of inorganic salts
- Regenerable
- Non-toxic
- Easy to handle
- Safe to store and long life time
- Easy and inexpensive removal from reaction mixture by filtration or centrifugation
- Tolerates a wide range of temperatures and pressures
- Easy and safe disposal

2.4.1 Heterogeneous catalyst

The majority of catalyst used in the industries is heterogeneous catalyst which generally was in the solid phase. This catalyst always use in the reaction of liquid or gas reactant because of the mechanical strength, high pressure and high temperature resistance and easy for separation form the reaction. For the reaction of liquid reactant, catalyst is mixed with reactant in the reactor. After the reaction, catalyst is separated by distillation. For the reaction of gas reactant, catalyst is packed in the reactor for the passing of gas to react on the surface of catalyst. Then the product obtained from the reaction is flowed out reactor in the other side.

Catalyst is composed of two main components, active component and supporter or carrier. The supporter always has high surface area which is useful in the reaction. Moreover, a few catalyst has only active component. However, the catalyst can promote by adding a few promoter to increase the activity, selectivity and stability



of catalyst. The active component is sorted into four groups by their function. They are metal, metal oxide, acid catalyst and bifunctional catalyst. For details is explained in many research. This study focus on the acid catalyst which explained in next topic.

The reaction of heterogeneous catalyst has seven step for the mass transfer to react on the surface of catalyst [9]. Figure 2.12 shows the classical seven steps for a heterogeneous catalytic reaction. First step is the external diffusion which is referred to the flow of reactant pass the external surface of catalyst. Next is the internal pore diffusion. This step is the diffusion of reactant on the catalyst surface into the internal catalytic surface. These two step are only a physical. Then, the reactant is diffused to the active site of catalyst. It is the adsorption step on the catalytic surface which had the chemical changing. This step is the adsorption between the molecule of reactant or adsorbate and the active site of catalyst or adsorbent. After that, the reaction is performed on the surface of the catalyst. Next step is the desorption of the product from the catalytic surface. This step is the last chemical reaction. Then, the product is diffused from the interior of the pellet to the pore mouth at the external surface of catalyst. Finally, the mass transfer of the products is performed from the external pellet surface to the bulk fluid.

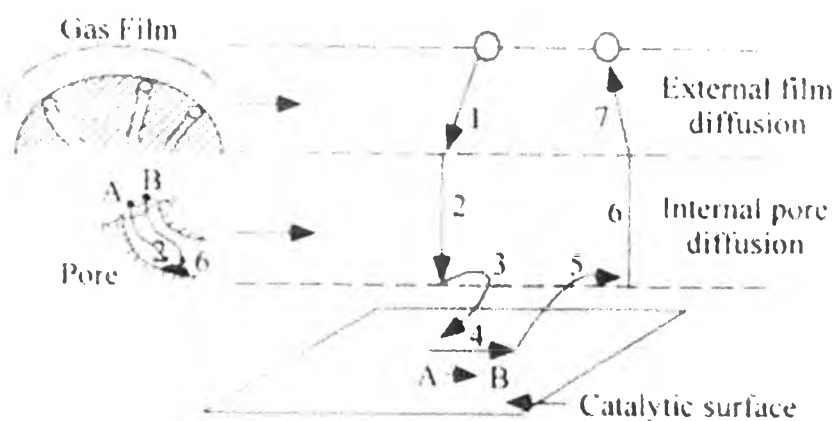


Figure 2.12 The classical seven steps for a heterogeneous catalytic reaction [9].

