

## CHAPTER II LITERATURE REVIEW

### Polybutene-1<sup>[4]</sup>

Polybutene-1 (PB-1) is a polyolefinic group polymer, solid at room temperature. Unlike poly-isobutylene (PIB), polybutene-1 is a semi-crystalline highly isotactic thermoplastic mostly produced by Ziegler-Natta catalysis of butene-1 monomer (shown in Figure 2.1). PIB is either an amorphous solid or a low molecular weight liquid. PIB is commonly used as a tackifier in the production of cling films.

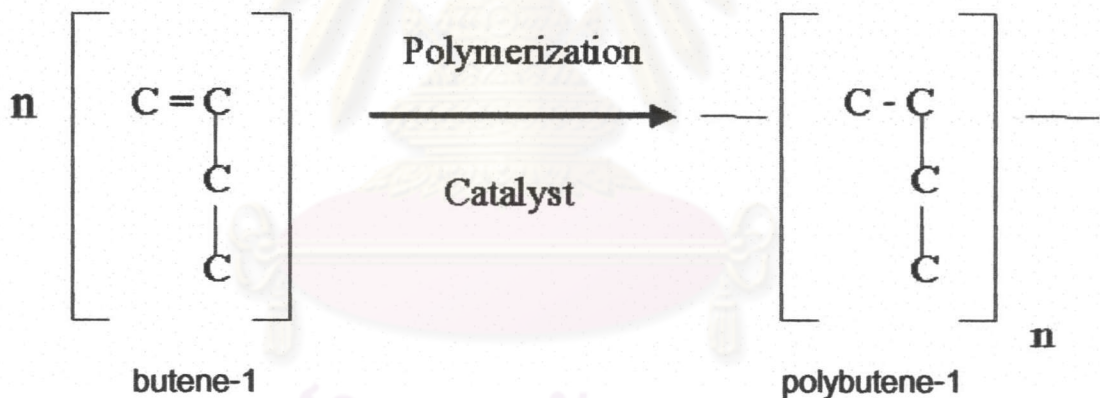


Figure 2.1 polybutene-1 structure

### 2.1 Technology in the Production of Polybutene-1

Normally technology to produce conventional polyolefins can be used for polybutene-1. Polybutene-1 can be prepared using several polymerization processes such as slurry polymerization, solution polymerization, gas phase polymerization and fluidized or mechanically agitated bed reactors. Solution and gas phase processes are the most popular.

A gas-phase process or solution process carried out in at least two polymerization reactors working conditions depend on technology such as concentration of molecular weight regulator, monomer concentration, temperature, pressure etc. This particular process allows to obtain polybutene-1 of different average molecular weight in the two reactors thus leading to a final product having a broad molecular weight distribution optionally of bimodal type. With respect to the use of a broad molecular weight distribution catalyst this method has the advantage that the various polymerization steps can be properly modulated so as to both produce a final product having the desired breadth of molecular weight distribution and properly tailoring the other properties like melt index, etc.

## 2.2 Polymerization of polybutene-1

The polymerization of butene-1 is affected in the presence of Ziegler-type catalysts which are composed of the reaction products of titanium trichloride with aluminum compounds such as aluminum triethyl or tributyl or aluminum diethyl monochloride. These compounds form 10% slurry in a diluent such as naphtha. The preparation of the catalyst for butane-1 polymerization is the most important step in the overall process. The composition of the catalyst as well as the shape and size of its particles are determinant for the properties of the polymer. A good catalyst should produce high yield of polymer per weight of catalysts, with a high content of isotactic polybutene-1, and with controlled molecular weight and morphology. Molecular weight distribution is generally broader when insoluble catalysts are used and much narrower with soluble catalysts. The different technologies that are used for the polymerization of butane-1 using Ziegler-type catalysts are the slurry process including the bulk process, the solution process and the gas phase process.

### 2.2.1 The slurry processes

The oldest and the major processes are the slurry processes. The polymerization resembles the Ziegler process described for polyethylene. It may be carried out either in stirred batch reactors in continuous loop reactors. The suspending liquid ( $C_4$ - $C_6$  paraffins), the catalyst and the butene-1 are metered separately into the reactor. The required isotactic polymer develops around the catalyst particles and forms slurry since it is insoluble in the diluent.

The slurry is centrifuged for the separation of the crystalline isotactic polymer from the diluent which contains the soluble atactic polymer and the solubilized catalyst. The polymer is washed and dried. Temperature and pressure are adjusted between  $45 - 80\text{ }^\circ\text{C}$  and  $1.7 - 3.5\text{ MPa}$ , respectively, in order to maintain the propylene in the liquid phase. Polybutene-1 results as a slurry in liquid monomer and is continuously withdrawn from the reactor when the slurry reaches  $30 - 50\%$  solids. In the flash chamber, the unreacted monomer is eliminated and the polymer forms a powder that is subsequently dried and palletized with stabilizers.

