

CHAPTER II

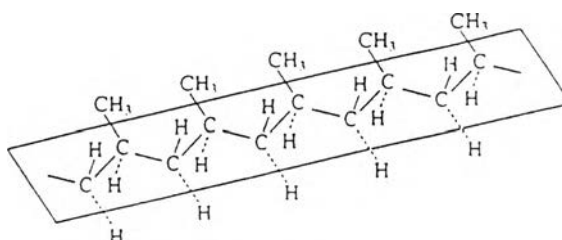
LITERATURE REVIEW

2.1 Polypropylene^[1]

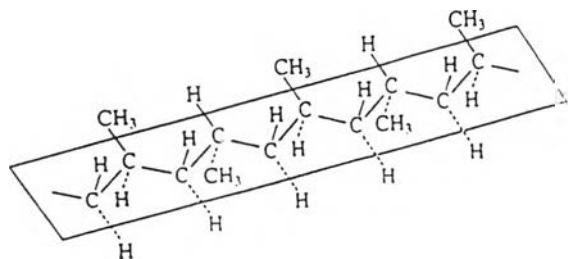
Polypropylene is a major volume thermoplastic material ranked third in the production of plastic, after polyethylene and polyvinyl chloride. Due to its cost effectiveness, versatility, overall competitiveness and excellent environmental aspects, polypropylene is the fastest growing commodity plastic. Advance polymerization processes in conjunction with highly developed compounding techniques make it possible to target polypropylene for engineering applications. The world production volume was about 19 million tons in 1995, including 4.7 million tons in the US alone.

Polypropylene is produced by the stereospecific addition polymerization of propylene. The common name of the polymer is polypropylene, which corresponds fairly well with the name recommended by IUPAC where the repeating propylene unit is in brackets. Commercial production of polypropylene started in 1957 at Montecatini, Italy, at Hercules, USA, and at Farbwerke Hoechst AG, Germany, and was the result of the discovery of heterogeneous stereospecific catalysts by Ziegler in Germany that effected the polymerization of ethylene in 1953. Using these catalysts, Natta in Italy obtained in 1954 crystalline polymers of propylene. Earlier efforts to polymerize propylene had only resulted in amorphous polymers without any use at that time. Natta classified the three geometric forms adopted by the polymer chain of polypropylene as follows.

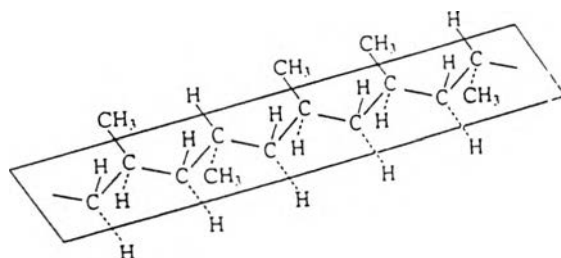
Isotactic; all methyl groups are situated on the same side of the chain.



Syndiotactic; methyl groups are on alternating side.



Atactic; methyl groups are situated at random.



Isotactic and syndiotactic polypropylene are crystalline, whereas atactic polymer is amorphous. As for ethylene, the raw materials for propylene are petroleum and natural gas from which the C_3 fraction is obtained after cracking and fractional distillation. Impurities such as water and methylacetylene must be carefully removed and the purity of propylene brought up to 99.7%. Three different categories of polypropylene materials are produced commercially: homopolymers, copolymers and blends.

The different technologies that used for the polymerization of propylene using Ziegler-type catalysts are the slurry processes including the bulk process, the solution process and the gas phase process.

- *The slurry process*

The oldest and the major processes are the slurry processes. It may be carried out either in stirred batch reactors or in continuous loop reactors. The suspending liquid (C_4 - C_6 paraffin), the catalyst and the propylene are metered separately into the reactor and the polymerization is conducted at 50 - 80 °C and 0.5 - 3.0 MPa (5 - 30 atmospheres). The slurry is centrifuged for the separation of the crystalline Isotactic polymer from the diluent that contains the soluble Atactic polymer and the solubilized catalyst. The slurry processes are increasingly giving way to superior gas phase technologies and to a combination of bulk and gas phase techniques.

