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ABSTRACT

Processing and Application of Polyolefin Plastics

By

Muhammad Khalid

This thesis describes the manufacturing, processing and application of polyolefin thermoplastics. Polyolefins have become one of the most important kinds of plastics. Polyolefin resin represents about one third of all plastics sold and its application for films and containers dominate the packaging industry. The objective of this thesis is to present the various processing methods and application of polyolefin thermoplastics. Polyolefin is produced by several different processes. Conventional low density polyethylene is made by polymerizing ethylene at high pressure and high temperatures while high density polyethylene is polymerized at relatively low pressure and low temperatures. Generally all polyolefin possess excellent electrical properties, excellent resistance to water and moisture and good resistance to chemicals. They are translucent, light weight, tough and flexible material. This combination of properties makes them suitable for film, blow, and injection molded parts, flexible sheet and extruded profiles, and tubing.

PROCESSING AND APPLICATION OF
POLYOLEFIN PLASTICS

by

Muhammad Khalid

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This thesis is dedicated to my family and friends for their
guidance and encouragement.

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CHAPTER 1

INTRODUCTION TO POLYOLEFIN PLASTICS

1.1 Polyolefins

Polyolefins are major polymers achieving significant growth each year. Their combination of useful properties, easy fabrication, and good economics has earned them global importance as commercial materials.

1.2 Category

Polyolefins are thermoplastic resins produced by high and low pressure processes using various sophisticated catalyst systems. The result is several families of polymers (low density, linear low-density, and high density), each having very different behavior and performance characteristics. Generally, all polyolefins possess excellent chemical properties, excellent resistance to water and moisture, and good resistance to organic solvents and chemicals. They are translucent, light weight, tough, and flexible materials.

1.3 History

The experimentation which lead to the discovery of polyolefins stemmed from studies of the effects of high pressures on chemical reactions, which were conducted by Alkali Div. of ICI in 1932. Currently A. Michels at the University of Amesterdam had succeeded in developing high

pressure experimental techniques, including a new pump capable of reaching 3000 atm pressure (44,000 psi, 300 MPa) at temperatures approaching 392 degree F (200 degree C). This equipment enabled the researchers at ICI to conduct a series of reactions, including those with ethylene and benzaldehyde, at 338 degree F and 20,000 psi (140 MPa). The resulting reaction caused a white, waxy solid to be deposited on the walls of the test vessel. The solid was identified as a polymer of ethylene.

Further experimentation was attempted in December 1935 using improved equipment. A larger, 80 mL experimental vessel was used that could be supplied with ethylene from a gas intensifier. After the experiment, the vessel was taken apart and 8 g of white, powdery solid were analyzed. It melted at approximately 239 degree F (115 degree C) and had a molecular weight of about 3000. Continued experimentation, early in 1936, led to larger samples of the polymer being produced. It was found to have higher electricity resistivity and was capable of being converted into thin, transparent films. By 1937, a continuously operating laboratory unit was in place, and a small scale pilot plant was designed.

Product application investigations were favorably aided by chance. A technical staff member at ICI, who previously had worked for the Telegraph Construction Maintenance Co. felt that the new material might be useful as a cable insulator.

A joint developmental project was established. Used for submarine telephone cable, the cable and its mechanical properties gave promising results. ICI committed to build a commercial plant, which became operational in the middle of 1939.

Additional early uses of polyethylene then called polythene, were accelerated by the needs of World War II. The unique insulating behavior of polyethylene was widely used in telephone cable jacketing and greatly added in development of radar. That the availability of this new insulation material should have coincided with the critical need for such a product was extraordinary. In the development of "radiolocation" (radar), the availability of polyethylene transformed the design, production, installation, and maintenance of air borne radar from a challenge that was nearly unsolvable to one that was comfortably manageable. The success of ICI's commercial operation resulted in considerable interest by U.S companies, who licensed the technology. By 1943, both Du Pont and Union Carbide were operating high pressure polyethylene production facilities.

Postwar application developments continued in communications and radar but also in such large scale uses as film extrusion and molding. Blown film extrusion found outlets in the packaging industries where quality and tear strength were required. Early molding uses in radar components were

economically extended until larger injection presses were developed in the 1950's particularly in the United States.

1.4 Polymerization

Continued experimentation and analysis of polyethylene showed it to have a molecular structure composed of both crystalline and amorphous regions. The high pressure (low density, or LDPE) polyethylene obtained by ICI had a rather low molecular weight, a broad molecular weight distribution (MWD), and a density of approximates 57 pound per cubic feet (0.920 grams per centimeter cube). Until 1940, polyethylene was regarded as a linear long chain hydrocarbon, but the advent of infra red studies revealed more methyl groups than could be accounted for as terminal end groups. Side chain branches had to be present to account for the mechanical properties of the polymer. Further work showed that if polymerization techniques were altered to favor the side chain branching reaction, then the physical properties of the polymer reflected those of a less crystalline, lower density material having highly branched side chains.

During the 1950's, discoveries of certain catalyst system permitted the low pressure polymerization of ethylene. In 1951, the Standard Oil of Indiana patented a process using a supported molybdenum oxide catalyst. In January 1953, Phillips Petroleum filed a patent for ethylene

polymerization based on supported chromium trioxide catalyst. Both companies built production facilities and widely licensed their technologies. The polyethylenes made from the Philips process were straight chain (high density, or HDPE) homopolymers having a very high density, with melt flow indices of 0.2 to 0.5 grams per 10 minutes.

Another dramatic advance occurred in late 1953. Karl Zeigler, at the Max Planck Institute in Germany, found the triethyle aluminum added to ethylene quite easily, resulting in the formation of higher aluminum alkyl compounds having low molecular weights in the range of 2000-5000. Zeigler sought a catalyst that would lead to higher molecular weight polyethylenes. Through continued investigation, Zeigler found that certain transition metal compounds could produce polyethylene in high yield. The most efficient catalyst found were those based on titanium compounds. These could produce polymers having molecular weights in the region of 300,000 and at a pressure approaching atmospheric conditions. The HDPE polymers produced by the low pressure Zeigler process were stiffer having a density of about 58.6 pounds per cubic feet, 0.940 grams per centimeter cube) than the high pressure LDPE polyethylene from the ICI process.