### 2.2.2 The solution process

In solution processes that are more expensive and hence used only for specialty products, higher temperatures ( $160$ - $250\text{ }^\circ\text{C}$ ) and pressures ( $2.7 - 8.0\text{ MPa}$ ) are employed in order to dissolve the native polymer in the liquid monomer. Polybutene-1 produced in this process has higher impact strength and lower brittleness temperatures than conventional polybutene-1.

### 2.2.3 The gas phase process

The reactor has two zones: the reaction zone at the bottom where the catalyst and the growing polymer particles are fluidized by the gas stream of monomer and the disengagement zone at the top where the unreacted monomer and the solid



particles are separated. The gas is recycled while the polymer particles fall down and are continuously withdrawn. The polymer may be obtained in granular form with spherical morphology which eliminates any palletizing operation.

### 2.3 Properties of polybutene-1<sup>[5]</sup>

Polybutene-1 is a semi-crystalline highly isotactic thermoplastic. Its properties include a high degree of flexibility, toughness and resistance to chemicals. The polymer also has excellent resistance to creep, pressure and environmental stress cracking, as well as high filler loading capability and retention of physical properties at elevated temperature. Table 2.1 shows typical properties of polybutene-1.

Table 2.1 Typical properties of polybutene-1

Property	Unit	Homopolymer	Copolymer		
			Low ethylene content	Medium ethylene content	High ethylene content
Melt flow index	dg/min	0.4, 2, 4, 20, 200	1, 2, 4	2	3, 45, > 1000
Tensile strength at yield	MPa	17.2-13.8	11.7	9	3.4
Hardness	Shore "D"	60-65	50	39	25
Melting point	°C	124-126	116	105	90
Glass transition temperature	°C	-18	-20	-28	-35

## 2.4 Processing and Applications<sup>[4,5]</sup>

The properties of polybutene-1 are well suited to uses such as domestic and industrial pipe, as well as specialty applications such as peel-seal packaging polybutene-1 film sealing and hot melt adhesive. Figure 2.1 showed the applications of polybutene-1.

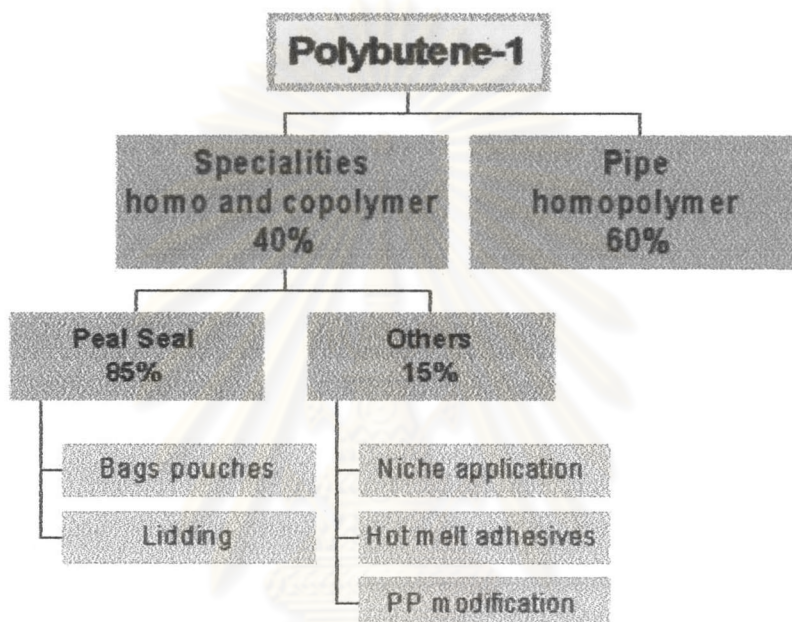


Figure 2.2 The applications of polybutene-1

### 2.4.1 Pipe

Polybutene-1 homopolymers are providing excellent high temperature creep and pressure resistance, with flexibility. This makes them the technically preferred choice for domestic and industrial heating and sanitary pipe when fully formulated to meet national and international codes and standards approval. Table 2.2 shows properties of polybutene-1 for water distribution pipe application.