- *The solution process*

In solution processes that are more expensive and hence used only for specialty product, higher temperature (160-250 °C) and pressures (2.7-8.0 MPa) are employed in order to dissolve the native polymer in the liquid monomer. PP produced in this process has higher impacted strength and lower brittleness temperature than conventional PP.

- *The gas phase process*

The gas phase fluidized bed process introduced by Union Carbide for the production of LLDPE has been adapted for the polymerization of propylene to homopolymers or block copolymers.

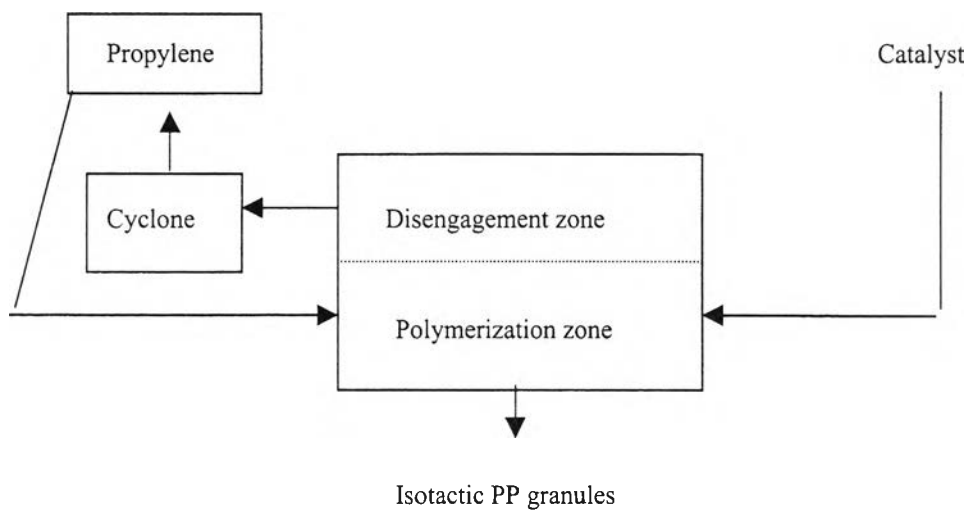


Figure 2.1 Gas phase fluidized bed polymerization of propylene

2.1.1 Properties

Polypropylene is a crystalline polymer and the rate and manner in which the crystals have been formed from the melt influence the crystalline structure. This in turn largely determines both physical properties and processing characteristics of the polymer. Nucleation agents (crystalline organic acids or metal salts) are added in amounts below 0.1% to provide additional crystallization sites and the formation of smaller and more numerous polymer crystals. This controlled morphology of the polymer, referred to as highcrystallinity polypropylene, results in higher bulk properties of the material, namely the softening point, the stiffness, the tensile strength, the modulus and the hardness.

The melting temperature, T_m , of isotactic polypropylene is 176 °C, some 40 °C higher than that of HDPE and this fact makes possible steam sterilization of many polypropylene articles strain-free articles retain their shape even at 135-140 °C.

The glass transition temperature, T_g , of polypropylene is situated at about 0 °C and below this temperature the impact strength comedowns and the polymer becomes brittle. A way to improve this behavior is by block copolymerization with ethylene. Some properties of polypropylene are density (g/cm³)= 0.903; tensile strength (MPa)= 35.5; tensile modulus (MPa)= 1380; flexural modulus (MPa)= 1690. The non-polar nature of polypropylene provides the material with excellent electrical properties similar to those of HDPE. Chemical resistance to most chemicals and solvents is exceptionally high. The polymer is insoluble at room temperature and dissolves in hydrocarbon and chlorinated hydrocarbons only above 80 °C. Unlike polyethylene, polypropylene does not suffer environmental stress cracking. Polypropylene differs from polypropylene by the present of methyl side branches and of relatively labile tertiary hydrogen atoms at every second carbon atom on the backbone.