Subsequent developments utilizing Zeigler type catalyst resulted in the production of many new ethylene polymers and copolymers. In 1954, Professor G. Natta of Italian Chemical

Institute announced that his discovery of stereoregulated polymers from alpha olefins, such as polypropylene. The catalyst work of Zeigler and the stereospecific polymerization work by Natta stimulated much research in polymer science.

Zegler/Natta type HDPE polyethylenes differed from those produced by Phillips and Standard Oil of Indiana. The later had higher densities of (59.7 - 60.2 pound per feet square, 0.958 - 0.965 grams per centimeter cube) and were linear with very few side chain branches and a high degree of crystallinity.

One disadvantage of Zeigler and Phillips process was that a separate catalyst removal step was required because the catalyst activity was so low. During the mid 1950s Phillips found that, at high yields, the polymer could be precipitated out of specific scientific solvents and there was need to remove the catalyst. This discovery lead to the development of a continuous slurry process (or particle-form process) carried out in loop reactors.

Phillips catalysts which are used in continuous reactors, generally provide broader MWDs than do Zeigler/Natta-type catalysts. Early, on low pressure, high density resins produced from the Phillips process were preferred for extrusion process, resins produced from the Zeigler process

found their greatest utility in injection molding. However refinements in Zeigler catalyst technology have allowed greater MWD resins to be produced, thus expanding their use by the plastic industry.

Phillips catalysts are primarily used in continuous single stage loop reactors. However Zeigler catalyzed systems can employ reactors set up in series in order to produce polymer having broader MWDs. Further to alter or control resin density, alpha-olephin comonomers can be introduced into reaction vessel. These affect the branching distribution and modify the physical properties of the polymer produced.

During the 1960s, Union Carbide produced a low pressure polymerization process capable of producing polyethylene in the gas phase that required no solvents. This process employed a chromium based catalyst. a commercial plant was in operation by the early 1970s. catalyst was continuously injected into a vertical reactor as ethylene gas was circulated through the system. Only a small percent of the ethylene was polymerized per pass, but the process had a low overall pressure drop and the energy required to circulate the gas through the system was small. While this gas phase polymerization process was simply compared to the other processes being used, it did not create much interest among polyethylene producers. The high density gas phase process had limited product range capabilities, and changing polymer

grades for various applications was difficult. However the gas phase process and the work done with it lead to the next major stage of polyethylene development: The advent in 1070s of low density resins produced at low [pressures and temperatures.

The low density high pressure process plants had been in operation for approximately 20 years and were capable of producing polyethylene copolymers having densities as low as 58.3 pound per feet cube (0.935 grams per centimeter cube)> However this was achieved with some difficulty because of agglomeration of resin in the reactor and reduced catalyst efficiencies. Then, in 1977, Union Carbide announced new technology, based on high density gas phase process, that permitted the economical production of low density polyethylene under low pressure conditions. The production plant was said to be less expensive than conventional high pressure plants and to have lower energy demands and operating costs. The products produced , using butene-1 as the incorporated comonomer, demonstrated superior mechanical properties and film drawing tendencies compared to conventional high pressure (low density) products. Films of resins from the new process could be made upto 20-25% thinner but could offer strength characteristics similar to those developed by existing high pressure resins. The process produced granules (powders) of polyethylene directed

from the reactor. Union Carbide stated that such resins could be used in unmodified form by fabricators.

During this same time period, The Dow Chemical Co. began producing polyethylene using a propriety solution process based on Zeigler/Natta-type catalysts. Resins were made at low pressures and high density in a system derived essentially from high density resin. technology. The resulting copolymers, based on the high molecular weight comonomers 1-octene, were introduced and marketed as linear low density polyethylene (LLDPE). Early commercial quantities of the resin were used for film fabrication, especially by the major producers of trash bags. Another difference of the Dow solution products from the gas phase products was that they were produced in standard pellet form, with any needed additives incorporated into the pallet. Therefore the resins could be handled by fabricators in conventional ways, without the need for equipment modification.

Union Carbide and Dow announced expansion plans for LLDPE resins, however, Du Pont of Canada had been producing LLDPE for over 20 years under the name Sclair resins. The Du Pont solution process was capable of making polyethylene over a wide range of melt indexes and densities, utilizing 1-butene as the incorporated comonomer. However, Du Pont of Canada

did not widely publicized or support its achievements in Polymer development.

Overall, LLDPE consists of linear molecules having short side chain branches. The length of the side chains are largely determined by the comonomer employed during polymerization. The chains can vary from a one carbon atom group (with propylene) as the comonomer to a six carbon group (with octene-1 as the incorporated comonomer). Depending on the resin density required for a particular grade up to 10 wt% comonomer is employed. All LLDPE resins are characterized as narrow MWD copolymers offering improved mechanical properties over conventional high pressure LDPE homopolymers. The MWD is largely determined by the catalyst; improved polymerization techniques are being researched to permit production of resin grades over a wide range of MWD, so that the resins can be tailored more specifically to suit the needs for particular applications. Broader MWD resins are for wire and cable and pipe applications because of melt strength requirements; narrower MWD resins are preferred for film extrusion and molding applications. The choice of higher alpha-olefin comonomers, in LLDPEs has a significant influence on resin and end product properties. With higher molecular weight comonomers, improvements are noted in impact physical properties improvements often can be realized by incorporating 1-butene over propylene, 1-hexene over butene, and 1-octene over hexene, respectively. Also the

placement of the short chain branches can enhance resin properties for specific applications. Branching located in the low molecular weight fraction can improve mechanical strength. However, a uniform side chain branching technique likely will be sought to yield the best overall physical property characteristics.

1.5 Description of Properties

Polyolefins are very versatile plastics earning volume uses in many applications areas, particularly in films and injection molding. Each end use requires balanced conditions among variables. The most important of these are melt index, density, molecular weight, MWD, and branching. A proper balance of those property variables is required in determining the best resin choice for a particular application. In order to characterize a particular resin adequately, at least three fundamental properties must be known. These are the melt index, density, and MWD. However, the effects of long chain branching are very important in understanding the nature of LDPE.

1.6 Applications

The characteristics relating to major commercial advantages of LDPE are excellent processability, excellent optical properties, and flexibility. These properties allow LDPE to be widely used in packaging applications. The presence of long chain branching in LDPE decreases some mechanical

properties, but a relatively broad MWD gives LDPE polymers good melt strength, which makes it particularly suitable for blown films uses.