2.4.2 Acid catalyst

The acid catalyst is able to catalyze many reaction. This catalyst often composed of two or more elements which bonded with strong bonding of oxygen for example, the compound of silica-alumina and zeolites. Moreover, the solid catalyst is prepared by attaching the halogen ion with the structure of alumina. The acid may

able to be Lewis, Bronsted acid or the coordinated with two types. The catalytic reaction is depended on the strong and nature of acid catalyst. Generally, the catalyst is categorized following the supporter. The interested acid catalyst is explained below;

- Alumina

Alumina or aluminium oxide (Al_2O_3) is common supporter with cheap and small size. Alumina is easily controlled the active site and pore size distribution in the preparation step. The commercial grade alumina has the surface area around 100-600 m^2/g . Alumina is prepared from bauxite mineral by the Bayer process. The common alumina is gamma-alumina which is prepared from the aluminium hydroxide dehydration at the lower temperature ($<900\text{ }^\circ\text{C}$). Generally, alumina can adsorb moist in the air. Calcination at high temperature ($>300\text{ }^\circ\text{C}$) generates the Lewis acid site (Al^{3+}) and Lewis basic site (O^{2-}). These active sites are suitable as catalyst in the dehydration of alcohol and isomerization of alkene.

- Mesoporous silica

Mesoporous SiO_2 is the mesoporous material which has exhibiting ordered pore systems and uniform pore diameters. The average pore size of prepared mesoporous SiO_2 is 20-45 Å. It can stable at high temperature (800-900 $^\circ\text{C}$). The advantages of mesoporous SiO_2 are high surface area (300-1300 m^2/g), high pore size (0.5-2.1 cm^3/g) and ordered pore systems. Moreover, the substitution at the silicon atom can increase the Bronsted acid of mesoporous SiO_2 . Mesoporous SiO_2 is prepared from the reaction of alkyltrimethyl ammonium halides and sodium silicate tetra ethoxy silicate or fumed silica at 100-150 $^\circ\text{C}$ for 24-144 h. Then, this materials are calcined at 500-600 $^\circ\text{C}$.

- Titania

Titania (TiO_2) is naturally found as anatase, rutile and brookite. Generally, anatase is prepared from the reaction of illmenite ($\text{FeO}\cdot\text{TiO}_2$) and sulfuric acid. Rutile is prepared by the chlorination of rutile mineral. Titanium chloride from the reaction is oxidized by the vapor-phase oxidation. This method generates the heat resistance rutile. However, acidity of titania is higher than alumina. Titania is used as the supporter in several catalyst, such as vanadia-titania catalysts in the conversion of o-xylene to phthalic anhydride.



- Zeolites

Zeolites are microporous crystalline solids with well-defined structures. Generally, they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Because of their unique porous properties, zeolites are used in a variety of applications with a global market. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as molecular sieves. Zeolites are prepared in the hydrothermal process by mixing alumina materials and silica. This process is catalyzed by base catalyst. Finally, they are slowly precipitated at 200 °C. Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Examples are the use of titanium ZSM-5 in the production of caprolactam, and copper zeolites in NO_x decomposition.

- Activated carbon

Activated carbon is the non-polar carbon solid which has high porosity and surface area. Activated carbon can be prepared from the carbon contained material such as coal, lignite and wood. They are heated in the absence of oxygen atmosphere for water and volatile elimination. The obtained product is the carbon material which is activated by the chemical treatment or the oxidation with steam or carbondioxide. The chemical treatment is performed by the strong dehydrating agent at 500-800 °C. The oxidation uses steam or carbondioxide to increase porosity and surface area of carbon material at 800-1000 °C. Activated carbon is studied as catalyst supporter in many researches [39].

- Polymer-based

The characteristic of polymer-based is an ion-exchange resin. The main structure is the crosslinked polymer which has anion in the center. The ion is stabilized



by cation. Generally, the cation are phenol group, carbonyl, sulfonic, phosphoric and carboic acid. Sulfonic acid is decided to be catalyst because it has high acidity. The high ion-exchange resin is prepared from the crosslinked copolymer, styrene and divinylbenzene. From these copolymer, they had high swell resistance in solvent. Then, they are reacted with sulfonic acid to form the high cation exchange resin. The most common cation exchange resin are explained below;

- Dowex

Dowex catalyst is plastic bead which formed from copolymer polystyrene crosslinked with divinyl benzene and functionalized with sulfonic acid groups. These tough plastic beads are insoluble in organic solvents, strong acids or base. The effective acidity is enhanced by the hydrophobic nature of the plastic backbone. The polymer matrix often stereochemically orients the reactants for greater selectivity or reduced by-product formation. Dowex dry catalysts are used for a wide variety of applications including phenol alkylation, aldol condensations, ester hydrolysis and esterification. It is able to resist temperature lower 150 °C.