Unlike polyethylene, which may be crosslinked by high radiation, by heating peroxides or by chlorosulfonation, polypropylene is degraded to lower molecular weight products by similar treatments. Polypropylene is produced in a large variety of melt flow index (MFI) from 0.3 to 800 g/10min. Weight-average MW of commercial polymers is in the range 220,000-700,000 and MWD is 5.6-11.9. Both MW and MWD are dependent on many factors such as the polymerization process, the

temperature, the pressure, the concentration of the monomer, the composition of the catalyst system. And the addition of hydrogen as chain transfer agent. A common practice to narrow the MWD is a post-reaction treatment usually with peroxides that also produces some chain scission.

2.1.2 Applications of polypropylene

Processing methods such as injection molding, blow molding, fiber extrusion and film manufacture (tubular bubble process or flat process) are the general processing techniques used with PP. The bulk of the film is used in biaxially oriented form, which provides higher strength and better barrier properties. PP grade 3300RC that used be material are random copolymer that have lower strength and crystallinity but higher clarity and improved impact strength than homopolymers. Using gas phase polymerization techniques produces them. Around 30% of PP and its related copolymers are used as fibers, coatings for wire piping or ducts, sheeting, film and filaments produced by extrusion.

2.2 Polystyrene (PS) ⁽¹⁾

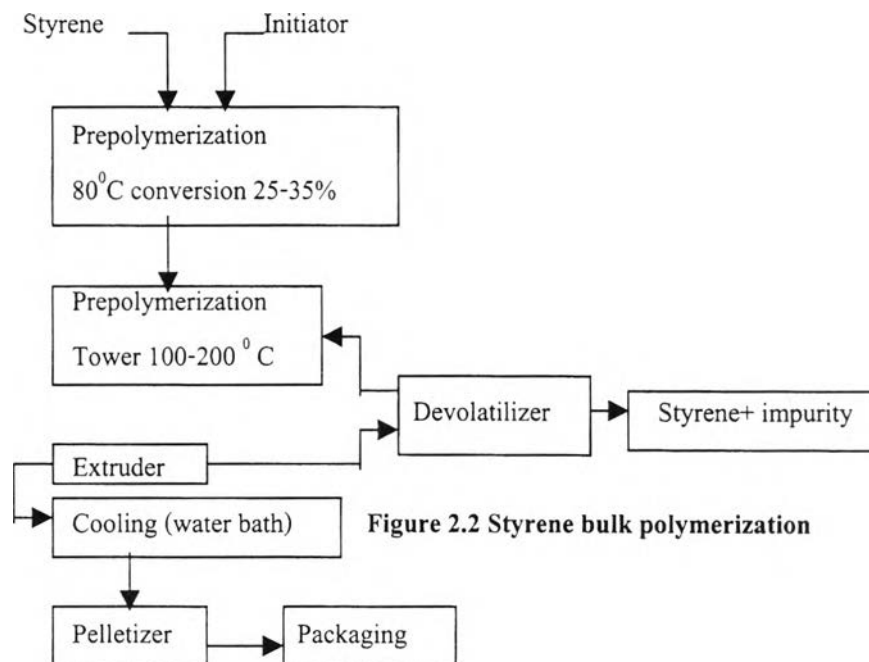
The polystyrene is a thermoplastic resin used in many applications because of its low cost and easy processability. It is available as a homopolymer (crystal) or a toughened graft or blend with elastomers (impact polystyrene (IPS) or PS copolymer are available that give exceed physical and thermal properties.)

Styrene, like many other aromatic compounds, is toxic, and concentrations in the atmosphere should not exceed 10 PPM. Styrene polymerization takes place in most cases through the radical thermal mechanism, with or without initiators (peroxides). The system needs heat only for starting as the reaction is exothermic (71 kJ/mol). As the temperature or initiator concentration increases, reaction rate increases and in the meantime, polystyrene MW decreases. At large scale, polymerization takes place in bulk, solution or the suspension technique.

