

CHAPTER II

THEORITICAL CONSIDERATIONS AND LITERATURE REVIEW

2.1 Polystyrene

Polystyrene is a thermoplastic resin used in many applications because of its low cost and easy processibility. It is available as a homopolymer (crystal) or toughened graft or blend with elastomers (impact polystyrene or IPS). Copolymers are available that give enhanced physical and thermal properties. With these categories are several grades such as standard impact polystyrene and crystal, environmental stress-crack-resistant (ESCR), UV-resistant, flame-retardant, abrasion-resistant, high flexural for part lightweighting, expandable, super-tough, and low-residual volatile. These resins are used every day in disposables, automobile, packaging, toys, construction, electronics, and housewares.[3]

2.1.1 Properties [3]

Typical properties of crystal polystyrene included the following:

Specific gravity	: 1.05 g/cm ³
Tensile strength	: 7000 psi
Flexural strength	: 12,000 psi

Typical shrinkage	: 0.0045 in/in
Coefficient of therm. exp.	: $5 \text{ to } 8 \times 10^{-5} \text{ in/in/}^\circ\text{C}$
Elongation	: 2 to 3%
Vicat softening	: 225 °F

Polystyrene has a natural resistance to property loss from gamma sterilization. It is soluble in aromatic solvents and certain ketones and can be solvent bonded with methylethylketone (MEK).

2.2.2 Toxicity [4]

Polystyrene is a low-toxicity product. The FDA for food contact applications approves almost all commercially available polystyrene. The polymer itself is not digestible and is not normally biodegradable.

2.2.3 Manufacture

Styrene is homopolymerized through the stepwise addition of monomer units. The polymerization is an exothermic reaction. Thermal means or the addition of peroxide initiators generally initiates the polymerization. The reaction can be shown schematically as in Figure 2.1.[4]

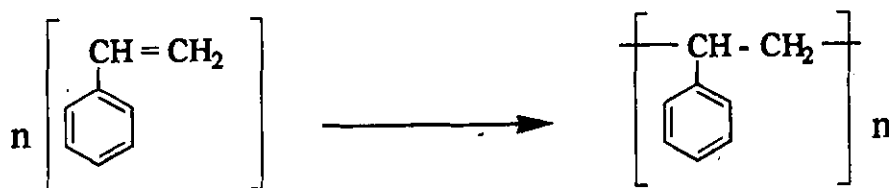


Figure 2.1 Polymerization reaction of styrene

Styrene monomer can be polymerized by all the common methods employed in plastic technology. Techniques of bulk, suspension, solution, and emulsion polymerization have been used for the manufacture of polystyrene and styrene copolymer, but processes relating to the first two methods account for most of polymers manufacture today. A free-radical polymerization of the monomer initiated thermally or with catalysts is generally employed.

The earlier commercial process was suspension polymerization for crystal polystyrene and mass suspension for impact polystyrene. Styrene monomer would eventually polymerized into hard beads. The final beads were then extruded into pellets.

Expandable polystyrene uses the same general process but incorporates a blowing agent (pentane is typical) during a steeping process with the resulting impregnated beads being classified and sold. Dissolving rubber into styrene monomer made impact polystyrene, and then drying and extruding the beads into pellets. Today's process is typically continuous process where

the styrene (for crystal) or the styrene-rubber solution (for impact polystyrene) is passed through a reaction train until optimal conversion is reached. The mass is then stripped of the unreacted component and pelletized.

2.2.4 Products and Applications

2.2.4.1 Crystal Polystyrene [5]

Crystal polystyrene or general-purpose (GP) polystyrene is a high molecular weight linear polymer. It is an amorphous polymer made from the addition polymerization of styrene monomer. It is clear and colorless with excellent optical properties and high stiffness. It is easily formed into finished products that need little maintenance; is light, versatile, and has excellent thermal and electrical properties.

Typical applications included packaging product (containers, lids, bottles), disposable medical ware, toys, tumblers, cutlery, tape reels, storm windows, consumer electronics, and many foam applications, i.e. egg cartons, meat packaging trays, "clamshells" for fast foods, and expanded polystyrene cushioning.