- Amberlyst® series

Amberlyst® series are ion exchange resins composed of copolymer polystyrene crosslinked with divinyl benzene and sulfonation with oleum sulfuric acid. This copolymer is stable which hardly dissolved in the solvent. The appearance is solid catalyst with high acid content. It is useful in the industries. Amberlyst has many type which decided by the code. Each code has the different in the acid content, surface area and the matrix resin. Generally, amberlyst is sorted in two types. First is macroporous which had the constant shape of pore such as Amberlyst-15 and Amberlyst-35. The other type is amberlyst with gel in the center. This type has the distribution in pore size such as Amberlyst-131 and Amberlyst-33.

Amberlyst® series are able to use as the excellent catalyst due to their high acid content and strong acid site. Moreover, their structure is the polymer base which was the hydrophilic group resulting the suitable for using as catalyst in the reaction which had water as by product. However, it is able to resist low temperature around 60-150 °C that unable to use in the severe condition. In this research, Amberlyst-15 with average pore size 300 Å, pore size 53 m²/g and the acid content 4.70 mmol/g is a promising heterogeneous acid catalyst for esterification of alcohol with carboxylic acid.



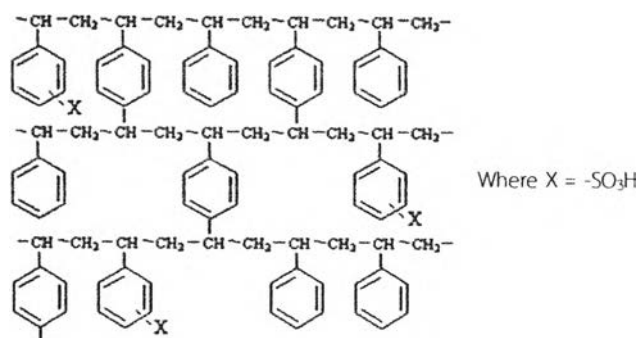


Figure 2.13 The chemical structure of Amberlyst resins.

2.4.3 Terms related to catalysis

Catalysis is studied by analyzing these term which is important to compare and develop the efficiency of catalyst in the reaction. First, the catalytic efficiency relates to the catalyst efficiency. It is analyzed as the turnover frequency (V) obtaining from the conversion of reactant per time. This value shows the reaction on the active site that decided as the turnover number (N). The turnover number is referred to the ratio of the turnover frequency of product to the concentration of reactant. For the heterogeneous catalyst, the active site can use as the concentration. The next is the catalytic cycle. This term is referred to the conversion of reactant and reusing of catalyst. The catalytic cycle of catalysis features the reaction mechanism which displayed the changing of reactant to the intermediates, and product from the reaction maybe conclude the changing of catalyst. When the reaction reaches to the equilibrium, the reaction rate and the ratio of selectivity to the concentration were found. Finally, the catalyst has to regeneration to use it again in the reaction. Generally, catalyst increase the reaction rate by decreasing the activation energy of reaction. From this result, Gibbs energy of activation in the reaction with catalyst has lower than without catalyst while the total energy of reaction was equal. This term is determined as the energetics of reaction. The performance of catalyst which catalyzed the reaction to reach the equilibrium is determined as activity. It is the quantity analysis of catalyst in the conversion of reactant to product. Generally, this value is performed in the Space-time yield or STY in the industries which referred to the obtained product content in limitation of reaction time and reactor size. The next is selectivity. It is the performance of catalyst to control the needed product from the reaction. The limitation of using catalyst in the reaction is analyzed as the life time of catalyst. The

good catalyst is able to reuse in the reaction for many cycle which was not deactivated. Lifetime of catalyst is also considered in the inactive site or deactivate. It is important to select catalyst that suitable for the reaction. Regeneration is the catalyst reusing in reaction. Before reusing, the used catalyst has to clean and reactivate for reuse in the reaction.