- *Bulk polymerization*

Discontinuous bulk polymerization with or without initiators is realized in glass forms where a solid PS is obtained. Because of the difficulty in removing the reaction heat and because of the low thermal conductivity of PS, non disperse product is obtained. In the

case of the thick blocks, where the polymerization is uncompleted, styrene traces lead to the polymer aging, a fact which may be visualized through cracking and pacification.



- *Emulsion polymerization*

Emulsion polymerization is less frequently used in the production of PS because the presence of the emulsifier traces in the final product affects some of its main characteristics.

- *Solution polymerization*

This process provides a high purity PS. The principal technical challenges are the control of the exothermic heat of reaction and the handling of the highly viscous polymer. This polymerization takes place at sequentially higher temperature from 90 to 180 °C, with a final conversion 60-90%. After the volatilization of solvent and remaining styrene, the PS melt is extruded and pelletized.

- *Suspension polymerization*

In this technology, styrene is dispersed in water with a dispersing agent (suspending agent) like poly (vinyl alcohol), calcium phosphate, magnesium silicates, etc.

2.2.1 Chemistry and properties

Crystal PS is an amorphous polymer made from the addition polymerization of styrene monomer. It is clear and colorless with optical properties and high stiffness. It is until biaxially oriented, at which and it becomes comparatively flexible and sable. Typical properties of crystal PS the following :

Specific gravity:	1.05	g. /cu.cm.
Tensile strength:	7000	p.s.i.
Flexural strength:	12,000	p.s.i.
Typical shrinkage:	0.0045	in./in.
Coefficient of therm. exp.:	$5 \text{ to } 8 \times 10^{-5}$	in./in./ $^{\circ}\text{C}$
Elongation:	2 to 3 %	
Vicat softening:	225 $^{\circ}\text{F}$	

PS has a natural resistance to property loss in gamma sterilization. It is soluble in solvents and certain ketones and can be solvent bonded with methylethylketone (MEK). Crystal comes in range of melt flows from 1 to 25 or higher. They can be supplied in high heat versions with Vicats to 225 $^{\circ}\text{F}$. Low residual monomer content grades also are available.

2.2.2 General-purpose polystyrene

General-purpose polystyrene, the parent of the styrene plastics family, is a high – molecular-weight linear polymer consisting of about 2000-3000 styrene units. General-purpose polystyrene (g. -p. PS) is often called crystal PS.

There are three common grades of commercial general-purpose PS: easy-flow, intermediate-flow and high heat. The choice of resin grade depends mostly on the fabrication method used and on the end-use application.

Easy-flow resins are the lowest molecular –weight resins, and usually contain 3 to 4 % added mineral oil to decrease melt viscosity and increase melt flow rate. Thus the low viscosity comes at the expense of heat distortion temperature and brittleness. They are mostly used for injection

molding, particular where thin-wall parts are needed. Very low-viscosity resins (melt flow rates > 20 g./10 min. at 392°F), are also available.

Intermediate-flow resins have melt flow and physical property between the other grades, intermediate molecular weight, and about 1 to 2% mineral oil added.

High-heat resins have the highest molecular weight and contain the fewest additives. No mineral oil or other flow aids are added; high heat resins generally contain only mold release or extrusion aids such as zinc stearate or stearic acid. Hence, a lower melt flow rate offsets the higher heat distortion temperature and less breakable parts from these resins.

Specialty grades are also available. These usually have some unique properties and are more expensive than commodity grades. Specialty grades include improved molding cycle time resins, food contact resins with ultra-low residual monomer concentration, very low-molecular-weight resins for specialty application, and higher-heat resins.