2.2.4.2 Impact Polystyrene [6]

Impact polystyrene is an amorphous polymer made from the graft polymerization of styrene monomer with an elastomer, or a physical blend of

polystyrene (typically polybutadiene). It is tough, usually white (these are clear grade available), and quit easily extruded and molded.

High-impact polystyrene (HIPS), rubber modified versions, was developed to meet the need for a tougher material. It has good dimensional stability, impact strength, and rigidity. Normal limiting factors are heat resistance, oxygen permeability, light(UV) stability, and resistance to oily chemicals.

Major markets of impact polystyrene included packaging and disposables, appliance, consumer electronics, toys and recreation, and buildings. The largest single use of high-impact polystyrene is in packaging and disposables, specifically for food packaging or food service. New high-impact polystyrene grades compete with engineering resin in some applications or represent upgraded products for existing applications. One of these areas is appliances and consumer electronics. One super-high impact/high heat grade has ever been approved for automotive interior trim applications.

2.2.4.3 Expandable Polystyrene [7]

Expandable polystyrene is a generic term for polystyrene and styrene copolymers, supplied as a compound with physical blowing agents and other additives, which can be processed into low density (0.7 to 10.0 lb/ft³) foamed articles. The most common form of this product is a crystal polystyrene bead containing pentane as a blowing agent.

Expandable polystyrene type materials can make products as a coffee cup, an energy-absorbing bumper for an automobile or a foam block for a protective packaging. Major end uses for expandable polystyrene are disposable drinking cups, cushioned packaging, and thermal insulation.

2.2.5 Monomer [8]

Styrene (phenylethylene, vinyl benzene, styrol, cinnamene) $C_6H_5CH=CH_2$, is the common name for the simplest and by far and the most important member of a group of unsaturated aromatic monomers comprised of variously substituted styrene derivatives. Styrene is used extensively for the manufacture of plastics.

Styrene (bp, 145 °C) is a liquid, which can be handle easily and safely. The activation of the vinyl group by the benzene ring makes styrene easy to polymerized and copolymerized under a variety of conditions.

Many different techniques have been investigated for the manufacture of styrene monomer. Of these, the following methods have been used or considered for commercial production.

1. Dehydrogenation of ethylbenzene.
2. Oxidative conversion of ethylbenzene to α -phenylethanol via acetophenone and subsequent dehydration of the alcohol.
3. Side-chain chlorination of ethylbenzene followed by dehydrochlorination.

4. Side-chain chlorination of ethylbenzene, hydrolysis to the corresponding alcohol, followed by dehydration.

5. Pyrolysis of petroleum and recover from various petroleum processes.

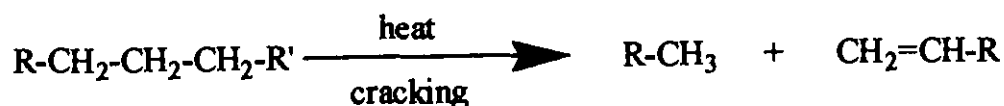
6. Oxidation of ethylbenzene to ethylbenzene hydroperoxide, which is reacted with propylene to give α -phenylethanol and propylene oxide. The alcohol is then dehydrated to styrene.

At present, all of the styrene manufactured commercially is made by the dehydrogenation of ethylbenzene.

2.2 Hydrocracking Reaction

Hydrocracking is a catalytic cracking process that take place in the presence of hydrogen. It is aimed at converting high boiling fraction and residue to lower boiling components. Cracking of long chain compounds and hydrogenation of the cracked products are the main reaction that take place.[9]

The mechanism of hydrocracking is that of catalytic cracking with hydrogenation super imposed. Catalytic cracking is the scission of a carbon-carbon single bond and hydrogenation is the addition of hydrogen to carbon-carbon double bond. An example of the scission of a carbon-carbon single bond followed by hydrogenation is the following



Cracking provides olefin for hydrogenation, while hydrogenation in turn provides heat for cracking. The cracking reaction is endothermic and the hydrogenation reaction is exothermic. The reaction actually provides an excess of heat because the amount of heat released by the exothermic hydrogenation reactions is much greater than the amount of heat consumed by the endothermic cracking reaction so that the hydrocracking reactions are exothermic.[10]