In this research, the possibility to reuse the oxidized rubber catalysts in the esterification is studied as the performance of catalyst. Moreover, the efficiency of catalyst is studied as the conversion of acid in the esterification. However, the catalyst recover is observed to determine the lifetime of the oxidized rubber catalysts.

2.5 Esterification of Alcohol with Carboxylic Acid

Esterification is the important reaction in several industries such as pharmaceuticals, fragrances, cosmetics and flavour. The products from this reaction are the ester compound. Esterification is the initiation step to synthesize the ester polymer, such as polyethylene terephthalate (PET), which is important in the textile and food packaging industry. Moreover, esterification is able to synthesize the emulsifier and additive. Currently, biodiesel and bio-fuel are synthesized by esterification.

In the industry, this reaction is performed under batch conditions in homogeneous liquid phase. To increase the efficiency of reaction, strong Bronsted acids are usually used as catalysts. The common Bronsted acids are sulfuric acid and hydrochloric acid [40]. However, these strong acids are corrosive which have to neutralise after reaction. Currently, solid acid catalysts have been studied as substitutes for liquid acid because of their advantages.

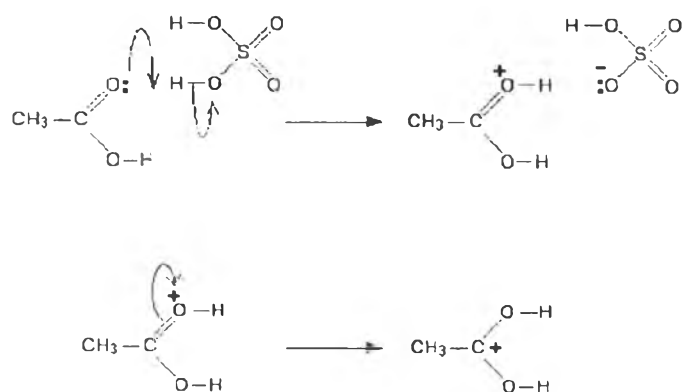
Typically, esterification is the chemical reaction by heating alcohol ($R_1\text{-OH}$) and carboxylic acid ($R_2\text{-COOH}$) for synthesis the ester compound ($R_2\text{-COO-R}_1$) with using acid as catalyst. The esters product from the esterification are important in the ranging from perfumes to biofuels industries. Figure 2.14 shows the general esterification



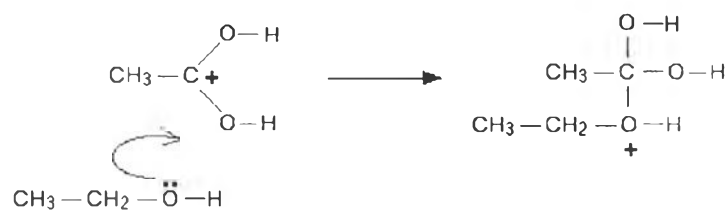
Figure 2.14 General esterification of carboxylic acid with alcohol in the presence of catalyst.

Generally, the synthesis method for the ester compound is the direct esterification of carboxylic acid with alcohol which is commonly performed in the liquid phase. For high conversion of carboxylic acid, the excessive alcohol are used in the presence of acid catalyst. However, the acid catalyst can be easily separated from the ester compound by using the solid catalyst. The mechanism of esterification is explained below [41];

- Step 1 : The protonation of hydrogen ion from the catalyst is attacked by lone pair electron of oxygen in carbonyl group of carboxylic acid. Then, carboxylic acid with positive charge is delocalized to form the carbocation.