2.2.3 Applications

Crystal PS resins are well suited for various end uses, especially where clarity is called for. Typical applications include packaging product (containers, lids, bottles), disposable medical ware, toys, tumblers, cutlery, tape reels, storm window, consumer electronics and many foam application—egg cartons, meat and poultry packaging trays, labels for bottles, and expanded PS cushioning materials.

Easy-flow resin applications include disposable medical ware and dinnerware, toys, and packaging. These resins also are employed in coextruded packaging applications.

Typical application for intermediate-flow resins are injection molded tumblers, medical ware, toys, and packaging; injection-blow molded bottles; and extruded and co-extruded food packaging products.

Common uses of high-heat resins are foam extrusion for food packaging; sheet extrusion-thermoforming for lighting, construction, and decoration; film extrusion for oriented food packaging; injection molding for CD jewel boxes ; and injection-blow molding for packaging containers.

Polystyrene is a commercial product after the second world war, as a result of a high production of styrene for synthetic rubber. Styrene, along with most of its substituted derivatives, can act as either an electron donating or electron-attracting center. Therefore, in addition to free radical polymerization, these monomers can be polymerized by all other primary propagation mechanisms: anionic, cationic and coordination (Ziegler-Natta)

The polymer with a MW of the order of 50,000 is used for coatings and a 200,000 – 300,000 MW polymer is suitable for processing through pressing or injection molding. PS is an amorphous polymer, which has a high degree of branching. Pure PS without extraneous groups and analyzed in vacuum has no absorption in near UV light, i.e. at 290-400 NM. It shows strong absorption at 250-280 NM due to phenyl groups. Above 150 °C in air, it darkens and thermal degradation starts. PS is very suitable to be processed through extrusion, injection and blowing. Due to PS flowing properties, the most widely used processing procedure is injection forming. PS has a lot of application in Electro and radio technique laboratory equipment, packaging for food and pharmaceutical supplies, pipes for acids, etc.

2.3 Polyethylene

Polyethylene is the most extensively used thermoplastic. It is characterized by being a flexible material, which is resistant to many chemicals. Polyethylene produced by free radical initiators is branched and is more flexible due to a lower crystallinity than linear high-density polyethylene. A new grade of low-density polyethylene, which is linear, is produced by the use of Ziegler catalysts. The polymer may be copolymerized with 1-butene to improve its properties.

Ethylene polymerization is highly exothermic, and heat control is very important. Heat removal is usually done by circulating the ethylene gas through heat exchangers, then compressing it for recycling to the reactor. Either a liquid or a gas phase process is used. In the liquid phase process a hydrocarbon diluent is added which requires a special recovery system.

The two most widely used grades of polyethylene are low-density polyethylene, LDPE, which has branched chains, and high-density polyethylene, HDPE, which is predominantly linear. Low-density polyethylene is produced by free radical initiated polymerization at high pressure while high-density polyethylene is produced by low-pressure process with a metallic oxide catalyst of the Ziegler type.

The main difference between the two grades of polyethylene is that LDPE is more flexible because of its lower crystallinity. This lower crystallinity is caused by the presence of branches of two or four carbons along the back-bone of the polymer. HDPE is more closely packed because of the absence of branches and thus the molecules are closer to the another and less permeable to gases.

Several processes can produce polymers with a wide range of densities that cover both the low and high-density ranges as well as medium density polymers.

2.3.1 Physical and chemical properties

Probably the most important property of polyethylene is its molecular weight and its distribution within a sample. Methods used to determine molecular weights are numerous. A widely used one is viscosity and the melt flow index, MFI, measure the extent of polymerization. A polymer with a high melt flow index has a low melt tensile strength.

Polyethylene is to some extent permeable to most gases. The higher density polymers are less permeable than the lower density ones. Polyethylene, in general, has a low degree of water absorption and is not attacked by dilute acids and alkalis. However, concentrated acids attack it. Its overall chemical resistance is excellent. Hydrocarbons and chlorinated hydrocarbons and swell slowly in these solvents affect polyethylene. Tensile strength of polyethylene is relatively low, but impact resistance is high. The use of polyethylene in insulation is due to its excellent electrical resistance properties.