For HDPE film applications, an excellent degree of mechanical strength can be achieved at thin gages. The best results are often obtained with HDPE resins exhibiting low melt indexes, high molecular weights, broad MWD for processing ease, plus linear molecular backbones for a high degree of orientation. Injection molding applications for HDPE require polymers having narrow MWDs to minimize warpage and shrinkage properties and to improve impact strength characteristics. Also higher melt index resins are needed to improve productivity and to keep overall molding cycles to a minimum.

LLDPEs attempt to develop the best characteristics of both LDPE and HDPE to achieve optimum end use physical properties. Compared to LDPE, LLDPE has improved thermal properties, a higher stiffness modulus at a comparable density and much improved environmental stress crack resistance and impact strengths. Further, LLDPE exhibits excellent drawdown capabilities, allowing performance films to be produced at much reduced gages. In molding applications also, high melt index LLDPE resins are capable of producing end products having reduced wall thicknesses while providing superior physical properties. The markets

targeted for LLDPE are thus supported by resin savings and end product properties. the markets targeted for LLDPE are thus supported by resin savings and end-product properties intermediate between those of HDPE and LDPE (compared to conventional low pressure, high density and to high pressure, low density polyethylenes).

The future uses of LLDPE are many. Besides effectively competing in traditional low and high density resin markets, specialized blends of LLDPE are being developed and targeted for specific application. Blends of LDPE and LLDPE in film markets are providing improved physical properties while being produced on modified extrusion equipment. Further, continued development work on polymerization catalyst is likely to achieve advances in MWD control, and in degree and placement of side chain branching. Also cost performance needs are encouraging experimentation with terpolymers to maximize production performance without the sacrifice of physical properties in the end products.

A recent noteworthy advance in LLDPE technology is provided by the commercialization of of extremely low density (56.1 to 57.1 pounds per cubic feet, 0.900 to 0.915 grams per centimeter cube) polymers that offer greatly improved strength properties. Union carbide offers them as very low density polyethylene (VLDPE) resins; Dow offers them, as ultra low density polyethylene (ULDPE) resins.

The significance of polyethylene has grown immensely since that first 8 grams of a white, powdery solid were scrapped off the walls of a reaction vessel approximately 50 years ago. The next 50 years offer technological challenges that will be met continued, directed process and research.

{For more detail refer to 14}

CHAPTER 2
TYPES OF POLYOLEFIN PLASTICS

2.1.Polyethylenes

Polyethylenes are characterized by toughness, near-zero moisture absorption, excellent chemical resistance, excellent electrical insulating properties, low coefficient of friction, and ease of processing.

In general they are not outstanding load bearing materials, but high density polyethylene can be used for some short term light loads.

Few thermoplastics have the excellent chemical resistance and electric properties of polyethylenes. Soluble in some organic solvents above 140 degree F, polyethylenes resist bases and acids at room temperatures. Their resistivity (both volume and surface) and dielectric strength are high.

Polyethylenes can be crosslinked to form infusible thermosetting materials with high heat resistance. Applications are in wire and cable coating, foams, and rotationally molded products.

- (a) 0.880 to 0.915 g/cu cm (called ultra or very low density)
- (b) 0.910 to 0.925 g/cu cm (low density)
- (c) 0.926 to 0.940 g/ cu cm (medium density)
- (d) 0.941 to 0.956 g/cu cm (high density)

The primary difference among the types are in rigidity, heat resistance, and ability to sustain loads. In general, as density increases, hardness, heat resistance, stiffness and resistance to permeability increases. So called conventional low density polyethylene (LDPE) are produced in high pressure reactors. Such polymers have highly branched structures with moderate crystallinity (50-65%).

Low density polyethylenes are quite flexible, with high impact strength and relatively low heat resistance (maximum recommended service temperature is 140-175 deg. F), although grades are available with heat resistance up to 200 deg F.

Traditional markets for LDPE are in packaging films, extrusion coating of papers, wire and cable coating, injection molding and pipe and tubing. Since the introduction of linear low density polyethylene,

conventional LDPE has been gradually displaced in some of these areas.

The high pressure route also is used to make copolymers of ethylene with polar monomers such as vinyl acetate or ethyl acrylate. The EVAs and EEAs that are produced have lower temperature flexibility and are used in tough films and as a component of multilayer constructions for low temperatures heat sealing. acid copolymers (with acrylic or metacrylic acid) are used for their hot tack and adhesive properties. Neutralized with metallic ions, these materials become clear ionomers, used in coating applications.

Linear polyethylenes, as the name suggests, have very little branching along the polymer chains. The polymerization of the linear polyethylenes at low pressures has been used to manufacture high density resins since the mid-1950s. Methods for making linear low density polyethylenes (LLDPE) did not become commercial until the 1970s.

Commercial LLDPE resins are made in gas phase reactors; the polymers typically contain up to 10% alpha olefin comonomers (butene, hexene, methyl pentene, or octene). The reactor output is in granular form, but normally is extruded and pelletized to incorporate additive systems.

LLDPE polymers, with little long-chain branching, have much greater elongation than LDPE. Their higher tear, tensile, and impact strength, along with improved resistance to environmental stress cracking, allow stronger products to be produced with the less material. This has been particularly important in film markets, where considerable downgaging has been accomplished. Ultra- and very low density polyethylenes (ULDPE and VLDPE) are essentially synonymous designations for linear polyethylene with densities down to 0.880 g/ cu in. Produced in gas phase reactors, they are finding applications as impact modifiers for other polyolefins and in film and sheet market.

Linear high density polyethylene (HDPE) can be produced via a slurry process or in gas phase reactors identical to those used to make LLDPE. HDPE polymers are highly crystalline tough materials that can be formed by most processing methods. Much HDPE polymer is blow molded into containers for household and industrial chemicals. It is injection molded into items such as crates, housewares, pails, and dunnage containers; extruded into pipe, tubing, and wire insulation; blown into film for packaging; and rotationally molded into containers, toys, and supporting goods.

Within the density range of HDPEs the stiffness, tensile strength, melting point, and chemical resistance all improve at high end. However materials with higher

densities have low stress crack resistance and low temperature impact strength.

High molecular weight HDPE polymers are a special class of linear resins with molecular weights in the 200,000 to 500,000 range. To obtain processability along with end use properties, control of molecular weight distribution is critical. Some materials are produced with a "bimodal" molecular weight distribution to obtain the necessary balance.