Table 2.2 Polybutene-1 properties for pipe application

Properties	Method	Unit	Value
<b>General Properties</b>			
Melt flow rate	ISO 1133-1981E	dg/min	0.4
Density	ASTM D 1505	g/cm <sup>2</sup>	0.926
<b>Mechanical Properties</b>			
Tensile strength at yields	ISO 1184-4983E	MPa	17.7
Tensile strength at break	ISO 1184-4983E	MPa	36.5
Elongation at break	ISO 1184-4983E	%	340
<b>Thermal Properties</b>			
Melting point	DSC	°C	124-126
Coefficient of expansion	ASTM D 696	cm/cm/°C	1.3x10 <sup>-4</sup>
Thermal conductivity (20 °C)	ASTM C 177	kg/m <sup>2</sup> /hr/°C/cm	19

#### 2.4.2 Easy-open packaging

Polybutene-1 copolymers provide easy open heat seal systems with cohesive peel mechanisms are being increasingly used in both flexible and rigid packaging for food, pharmaceuticals and medical device application. Most of polybutene-1 homopolymers and copolymers meet FDA requirements for direct food contact.

Seal security and tamper evidence are particular features for polybutene-1. One of the most successful applications of easy-open packaging has been for vacuum-packed ground coffee.



### 2.4.3 Bi-oriented polypropylene film coating

Polybutene-1 copolymers with low and medium ethylene content have a lower melting point than homopolymer grades and lower crystallinity. Blending of these products with polypropylene copolymers provides effective heat seal coating for cast or bi-oriented polypropylene film where low heat seal initiation temperature is required. Multilayer films can be produced either by coextrusion or lamination.

### 2.4.4 Hot melt adhesives

Polybutene-1 is one of hot melt adhesive and sealant formulations give high adhesive strength property, wide range of service temperature and compatibility with a variety of tackifying resins, wide range of viscosity, good adhesion to non-polar substrates, high filler loading and good thermal stability. Its makes non-rigid bond adhesion property for use in packaging, automotive, construction, non-woven or disposable textile applications. The polymers can be applied by spray extrusion, foam or conventional hot melt application techniques.

### 2.4.5 Polyolefin modification

Polybutene-1 is completely miscible in all proportions with other polyolefins such as polypropylene and polyethylene.

## 2.5 Literature Reviews

Shabtai et al.<sup>[6]</sup> studied the solid superacid-catalyzed depolymerization-liquefaction (DL) reactions of high-density polyethylene (HDPE), isotactic polypropylene (PPR), and *cis*-polybutadiene (PB) samples were systematically investigated as a function of processing conditions, such as temperature (350-450°C), time (0.5-3.0 h) H<sub>2</sub> pressure (500-2000 psig), catalyst type and concentration, and the presence of

solvents. Catalyst used included  $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ , and a Pt-modified  $\text{SO}_4^{2-}/\text{ZrO}_2$ . At temperature greater than 400 °C, with 1-2 wt% of  $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$  or  $\text{SO}_4^{2-}/\text{ZrO}_2$  as catalyst, there is an overlap of catalytic and noncatalytic, thermal depolymerization-liquefaction reactions. Under such conditions HDPE yields a liquid product consisting of  $\text{C}_5$ - $\text{C}_{30}$  (mostly  $\text{C}_5$ - $\text{C}_{12}$ ) normal and branched paraffins, accompanied by small amounts of cycloparaffins and olefins. Selective catalytic depolymerization-liquefaction of HDPE was achieved at lower temperature (350°C) in the presence of 17-33 wt% of  $\text{SO}_4^{2-}/\text{ZrO}_2$  or the more active Pt/ $\text{SO}_4^{2-}/\text{ZrO}_2$  catalyst, preferably in the presence of a chemically compatible solvent, such as *n*-octadecane. Under such conditions the high yield (more than 90 wt%) product predominantly consists of branched paraffins in the gasoline boiling range. PPR, which shows high depolymerization-liquefaction reactivity due to its multiply branched polymeric chain structure, yields a similar gasoline-like mixture of  $\text{C}_5$ - $\text{C}_{12}$  branched paraffins as main product. The change in product composition from HDPE and PPR as a function of temperature and reaction time allows for elucidation of mechanistic aspects of the stepwise DL reactions of these polymers. For HDPE results are rationalized in terms of a carbonium ion mechanism involving extensive skeletal isomerization and attendant  $\beta$ -cleavage reactions leading to low-branched paraffins as final products. Results obtained demonstrate that at mild temperatures, under properly designed catalytic conditions, waste HDPE and PPR feeds could be effectively converted into desirable multi-branched paraffins which represent potential blending components for reformulated, nonaromatic gasoline. Depolymerization-liquefaction reactions of polybutadiene, unlike those of polyethylene and polypropylene, yield cyclic compounds as predominant products. Formation of the latter can be tentatively explained on the basis of previous studies of the thermal reactions of butadiene. Monomeric butadiene, and possibly also some higher dienes, derived by initial depolymerization can undergo fast Diels-Alder cyclodimerization to form 4-vinylcyclohexene (and alkyl-substituted derivatives), which by a sequence of rearrangement and hydrogen transfer reactions yield a full range of alkylbenzenes and alkyl-substituted naphthenes. Some bicyclic arenes can be produced by secondary Diels-Alder additions of butadiene to unsaturated monocyclic intermediates and/or intramolecular cyclization of alkyl or alkenylbenzenes.