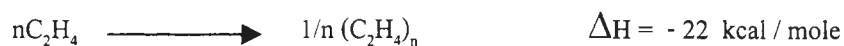
Table 2.1 Typical properties of polyethylene

Polymer	Melting Point Range °C	Density	Degree of Crystallinity %	Stiffness module psi x 10 ³
Branched, low density	107-121	0.92	60-65	25-30
Medium density		0.935	75	60-65
Linear high density				
Ziegler type	125-132	0.95	85	90-110
Phillips type		0.96	91	130-150

Polyethylene, $n(\text{CH}_2\text{-CH}_2)_n$ is the most extensively used thermoplastic. The ever-increasing demand for polyethylene is partly due to the availability of the monomer, ethylene, from abundant raw materials: associated gas, and naphtha. The ease of processing of the polymer, its relative low cost, its resistance to chemicals, and its flexibility are also strong influences. All these and other factors lead to generally strong market demand for polyethylene.

High-pressure polymerization of ethylene was introduced in the 1930's. The discovery of new titanium catalysts by Karl Ziegler in 1953 opened a new era for the polymerization of ethylene at lower pressures. The two most widely used grades of polyethylene are low-density polyethylene, LDPE, which have branch chains, and high-density polyethylene, HDPE, which is predominantly linear. Low-density polyethylene is produced by free radical initiated polymerization at high pressure while high-density polyethylene is produced by low-pressure process with a metallic oxide catalyst of the Ziegler type.

Polymerization

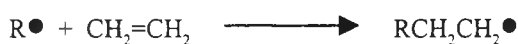


Decomposition



Low-density polyethylene

Low-density polyethylene is made by free radical polymerization. The reaction is carried out at temperatures from 80 to 300 °C and pressures in the range 1000 to 3000 atm. Either oxygen or organic peroxide is used as the initiator. Initiation and propagation occur as follows:



etc



As we will see shortly, the branching has a profound effect on the properties of the polymer.

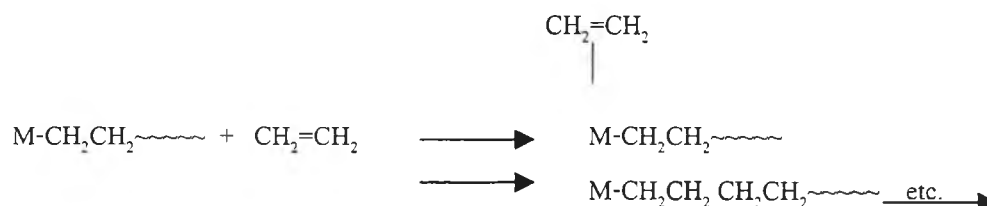
The pressures used in the manufacture of low-density polyethylene are exceptionally high for a chemical process. Since the use of such pressures is expensive both in terms of capital costs and of operating cost, the question arises as to why they are used. The reason is that it is only at very high pressures. i.e. at high ethylene concentrations, that the propagation reactions are fast enough for high molecular weight polymer to be formed.

High-density polyethylene

An entirely different type of process, called co-ordination or Ziegler polymerization makes high-density polyethylene. Karl Ziegler discovered this in 1953, and the first commercial production of HDPE was about two years after that.

The catalyst systems developed by Ziegler consist of complexes formed from aluminum alkyls and transition metal halides, typically triethylaluminium and titanium tetrachloride. In the presence of such catalysts, polymerization of ethylene occurs at about 100°C and at moderate pressures. Originally the reaction was carried out in an inert solvent such as hexane, but now it is also carried out in the gas phase. Quite separately from Ziegler, other workers developed system for carrying out this type of polymerization over transition metal oxide catalysts. The mechanism of co-ordination polymerization is complicated.