HMW-HDPE is made into blown film for packaging, extruded into pressure pipe, ,and blow molded into large shipping containers. Extruded sheet is also used to form truck bed liners and pond liners.

At the highest end of the spectrum is ultra high molecular weight high density polyethylene. Its weight average molecular weight is over 3 million. Because the resin does not flow when melted, it normally is compression molded into thick sheets or ram-extruded.

High strength, chemical resistance, and lubricity make UHMW-HDPE ideal for gears, sliders, rollers, and other industrial parts. It also is used to make artificial hip joints. In fibre form, the UHMW-HDPEs linear structure exhibits liquid crystal properties that are useful in reinforcing composite

structures. The fibre also can be woven into light weight ultra strong fabrics.

2.2 Polymethylpenten (PMP)

Based on 4-methylepentene-1, this crystalline polyolefin is characterized by transparency (90% light transmission), low specific gravity (0.83), and a high melting point (464 F). Its draw backs are brittleness and poor UV resistance. PMP has found applications in making injection molded and blow molded laboratory ware and medical products, food processing equipment, and microwaveable packaging. Glass fibre-reinforced grades, with heat distortion temperatures up to 440 F, can compete with more expensive engineering resins for electrical/electronic and automotive applications.

2.3 Polypropylene

This polyolefin has turned out to be the most versatile of the family, accounting for the continuing rapid increase in its use. First produced in the 1950s, first polypropylenes (PPs) suffered from low yields from polymerization, high percentage about 10%, of atactic polymer, and poor control of molecular weight.

The development of high activity catalysts in the 1970s improved the yields dramatically and almost eliminated

production of the atactic form. The resulting isotactic polymers were highly stereoregular.

Polypropylenes have better resistance to heat (heat distortion temperature at 66 psi : 200-250 F) and resist more chemicals than do other thermoplastic materials of the same cost. Also, polypropylenes have negligible water absorption and excellent electrical properties, and they are easy to process.

In much the same way that density is important in determining the mechanical properties of polyethylenes, the stereoregularity (related to the repeated units in stereoregular molecular chain) of a polypropylene very often determines the characteristics of the material. An increase in the stereoregularity of a polypropylene will sharply increase the yield strength of the material. The hardness, stiffness, and tensile strength also increase. On the other hand, as the stereoregularity decreases, elongation and impact strength increases.

The ability to carry light loads for long periods and over wide temperature ranges is one of the properties that make polypropylenes valuable in engineering applications. Polypropylenes do not have outstanding long term creep resistance but their fatigue endurance limit is excellent.

In fact polypropylene often is referred to as the "living hinge" thermoplastic.

One of the limitations most often mentioned for polypropylene is their low temperature brittleness (-4 F) . However polypropylene copolymers have been developed with brittleness point of about -20 F.

Like all other polyolefins, polypropylenes have excellent resistance to water and to water solutions, such as salt and acid solutions that are destructive to metals. They also are resistant to organic solvents and alkalis. Above 175 F, polypropylene is soluble in aromatic substances such as toluene and xylene, and in chlorinated hydrocarbons such as trichloroethylene.

Polypropylenes have excellent electrical resistivity (both volume and surface), and their dielectric strength is high. The greatest commercial uses for homopolymer PP are in fibres and filaments. PP fibres are woven into fabrics and carpets, and they are also used to produce woven to produce nonwoven fabrics for disposables. Slit tape filaments are used as jute replacements in carpet backing and sacks. PP also is made into unoriented films for packaging, which have largely replaced cellophane and glassine. Homopolymer PP is injection molded into caps and closures, appliance components, and auto parts. {For more details refer to 12}.

CHAPTER 3

PROPERTIES OF POLYOLEFIN PLASTICS

3.1 Properties Common to All Polyolefin Plastics

Polyolefins are long chain aliphatic hydrocarbons; this means that they belong to same general class of chemical compounds as paraffin wax. Many of the properties of Polyolefin plastics can be understood by analogy with wax, while others are quite different. We will start with simple wax like ones.

3.1.1 Water Resistance

Polyolefin plastics are highly water resistant; they absorb practically no water and are quite resistant to the passage of water either in liquid or vapor form. The lack of water absorption means that they do not change dimensions in accordance with changes in atmospheric humidity. They are also very resistant to chemicals in water solution, inorganic salt solutions, acids, and other materials that are highly corrosive to metals but that have little effect on polyolefins. They are equally resistant to strong alkalis and to hydrofluoric acid which attack glass.

3.1.2 Solvent Resistance

The polyolefin plastics are generally insoluble in solvents at room temperature, although they can be dissolved at elevated temperatures in a variety of solvents, especially

the aromatic hydrocarbons. Polyolefin plastics generally obtain a fraction that can be extracted by hydrocarbon solvents at room temperatures, and many solvents and oily materials pass through them readily.

3.1.3 Gas Barrier Properties

As a gas polyolefin plastics are not very good barriers to oxygen, nitrogen, carbon dioxide, or other gases, but this varies considerably from one polyolefin to another.

3.1.4 Density

The polyolefins are light weight materials, non having the density above that of water. Poly-4-methylpentene (TPX) is the lightest and linear polyethylene the heaviest. In the overall group, density has little relationship to other physical properties, but with in the polyethylenes there is a close relationship between density and the other properties. Since the polyethylenes vary nearly span the range of the polyolefins in many properties, it is useful to consider all the polyolefins in the relation to the polyethylene spectrum. As polyethylene density increases, tensile strength, stiffness, heat resistance, yield strength, and hardness all increase. Permeability, stress crack resistance, impact strength, and tear strength decrease at the same time.

Table 1 Effect of Density on Properties of Polyethylene

Increasing Density	
Increases	Decreases
Stiffness	Permeability
Tensile Strength	Stress Crack Resistance
Yield Strength	
Heat Resistance	Impact Resistance
Hardness	Tear Strength

3.1.5 Tensile Strength

In tensile strength all of the other polyolefins fall with in the polyethylene spectrum with polypropylene, poly-4-methylepentene, and the ionomers in the high density polyethylene range, and EVA copolymers in the low density range.

3.1.6 Stiffness

Tensile modules, however, shows a different picture, and we see that un modified polypropylene and poly-4-methylepentene are both stiffer material than linear polyethylene, while the EVA copolymers may be very considerable less stiff than low density polyethylene. In the copolymer, stiffness depend on comonomer content, with comonomer content giving more flexible materials. While no figures are given for other copolymers of ethylene with polar monomers, such as the acrylates, these too are less stiff materials whose properties can be best understood as extension of the polyethylene property spectrum on the low density side.