Hydrocracking reactions take place on a fixed-bed catalyst operating at 250-430 °C and a hydrogen pressure of 200-2000 psi. The catalyst used are the bifunctional or dual-function, i.e. those with hydrogenation-dehydrogenation and acidity functions. On acid centers, carbonium ions are formed and isomerized to the thermodynamically most stable ions. On hydrogenation-dehydrogenation centers, dehydrogenation of the C-C bond and formation of initial olefinic intermediate product takes place, as well as hydrogenation of all olefinic products formed by the reaction.[11]

Side reactions is coke formation, the formation of high molecular weight aromatic or highly unsaturated carbonaceous solids on the surface of catalyst and takes place simultaneously with the isomerization. Cokes usually

contain polycyclic aromatic structures. Coking is undesirable because the coke can be plug the pores or occlude the surface of the catalyst, reducing or destroying the activity of the catalyst. The catalyst surface can be regenerated by carefully burning off the coke.

2.3 Bifunctional Catalyst [12]

Modern hydrocracking process calls for the availability of a catalyst having the ability to function as an aid to both hydrogenation and dehydrogenation processes. This is best attained by the dispersion of a reduced metal on an inert support. Bifunctional catalyst is prepared by impregnation method. Impregnation is done by depositing a metal salt on a porous support, converting this salt to oxide and then reducing it to the metallic state.

In multimetallic catalytic composites, the various metals may be deposit in any desired order but in most method group VIII metal is deposited after tin and then impregnated with ammonium fluoride. Finally, the impregnated catalysts are reduced by hydrogen gas in the 400-600 °C temperature range.

The preparation of metal impregnated alumina by chloroplatinic acid is shown in Figure 2.2.

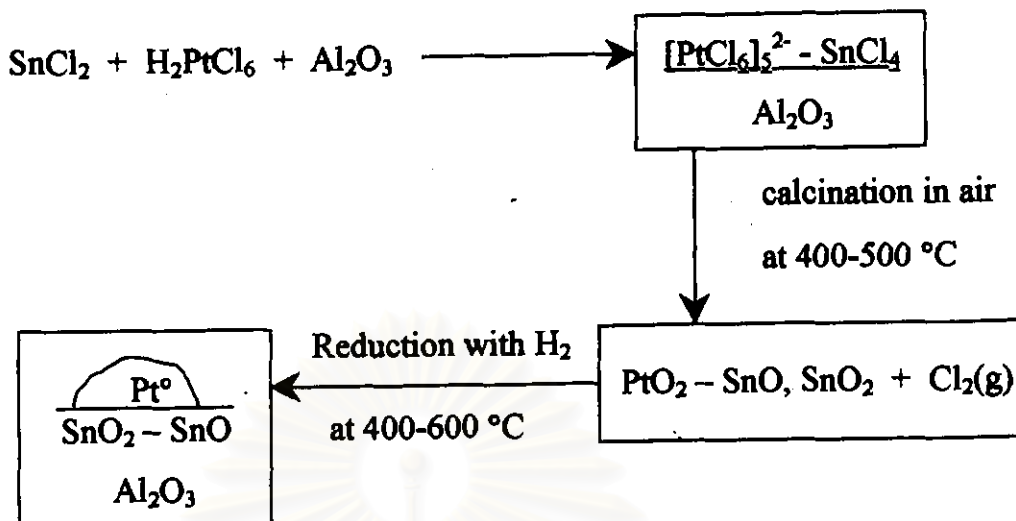


Figure 2.2 The preparation of metal impregnated alumina

Impregnation with NH_4F enhances both acid activity of SnO , SnO_2 by forming SnF_2 or SnF_4 and of alumina by inductively withdrawing electrons from the aluminium atom. Because fluoride has higher electronegativity than oxygen, it cause the residual hydrogen atom on the surface to become more acidic. The effectiveness of tin is greatly enhanced by the addition of halogen acid or ammonium halide.