The polymer chain grows at active metal sites on the catalyst, molecules of ethylene being first co-ordinate to the site, and then inserted between it and the growing chain:



Chain transfer to polymer does not occur, and the polymer obtained is linear. It is this fact that accounts for the difference between its properties and those of low-density polyethylene.

One of the reasons why polymers have useful mechanical properties is that there are large attractive forces between the very big polymer molecules. In non-polar polymers like polyethylene the attractions are due to Van Der Waal's forces. In other polymers, dipole-dipole interactions or hydrogen bonding may be involved. It can be appreciated that the more closely and regularly the polymer molecules can pack together, the stronger will be the forces between them.

In high-density polyethylene, with its regular linear structure, the molecules can pack together very closely in orderly arrays, called *crystalline regions*, for most of their lengths. In low-density polyethylene the branches tend to get in the way, and a much smaller proportion of the total length of the molecules is in close packed ordered regions. This results in the polymer being softer, less strong and having a lower melting point than the linear polymer, and also, as is indicated by the name, in its having a lower density.

The two products have different ranges of application, reflecting their different properties and also the fact that low-density polyethylene has traditionally been cheaper than high-density polyethylene. This price relationship may seem strange in view of the costs associated with the operating pressures in the low-density polyethylene process. It arose from the fact that, originally at least the cost of making and handling the catalyst in the HDPE process, and the cost of removal of catalyst residues from the polymer, more than outweighed the cost of high pressure operation. With modern high activity catalysts this is probably no longer the case, and the price differential probably reflects the fact that for many applications high density polyethylene is the superior product.

2.3.2 Application

Products made from polyethylene are numerous and range from building materials and sheets. It is an inexpensive plastic that can be molded into almost any shape, extruded into fiber or filament, and blown or precipitated into film or foil. Because it is more flexible and more transparent, the low-density polymer is used in sheets, films, and injection molding. High-density polyethylene is extensively used in blow-molded containers. About 85 percent of the blow-molded bottles are produced from HDPE. Irrigation pipes made from polyvinyl chloride and high-density polyethylene, HDPE, are widely used. Pipes made from HDPE are flexible, tough, and corrosion resistant. These pipes are used for carrying corrosive and/or abrasive materials, such as gypsum, slurry, and various chemicals. Corrosion resistant pipes are also used in well drilling and crude oil transfer. Spun-bounded polyethylene is extremely fine fibers interconnected in a continuous network. Their use includes

notebook and reference book covers, wall covering tags labels, etc. The point-bonded, spun-banded polyethylene are used, for example, as laboratory coats, aprons, garments and sleeping bag liners.

2.4 Literature reviews

Huffman et al.,^[3] investigated the direct liquefaction of medium and high density polyethylene(PE), polypropylene(PPE), poly(ethylene terephthalate) (PET), and a mixed plastic waste, and the coliquefaction of these plastics with coals of three different ranks. The results established that a solid acid catalyst (HZSM-5 zeolite) was highly active for the liquefaction of the plastics alone, typically giving oil yields of 80-95% and total conversions of 90-100% at temperatures of 430-450 °C. In the coal liquefaction experiments, 50:50 mixtures of plastic and coal were used with a tetralin solvent(tetralin : solvent = 3 : 2). Using ~1% of the HZSM-5 catalyst and a nanoscale iron catalyst, oil yields of 50-70% and total conversions of 80-90% were typical.

Anderson et al.,^[4] studied coliquefaction of coal and waste polymers. Coal can be converted into distillable liquid fuels with the addition of hydrogen. Waste polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) contain hydrogen at levels of approximately fourteen percents since such a small fraction of the plastic and other polymer materials are currently recycled, these materials could, in principle, provide the hydrogen to aid in the liquefaction of coal. Coal alone and pure waste polymers, as well as a commingled waste polymer mixture, have been liquefied separately and mixtures of coal and various polymers have been coprocessed. Thermal and catalytic processing shows that such coprocessing can be a viable method to produce high quality liquid fuels and to mitigate the disposal problem of waste polymers.