Nakamura et al.<sup>[7]</sup> 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.

Phungtum<sup>[8]</sup> studied the conversion of polypropylene into oil product using iron on activated carbon catalyst in a microreactor, width of 30 ml, by varying operation conditions as pressure of hydrogen gas range of 28 to 50 kg/cm<sup>2</sup> reaction temperature between 395 and 455 °C and reaction time 30 to 90 min for each catalyst. The results, it was found that reaction temperature of 435 °C was the temperature that yielded the highest quantity of oil product. The analyzed oil product from gas chromatography was found that iron on activated carbon was suitable and used as catalyst at 435 °C, hydrogen pressure at 30 kg/cm<sup>2</sup> and reaction time 60 min. The product yield was in the range of 40-65% naphtha, 12-14% kerosene, 10-13% gas oil, and 4-5% long residue.

Luo and Curtis<sup>[9]</sup> studied coprocessing of waste plastics with coal. They investigated at reaction condition typical of direct liquefaction using slurry phase Mo and Fe hydrogenation catalysts. Reaction were performed with individual model polymers including polyisoprene, polystyrene and high and low density polyethylene and with coal alone in the presence and absence of a hydrogen donor solvent and catalysts at 400 °C and initial H<sub>2</sub> pressure of 5.6 MPa. Polyisoprene and polystyrene liquefied readily at these conditions; however, neither HDPE nor LDPE liquefied much with these catalysts or conditions. The conversion to THF soluble and product distribution from coprocessing reactions with coal and each polymer performed at the same reaction conditions were compared to those obtained with individual polymers. The coprocessing reactions with polyisoprene and polystyrene yielded thermal and catalytic conversion in the range of 20.2 to 43.2%. Catalytic reactions using carbon

black, minerals and fluid catalytic cracking catalysts were performed with HDPE and LDPE to evaluate their effect on conversion. After pretreatment, the fluid catalytic cracking catalysts showed activity for converting LDPE at 440 °C with an initial H<sub>2</sub> pressure of 5.6 MPa. Subsequent coprocessing reactions of LDPE and coal and commingled plastics and coal were performed with four fluid catalytic cracking catalysts and zeolite HZSM-5. HZSM-5 was the most effective catalyst for converting both coprocessing systems although more gaseous products were produced than with the fluid catalytic cracking catalysts. The coprocessing reactions with commingled plastics, which consisted primarily of HDPE with some polypropylene, and coal yielded less conversion and less hexane-soluble materials than the LDPE coprocessing systems.

Anderson et al.<sup>[10]</sup> 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 percent. Since such a small fraction of the plastic and other polymer material 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.

Williams et al.<sup>[11]</sup> 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 yields 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 were 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 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.

Zmierczak et al.<sup>[12]</sup> investigated the depolymerization-liquefaction reactions of representative polystyrene and styrene-butadiene copolymer (non-vulcanized SBR) samples as a function of processing variables, temperature (350-450 °C), time (15-120 min), H<sub>2</sub> pressure (500-2500 psig), and the presence of catalysts. Two solid superacids, i.e. Fe<sub>2</sub>O<sub>3</sub>/SO<sub>4</sub><sup>2-</sup> and ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>, which differ in acidity were used in the study. The detailed composition of products was determined by GC/MS. Typical products from a polystyrene sample (average MW, 280000) contained benzene, toluene, (C<sub>2</sub>-C<sub>5</sub>) alkyl- and alkenylbenzenes, 1,3-diphenylalkanes and triphenylalkanes, accompanied by some indanes, tetralins, naphthalenes and polyphenyls, whereas products from non-vulcanized SBR (MW, 140000) contained, in addition to the above, C<sub>5</sub>-C<sub>9</sub> paraffins and cycloparaffins, (C<sub>5</sub>-C<sub>8</sub>) alkyl- and alkenylbenzenes, cyclopentylbenzenes, and cyclohexylbenzenes. The changes in product composition as a function of the above processing variables were determined and conditions for preferential (greater than 85 wt%) production of gasoline-range liquid fuels established. The observed change in



composition as a function of reaction time and temperature allowed for elucidation of mechanistic aspects of high-temperature depolymerization-liquefaction processes, including the role of catalytic effects.



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