- Step 2 : The positive charge of carbocation is attacked by lone pair electron of oxygen in alcohol giving the tetrahedral intermediate. This step is the rate determining step.



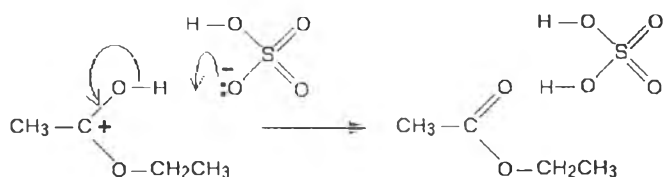
- Step 3 : The rearrangement of positive charge is transferred.



- Step 4 : The intermediate spilt out water molecule which form the carbocation.



- Step 5 : The hydrogen atom in carbocation leaves out the molecule by attacking of lone pair electron from oxygen in the acid catalyst. This occur possess the catalyst can catalyze again. Carbocation with losing proton is rearranged to the ester product.



The research of Miao S. *et al.* studied the heterogeneous acid catalyst which was prepared using the co-condensation method, mesoporous silica materials-supported organic acid or SBA-15 on the esterification of acetic acid with methanol. This catalyst had high surface area, good control of the acid moieties, no significant Lewis acidic sites and good stability without swelling in organic solvents. They modeled the esterification mechanism of acetic acid with methanol by using propylsulfonic acid-functionalized SBA-15 as catalyst in Figure 2.15 [6].

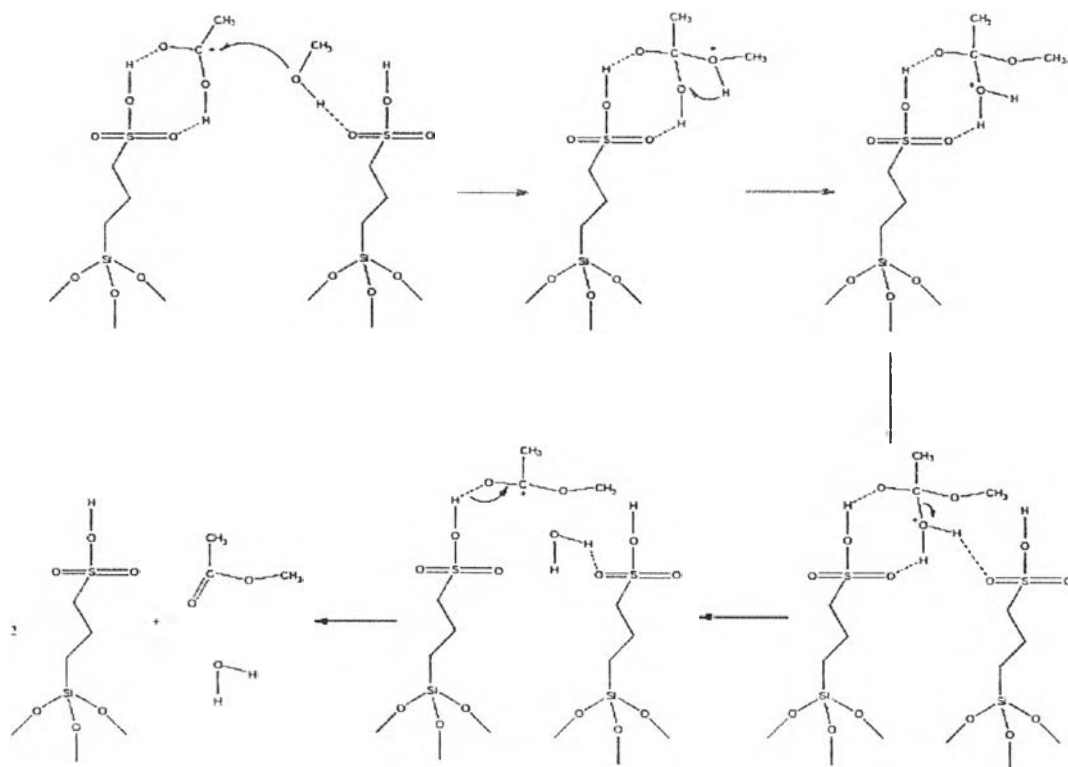


Figure 2.15 Possible esterification mechanism of methanol with acetic acid by using propylsulfonic acid-functionalized SBA-15 as catalyst [6].