Hyun et al.,^[5] investigated coprocessing of waste plastics with petroleum resid to determine the effect of resid on reactivity and conversion. The coal used in this study was Blind Canyon bituminous coal, the resids were Maya and Maniji, and the model plastics tested were polystyrene, poly(ethylene terephthalate) (PET), and low-density polyethylene(LDPE). Three systems, the individual species, binary combinations, and ternary combinations, were reacted at conditions of 430 °C and 8.7 Mpa of H₂ introduced at ambient temperature for 60 min of reaction time. Presulfided NiMo/Ai₂O₃ was used as the catalyst, typically at 1 wt% loading, although other catalyst loading levels of 3 and 10 wt% were tested. Under these conditions polystyrene and PET reacted readily, while LDPE was difficult to convert. Binary reaction with

resids resulted in high conversions of ~94% from polystyrene and PET, while the reactions with LDPE somewhat less conversion of ~72%. By contrast, reactions of plastics with coal converted substantially less, ranging from 70.2% for polystyrene and coal to 39.9% for LDPE and coal. Ternary reactions with coal, plastic, plastic, and resid resulted in high conversions for all systems (~89-95) except those with LDPE (~77-81). The effect of coprocessing binary and ternary systems compared to individual systems on the basis of conversion, hexane solubles, and gas productions was determined. The effect of adding a third species into the binary systems was also evaluated. The hexane-soluble products from the three reaction sets were analyzed by simulated distillation to determine the amount of the reaction product boiling at less than 500 °C. Reactions containing LDPE produced substantially less material that boiled 500 °C than did the other reactions.

Kaoru et al.,^[6] studied an iron supported coal-derived active carbon catalyst which shown excellent activity for liquefaction of polypropylene(PP) at low temperature (380 °C) to give good selectly of colorless distillates (92 wt%). Free radical on active carbon should initiate cracking reaction by hydrogen abstraction from polypropylene to form hydrocarbon radical. However, the consecutive cracking of the hydrocarbon radical is suppressed by hydrogenation on the iron particle to give colorless distillates selectively.

Williams et al.,^[7] studied interaction of plastics in mixed-plastics pyrolysis. The pyrolysis of mixed-plastic waste has been proposed as a means of recycling to produce petrochemical feedstock. The interaction of the main plastic types in plastic mixtures is significant in predicting the likely yield and composition of products from different plastic mixtures. The six main plastics in municipal solid waste are high-density polyethylene(HDPE), low-density polyethylene (LDPE), polypropylene(PP), polystyrene(PS), poly(vinyl chloride)(PVC), and poly(ethylene terephthalate)(PET). Each of the plastics was pyrolyzed individually in a fixed-bed reactor heated at 25 °C/min to a final temperature of 700 °C. Polystyrene was then mixed with each of the other five plastics in a ratio of 1:1 and pyrolyzed in the fixed-bed reactor under the same pyrolysis conditions. The yield and composition of the derived oil/wax and gases was determined. The main gases produced from the individual plastics were hydrogen, methane, ethane, propane, propene, butane, and butene and for the PET plastic carbon dioxide and carbon monoxide. Hydrogen chloride was also produced with PVC. Analysis of the oil/wax showed that the polyalkene plastics, HDPE, LDPE, and PP, gave a mainly aliphatic composition consisting of a series of alkanes, alkenes, and alkadienes. PVC gave a mainly aromatic oil, and PS and PET, which have aromatic groups in their structures, also showed a more aromatic composition. There was a higher gas

yield from the mixtures of the plastics with PS than would be expected from the pyrolysis of the individual plastics, coupled with a reduction in the oil/wax phase. The average molecular weight of the oil/wax from the mixed plastics was less than expected from the individual molecular weights. Compositional analysis of the oil/wax showed that changes in the concentration of aromatic hydrocarbons and polycyclic aromatic hydrocarbon were produced with the mixture compared to that expected from the individual plastics.