2.3.1 Metallic Component

Transition metals are hydrogenation/dehydrogenation sites because they have valency d-orbitals in their atoms, accepting electron for sharing into chemisorption bonds. Either molecule hydrogen or alkanes tend to be dissociatively chemisorbed to atomic hydrogen. On the other hand, chemisorption of alkenes involves the sharing of one pair of electrons from the multiple bonds into the valency orbital.

2.3.2 Acidic Component

Molecular Sieve [12]

“Molecular Sieve 3A, 4A and 5A”, which are the alternative names for the ion-exchange form of synthetic zeolite A first produced by the Linde Corporation (now part of Union Carbide)

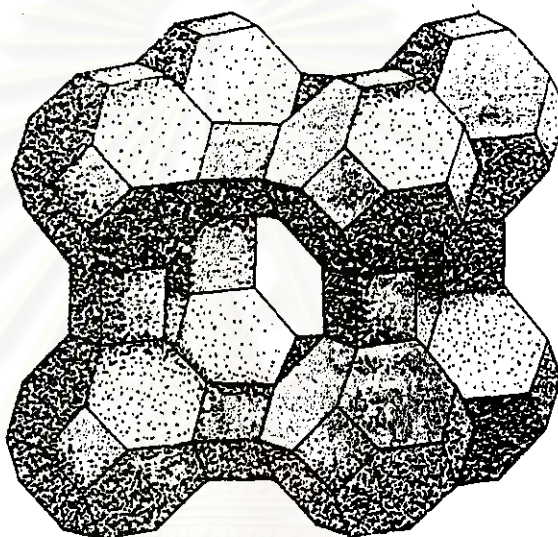


Figure 2.3 Structure of Zeolite A

Zeolites are well-defined class of crystalline naturally occurring aluminosilicate minerals. The general formula of zeolites may be represented in the form $(M^{n+})^{x/n}(AlO_2)_x(SiO_2)_y \cdot mH_2O \cdot M^{n+}$, where n is charge of metal cation M , m is the number of water molecules of crystallization and $(x+y)$ is the number of tetrahedral in the unit cell. They have three-dimension structures arising from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedral linked by all their corners. The aluminium atoms are bonded to three oxygen atoms whereas the silicon atoms in silica are bonded to four oxygen atoms. The

frameworks generally are very open and contain channels and cavities in which are located cations and water molecules.

The property of “molecular sieving” is characteristic property arise from their molecular framework structure in that the assemblages of tetrahedral creating their porous structure happen to create regular arrays of apertures. These apertures are of such a size as to be able to selectively take up some molecule into their porous structure, whilst rejecting others on the basis of their larger effective molecular dimensions. This property is largely unique to zeolites and responsible for their first commercial success. It can be conjectured that every chemical laboratory in the world has on its shelf bottles of molecular sieve.

The series of commercial molecular sieve produced by Union Carbide were the “Linde Molecular Sieve 3A, 4A and 5A”, again the number suggests the pore dimension and the difference between the sieve in the cation present. The sodium form (as synthesized) is 4A, which can be modified by introducing the potassium cation (3A) or the calcium cation (5A), via ion exchange, again cations have a specific role in controlling effective pore dimension.

Ion exchange provides a route for the introduction of metal cations with a view to their subsequent reduction to metal particles. There exist in the so-called “bifunctional” zeolite catalysts used to effect both hydrogenation and dehydrogenation reactions.

Most industrial applications of zeolites are based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction. This means that the activity required is based upon the production of Bronsted sites arising from the creation "hydroxyls" within the zeolite pore structure. These hydroxyls are usually formed either by ammonia or polyvalent cation exchange followed by a calcination step:

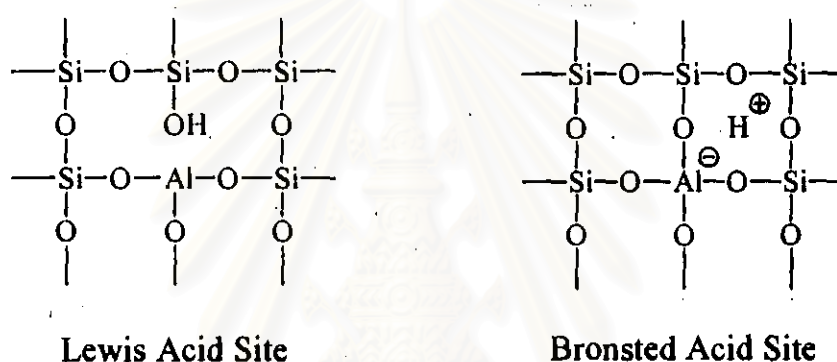


Figure 2.4 Representations of the Lewis and Bronsted acid sites in silica-alumina