2.6 Literature Reviews

In 2012, Dubkov *et al.* [21] studied the waste rubber reclamation by using nitrous oxide. This study was started by cleaning crumb rubber of 1-2 mm particle size with the solution of trichloromethane and acetone with ratio 2:1 V/V at 70 °C. After that, the cleaned crumb rubber was mixed with benzene before the feeding in the reaction with nitrous oxide. Then, they were fed in the reaction which controlled the condition at 180-230 °C in 2-5 MPa for 6-12 h. At the end of reaction, the conversion of nitrous oxide was analyzed by gas chromatography (GC). It found that the conversion of nitrous oxide and the ketonisation increased with the increasing in temperature and reaction time. The solid product from reaction was likely the plastic material. Moreover, the sol/gel ratio was analyzed by immersing the solid product in acetone at the ambient temperature for 12 h. The result showed that the sol ratio was a viscous dark-brown liquid which composed of the diene oligomers and the sol ratio was increased by the increase in amount of ketone from the ketonisation. On the other

hand, the gel ratio was black particle which was consisted of carbon black from the original crumb rubber. However, the sol ratio had oligomers of isoprene, butadiene and styrene as the main component which was analyzed by ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR). The mole ratio of isoprene to butadiene was higher than styrene to butadiene. Moreover, oligomers of ketone and aldehyde was lightly found in the sol ratio.

In 2004, Yehia *et al.* [42] studied the properties of rubber which obtained from mixing of the chemically modified rubber with virgin rubber. This process was performed by the oxidation of the waste rubber powder 125-500 micron. The oxidizing agents with controlled condition were hydrogen peroxide 30% at $100\text{ }^{\circ}\text{C}$ for 3 h and nitric acid 10 20 30 60% at ambient temperature for 3 h. From the FTIR result showed that the chemically modified rubber was found the carbonyl group on the IR bands at 1710 and 1720 cm^{-1} . This functional group increased the polarity of the modified rubber. When the virgin rubber was mixed with the modified rubber, the rheometric characteristic and physicochemical properties of mixed rubber decreased. The rheometric characteristic were torque, scorch time and cure time while the physicochemical properties were modulus, tensile strength, elongation and swelling.

In 2006, Rios *et al.* [1] studied the oxidation of the vulcanized styrene-butadiene rubber by using nitric acid 63% at 1 2 4 6 and 10 h. The oxidized rubber was analyzed by FTIR. The results found the IR bands at 1650 and 1550 cm^{-1} which related to nitro group ($-\text{NO}_2$). Moreover, the IR bands of the carboxylic acid group was found which composed of $\text{C}=\text{O}$, $\text{C}-\text{O}$ and $\text{O}-\text{H}$. From the thermo gravimetric analysis (TGA), styrene-butadiene rubber had 2 step weight loss. First step referred to the loss weight of polymer at $350-450\text{ }^{\circ}\text{C}$. Next step was belonged to carbon black at $560-850\text{ }^{\circ}\text{C}$. After the oxidation, the weight loss of new species which contained $-\text{COOH}$ and $-\text{NO}_2$ was found at $250-350\text{ }^{\circ}\text{C}$ while the weight loss of polymer was remained at $350-450\text{ }^{\circ}\text{C}$. However, the weight loss of carbon black was disappeared after the oxidation. The oxidation by using nitric acid broke the bonding of sulfur ($\text{S}-\text{S}$) which crosslinked in the rubber structure. This results was examined by gel permeation chromatography (GPC). The increase in concentration of nitric acid and oxidation time affected to decrease the molecular size of rubber which became to the hydrophilic material. In the other hand, the oxidation by using nitric acid was able to oxidize disulfide to sulfonic acid group and finally transform to sulfate ion (SO_4^{2-}).