3.1.7 Heat Resistance

When heat deflection temperature is considered, an even more marked extension of the polyethylene spectrum can be observed. All of the polypropylene, polybutene-1 and poly-4-methylpentene are more heat resistant than the most heat resistant linear polyethylene. This extension of the spectrum is particularly important because, of we consider

Table 2 Comparison of Rheological Behavior

Shear rate, s ⁻¹	Frac MI LDPE (A)	Octene LLDPE (B)	Linear Grade LDPE (C)
3	98,996	55,570	27,851
7	59,662	44,878	19,852
15	39,598	35,639	13,991
30	26,069	27,785	10,032
75	15,021	18,822	6,336
150	9,768	13,332	4,395
300	6,435	8,910	3,029
750	3,696	4,778	1,816
1,500	2,323	2,785	1,214
3,000	1,419	1,657	792

the 66 psi distortion temperature, we see that this goes above the boiling point of the water on these materials. Since many plastic applications involve temperature at or near the boiling point of water, it can be seen that a really useful extension of the polyolefin applications results from this improved heat resistance. The EVA copolymer stiffness is below that of low density polyethylene, its 66 psi heat distortion temperature falls in the range of high density polyethylene. This means that it is a flexible but relatively heat resistant material. Polybutene-1 has stiffness in the low density polyethylene range, and higher heat distortion temperature than low density polyethylene. This useful combination of properties is shared by some of the other ethylene polar copolymers as well.

3.1.8 Elongation

The wide ranges given for the elongations of the most of the materials shown result from the phenomenon of cold draw. Cold draw is very important in many of the polyolefin plastics processing techniques where the processing consists in part of drawing the material at a temperature well below its melting point. These elongations are similar in size to the elongations shown by some rubber but are entirely different in nature. the rubber elongation is entirely reversible and the plastic elongation is permanent and irreversible in most cases. The polar copolymers may have a

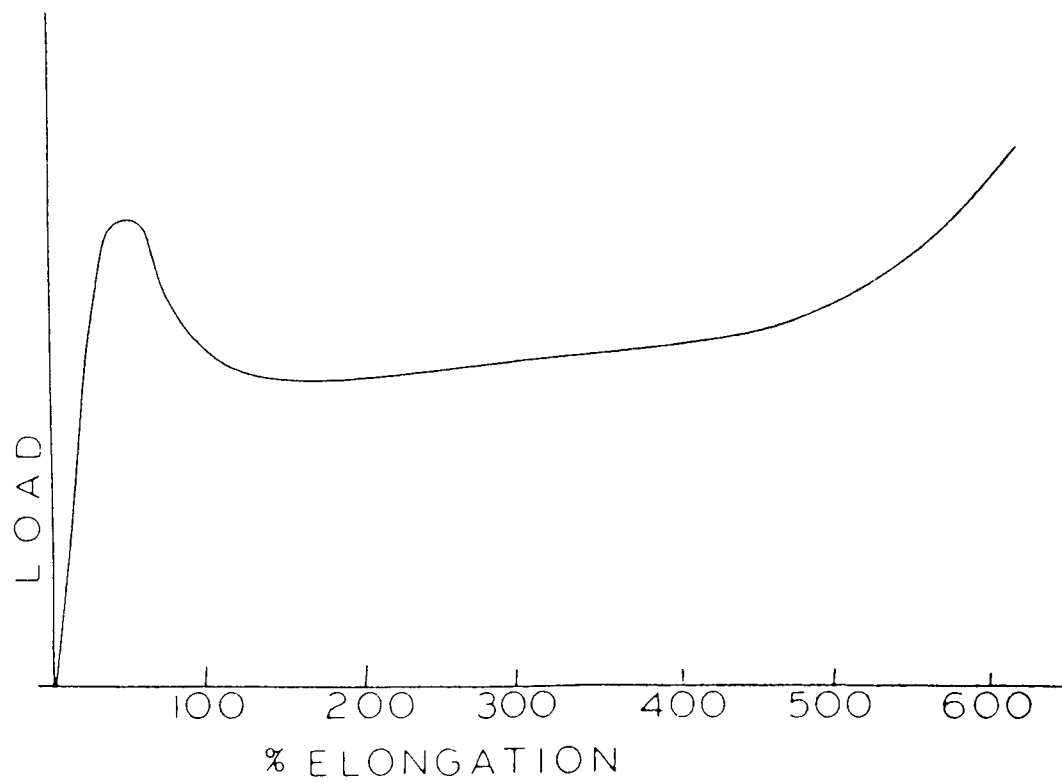


Figure 1 Typical Polyolefin Stress-Strain Curve

reversible elongation, which gives them a rubbery characteristic, and to some degree the ionomers also have this nature. At this time we cannot judge whether the low elongation of poly-4-methylpentene is characteristic of the entire line of such polymers, or if it is only a property of the first resin of this class that has been produced.

3.1.9 Impact

The impact strength of polyolefin plastics varies a great deal. This variation is not so much between resin types as with in types. Certain polyolefins, low density polyethylene and polar copolymers do not break in the Izod impact test; they just bend. Even the lowest numbers given represent quite respectable impact values. There are many usable plastics with Izod impact values only a few hundredth of a ft pound per inch. This means that 0.5 ft pound per inch is really quite impact resistant. On the other end of the scale, the very high impact strengths of some linear polyethylenes and polypropylene copolymers represent formulation designed to optimize these properties.

In the case of linear polyethylene, high impact strength is obtained by copolymerization with higher alpha olefins. These have not been specifically mentioned before because they form a continuous property spectrum with the homopolymers. Linear polyethylene with a density below about 0.995 is produced by copolymerisation. The high impact strength of some of polypropylene is also produced by

copolymerization, but, in this case, the comonomer is usually ethylene.

3.1.10 Flexure Modules

This is just another measure of stiffness, it is generally somewhat higher than tensile modules, and varies in similar manner. Theoretically they should be the same but the different method of test gives slightly different values.