In the Lewis structure, oxygen atom from hydroxyl group bonded with silica atom can share a lone pair of electrons with Al atom to form a fourth bond of Al with a proton to unsaturated hydrocarbons in the process of its chemisorption to obtain carbonium ion.

Literature Review

Early studies for the recycling of used polystyrene have been demonstrated in the following literatures:

Albright and Keller, II [13] studied thermal cracking of thermoplastic polymers to valuable products by converting the polymer into a liquid or fluidized stage. The liquid polymer was mixed with a hot inert gas or mixture of hot inert gas. The temperature of the gas heated the polymer in the range about 800-1050 °C, the pressure was maintained in the range about 10-25 psig and the residence time in the reaction zone was about 10-100 milliseconds. The product consisted of ethylene, propylene, butadiene, benzene, toluene, xylenes and other.

Chen and Yan [14] converted ash-free solid polymeric wastes, which comprised mixing rubber and/or plastic waste, to liquid and gaseous fuels and chemicals, by heating polymeric wastes in the presence of a petroleum oil, at temperature between 65-370 °C, in the absence of air and added molecular hydrogen. This resultant liquid resembled a crude oil and was catalytically cracked or mixed with conventional cracking stock and then cracked to gasoline and distillates.

Matsuzaki [15] immersed waste plastic material, e.g. hard plastic waste constituted of vinyl chloride, polyethylene and foam polystyrene, soft plastic waste or other plastic waste containing metal fragments, in a vegetable or mineral oil heated to 110-180 °C for melting into a saturation of plastic waste. The melted plastic material was mixed with neutralizing agent, e.g. calcium hydroxide, at a temperature of 220-300 °C. The resultant mixture, in which a quantity of the oil was entrapped, was shaped into a solid fuel that would generate no toxic gas while it was burnt, or it would generate appropriated formed for safe disposal in a landfill. In this process, the preparatory procedure of crushing, cutting or grinding a waste plastic material to be fed was eliminated, and the waste plastic material was easily softened and melted down without generation of toxic gases.

Butcher, Jr. [16] cracked polymeric materials, such as polyethylene, polypropylene, polystyrene and the like, by alkali fusion, comprising a step of preparing a molten reaction mixture consisted of NaOH and KOH, Cu_2O and polymeric material and reflux at 200 °C for 5-20 minutes. This process produced 40-50% yield of liquid hydrocarbon mixture having a boiling range and chemical properties resembling kerosene or diesel fuel.

Northemann [17] recovered monomeric styrene from plastic waste containing styrene polymers by thermal depolymerization, wherein the

waste in liquid or solid form was transported into a fluidized bed of magnesium aluminium silicate, as a heat transfer agent, heated from 400-700 °C and was cracked or depolymerized in an average residence time of less than 60 seconds. The process took place purely thermally so that no catalyst was required for the reaction. The styrene was recovered in a yield of at least 80%.

Khomentrakarn [18] transformed polystyrene to liquid hydrocarbon in high yield by cracking with bifunctional catalyst (Fe(5%)/Sn(5%)/F(2%) on molecular sieve). The optimum condition for hydrocracking was 400 psig hydrogen pressure and 15% by weight of catalyst at 350 °C for 1.5 hours. The main component was ethylbenzene. Toluene and isopropylbenzene were the second and the third component, respectively.

Yang [19] treated waste plastic, include polypropylene, polyethylene and polystyrene except polyvinyl chloride, by catalytic cracking without any cleaning or pretreatment operation. The process was operated at 280-480 °C, using catalyst, which comprised a silica carrier and a mixture of active components. High quality gasoline and diesel oil were obtained at least 80% yield.