In 2012, Qu *et al.* [13] studied the adsorption of heavy metal using the synthesized adsorbent. Their adsorbent was started the preparation with hydrolysis of



3-mercaptopropyltrimethoxysilane which transformed to silica with thiol group ($\text{SiO}_2\text{-SH}$). After that, it was reacted with hydrogen peroxide. Then, water and methanol was taken to clean the product. Finally, the obtained product was oxidized with sulfuric acid 0.1 M to generate the adsorbent which was silica with sulfonic acid group ($\text{SiO}_2\text{-SO}_3\text{H}$). This adsorbent was tested by adsorption heavy metal ion in aqueous phase. FTIR technique was taken to analyze the functional group in the adsorbent. The result found the strong IR band at 2556 cm^{-1} which referred to thiol group in the sample before reacted with hydrogen peroxide. After the reaction with hydrogen peroxide, the intense IR band at 1169 cm^{-1} was found which presented sulfonic acid group in the structure. This adsorbent was able to adsorb the heavy metal ion. The adsorption of Pb^{2+} was better than Cd^{2+} and Cu^{2+} , respectively. The pH value of 4 gave the best adsorption. The increase in surface area of the adsorbent increased amount of adsorbed heavy metal ion. Moreover, reuse of the adsorbent was studied by using ethylenediaminetetraacetic acid (EDTA) as the stripping agent which was able to strip adsorbed heavy metal ion out of the adsorbent and reuse it again.

In 2009, Caetano *et al.* [15] studied the catalytic esterification of ethanol with palmitic acid at $60\text{ }^\circ\text{C}$ by using the heterogeneous acid catalyst obtained from the modification of polyvinyl alcohol crosslinked with sulfosuccinic acid (PVA_SSA) and polystyrene crosslinked with sulfonic acid (D50W). From the FTIR technique, PVA_SSA had the IR band at 1037 cm^{-1} which referred to sulfonic acid group in the structure. The acid content was analyzed by titration which found that the increase in the crosslinked density increased the acid content of catalyst due to the increase in the sulfonic acid group from the crosslinked structure. In the esterification of ethanol with palmitic acid by using PVA_SSA and D50W as catalyst. The palmitic acid conversion in case of using PVA_SSA was 94% at 24 h which was higher than D50W while the selectivity in esterification of using PVA_SSA and D50W were equal. The reusability was performed by filtration and cleaning the catalyst with methanol after the esterification. When it was dried overnight at $80\text{ }^\circ\text{C}$, it was reused in the esterification again. The efficiency of catalyst slightly decreased after reuse in 7 times.

In 2011, Tian *et al.* [43] studied the esterification of methanol with acetic acid by using sulfonic-acid-functionalized porous benzene phenol polymer and carbon as catalyst. This research started with the synthesis of porous benzene phenol polymer by mixing phenol and formaldehyde in sodium hydroxide solution. After that, water and pluronic 123 were added to the mixing. The sediment from this reaction was kept and dried at the ambient temperature to carbonization at the different temperature.

Then, this sediment was immersed in concentrated sulfuric acid. DI water was added into the solution to form black precipitate. Finally, the solid was cleaned until became the neutral which was able to use as catalyst. FTIR technique was used to check the IR bands in the catalyst. The result found the IR bands of sulfonic acid at 1032, 704 and 610 cm^{-1} while C-S was found at 630 cm^{-1} . In the catalytic esterification, the catalyst can decomposed in the reaction from the hydrolysis of sulfonic group. However, the catalytic performance decreased after the second run.