3.1.11 Thermal Conductivity

The difference in conductivity is related to the basic raw material. Polyethylenes generally have higher conductivities than polymers of other olefins; and among polyethylenes conductivity increases with density. This difference is important in processing because most processing methods involve putting heat into the plastic and then taking it out again. When this heat involves conduction, it is easier with a resin of higher thermal conductivity. This gives linear polyethylene a considerable advantage over polypropylene in processing such as thermoforming, bottle blowing, and injection molding. Cycle time can be shorter than polyethylene heat transfer is faster. The thermal conductivity of all polyolefin plastics is very low compared to metals, and many other materials. This means that they have some degree of thermal insulating value.

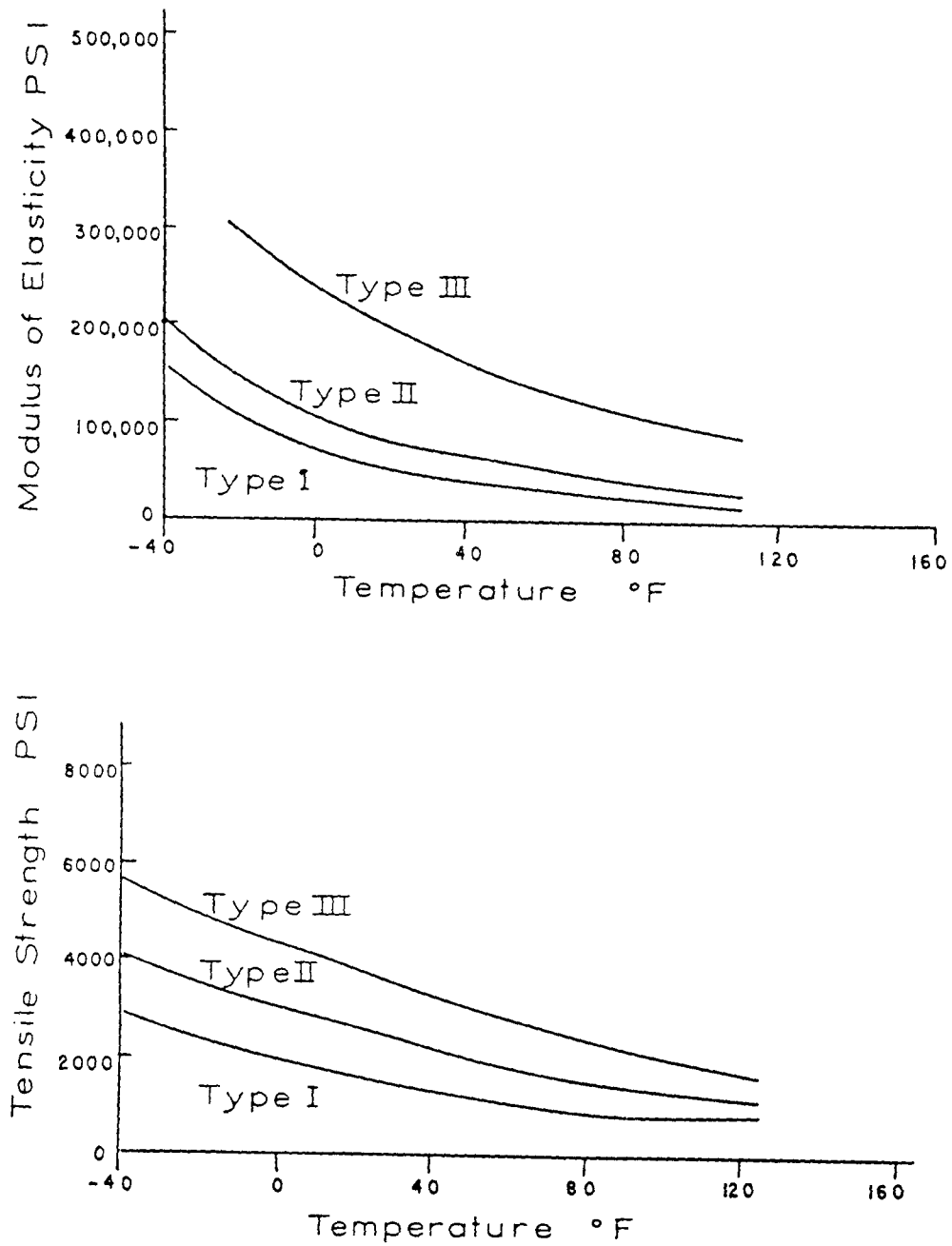


Figure 2 Temperature dependent of Selected Physical Properties of Polyethylene.

3.1.12 Specific Heat

Speed of heating and cooling depends not only on thermal conductance but also on specific heat. The difference in specific heat is not very great between polyolefin plastics. Polypropylene has a little advantage over polyethylene in this respect, but it generally does not compensate for the difference in thermal conductivity. It would be significant only in the case the limiting factor in a production process was the ability of the machine to handle the heating or cooling load.

3.1.13 Thermal Expansion

Polyolefin plastics have high thermal expansion compared to metals and other construction materials. This must be taken into consideration when they are used in some product along with other materials. If polyolefins are rigidly fastened to other materials with lower thermal expansion, like steel for instance, excessive stress could be built up when the temperature changes. This is not important with flexible polyolefins, like low density polyethylene or polar copolymers, but can be serious with the stiffer materials especially with the large size parts. Methods of joining should provide flexibility to compensate for the expansion differences.

3.2 Polyolefin Properties Related to Melt Index

Melt index is brought up at this time in relation to its influence on physical properties. In many processing methods it is convenient to have a resin that flows very readily. This means a high melt index resin. While it is, of course, necessary to use a melt index high enough to make the process practicable, the use of high melt index materials entails certain penalties in other physical properties.

The most striking melt index dependent property is environmental stress crack resistance, which drops very sharply as the melt index is increased. This is in the strictest sense a polyethylene property, for the other polyolefins do not have the same susceptibility to Igepal, the standard stress cracking reagent. The other polyolefins, however, all have reagents or environmental materials that attack them and cause premature failure, and their susceptibility to such failure is greater for high flow materials. This can be interpreted very generally in terms of service life and general resistance to deterioration by outside influences. Resistance to aging can, of course, be improved sharply by certain additives which protect against specific dangers, such as oxidation or ultraviolet irradiation, but along with these there is also a component related to flow. Higher flow materials within a group also show some loss in physical properties such as tensile

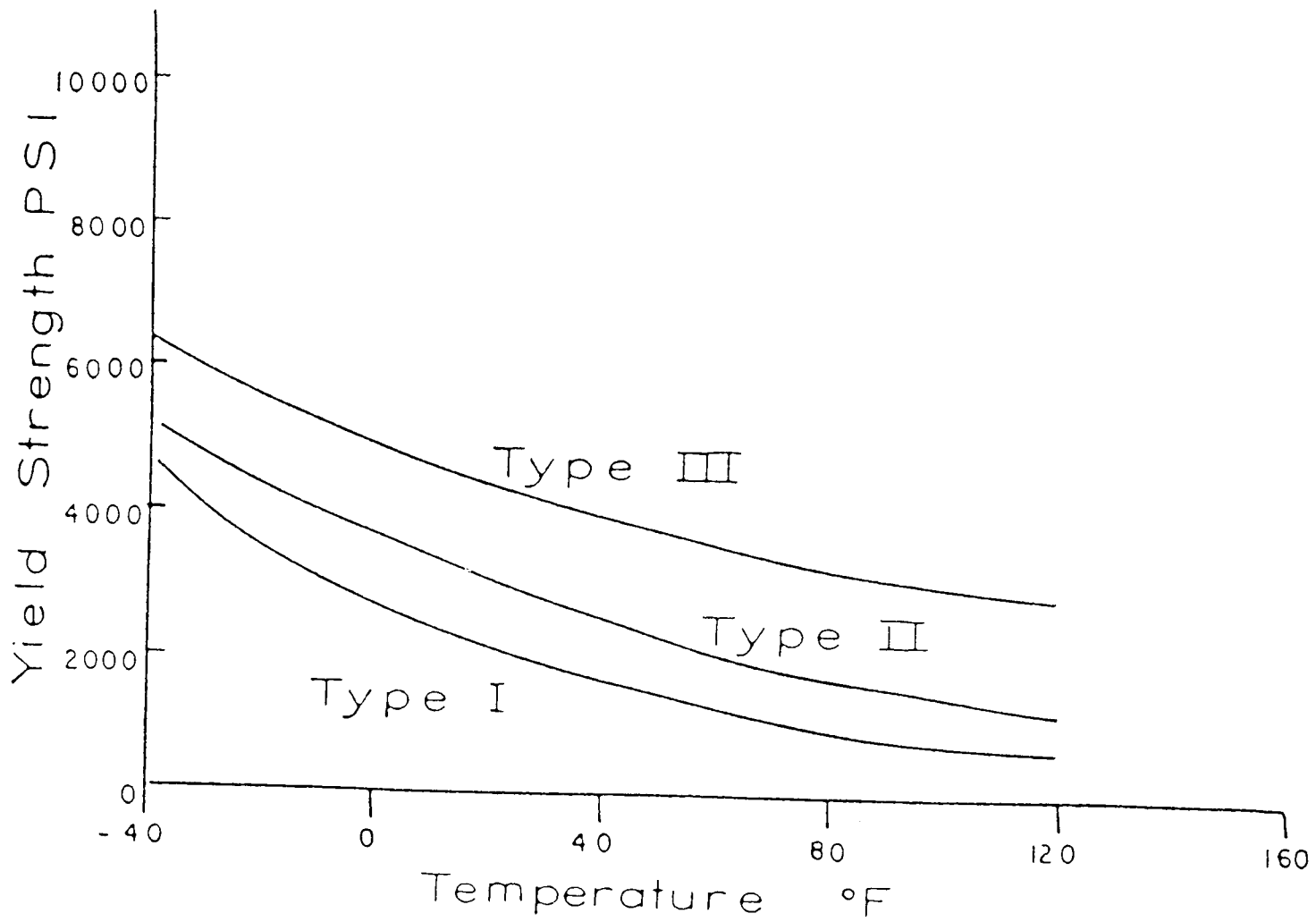


Figure 3 Temperature Dependent of Tensile Impact of Several Type of Polypropylene.

strength, but this is only true of extreme differences, and in some cases, such as in polypropylene, there may even be higher tensile strengths with higher melt index. Elongation however is much more flow dependent, and the technologies that make use of the strength increasing effect of the elongation, are effective mainly on relative low melt index polyolefin plastics.

Impact strength generally is lower in high melt index materials. The flow properties of a polyolefin plastic are related to melt index but are not entirely specified by it. In particular, melt index cannot be compared between different type of olefin plastics, and even resins of same class, the flow behavior of the resin with same melt indexes may differ appreciably.

3.3 Temperature Dependent of Physical Properties

A few general statements may be made to illustrate the value of these curves. Up to this point we have mainly discussed room temperature physical properties, built the physical; properties of all polyolefins are dependent to a great degree on temperature.

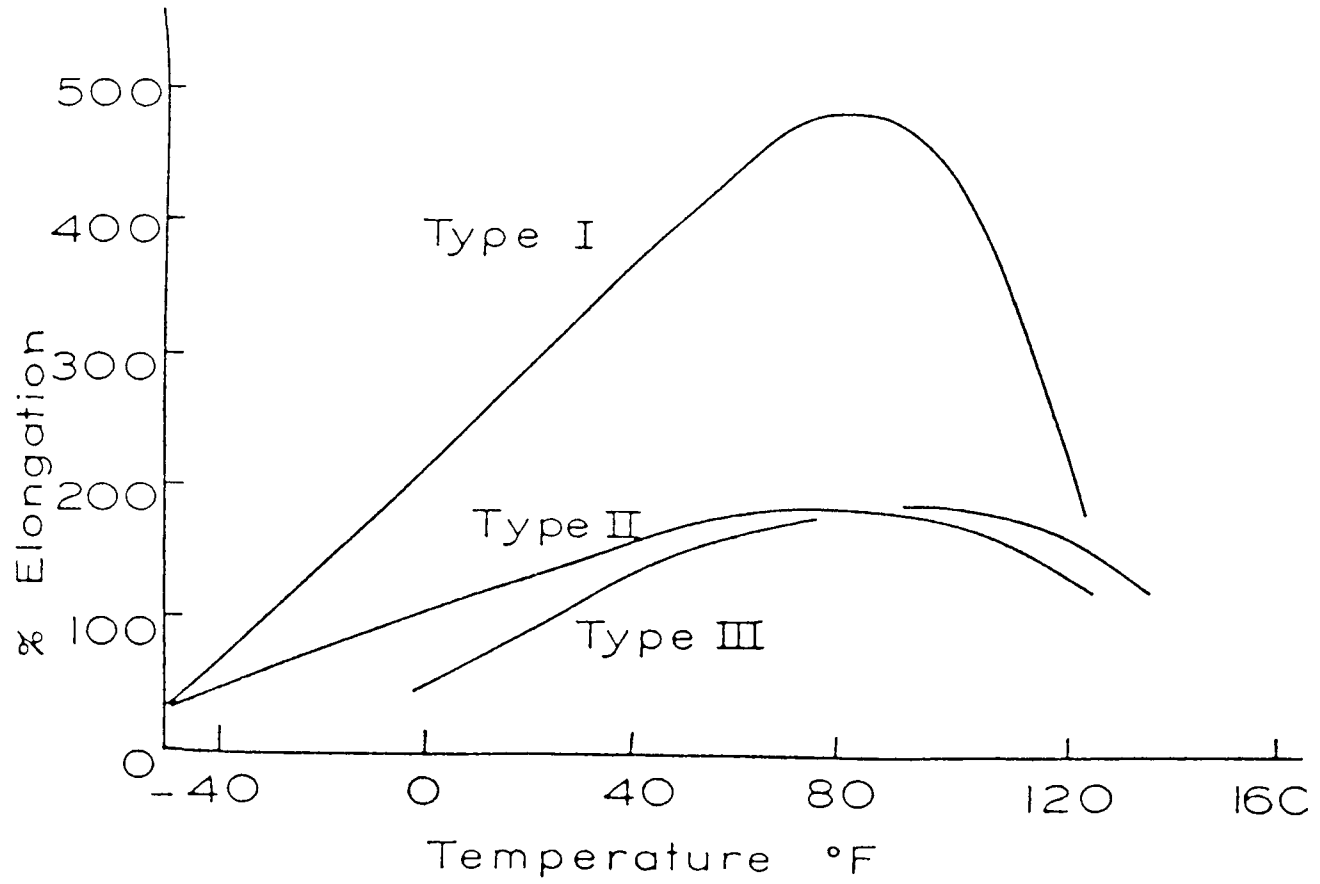


Figure 4 Types of Polyolefins

Polyethylene

To illustrate some of the properties are shown in figure plotted against temperature. In these curves the three types represent density ranges.

Type 1	Low Density	0.910-0.925
Type 2	Medium Density	0.925-0.940
Type 3	High Density	0.940-0.960

It can be seen that yield tensile strength, ultimate tensile strength, and modules of elasticity, are all high at low temperature and drop sharply as the temperature increases. Elongation is quite different and rises to a maximum, which is at a higher temperature with the higher density resin, and is also much more marked in Type 1.

3.4 Crystallinity

The relationship between the density of the polyethylene and its physical properties was mentioned earlier without detailing the reason for the relationship.

The reason why the density plays a such an important part in polyethylene properties is that it is measure of

crystallinity. Polyethylene crystals are more dense than amorphous polyethylene. Therefore the density of the aggregate reflects the degree of crystallinity. The other polyolefins have lower crystal densities than polyethylene, so have lower mass densities, even at higher degree of crystallinity.

It would seem more logical, therefore, to report the percent crystallinity rather than density, but this is not readily done. Crystallinity has been measured by X-ray diffraction, by infra red absorption, and by differential thermal analysis (DTA), but these different methods do not measure quite the same quality. Therefore, there is no generally accepted definition reliably comparable data available on crystallinity.

A complicating factor in the relationship of physical properties to the crystallinity is that the size of the crystalline aggregates, as well as the total amount of the crystallinity effects the physical properties. Large crystalline stiffens the polymer and causes it to become brittle. This is one reason for the loss of flexibility on aging. Time, particularly at elevated temperatures, causes an increase in the size of the crystalline aggregate as well as the gradual increase in total crystallinity.

One of the reasons why high molecular weight polyolefins show superior aging characteristics is the tendency for very long chains to limit crystallinity and crystal size.

Crystallinity is responsible for much of the tensile strengths of the polyolefins. The bonds between the molecules are very weak. When the resin crystallizes, the molecules conform more closely, so that the weak molecular forces have the greater chance to become effective, and this is what gives the plastic its strength.

3.5 Standard Test Methods

For the detailed study of the physical properties whose values are the result of numerous tests. While we cannot attempt to describe these tests in detail, a short description of each test will be given, and reference will be made to the appropriate test procedure of the American Society for Testing of Materials (ASTM), or other standard reference, for those who need to know the details. A brief comment on meaning of the test will be made.

3.6 Resin Tests

3.6.1 Melt Index (ASTM D1238-62T)

The polymer is packed into an accurately controlled, heated cylinder which has a small orifice at the bottom. A weighted

piston is loaded at the top of the polymer mass, forcing a stream of molten polymer out of the orifice,. The extrudate is collected over a carefully time interval and weighed. The weight of polymer extruded in ten minutes is called melt index, abbreviated M.I. This test is a widely used means of classifying polyolefin plastics. It is also an indication of how a material will flow in processing, although identical melt index does not necessarily mean identical flow.

3.6.2 Flow Rate (D 1238-62T)

Flow rate is a value similar to the melt index but determined under conditions different from the standard melt index conditions. Flow rates are often referred to as melt index, but this results in confusion. For instance, The abbreviation M.I 10 is used to indicate a flow rate under the same conditions as melt index except that a 10,000 gram weight is substituted for the standard weight. This same designation is used by others to indicate a flow rate at ten times the standard weight, or 21,600 grams. This ASTM procedure lists conditions suitable for determining flow rate for almost any purpose, and provides a positive means for identification for them.

These tests are indications of how the polymer will flow in processing. Using other conditions than standard melt index permits the choice of conditions more suitable to the polymer in question.

3.6.3 Flow Rate Ratio

This is also referred to as Melt Index Ratio (M.I.R.). There is however no industry wide standard, so that the exact meaning must be explained with the data to make it meaningful. When the ratio $M.I._{10} / M.I.$ has a high value, it indicates good flow at higher shear rates.

3.6.4 Density (ASTM D1505-63T)

Density is the weight in grams of a cubic centimeter of the material. It is commonly determined by means of density gradient column. A density gradient column consists of a cylindrical liquid, usually for polyolefins a mixture of an alcohol and water, which has been so constructed as to have a higher proportion of water in the bottom and a higher proportion of alcohol on top with a smooth gradient of concentrations in between. The proportions of alcohol and water are chosen to match the density of the sample being tested near the middle of the column. Accurately calibrated glass floats, representing density steps within the range of interest, are then dropped into the column. The floats will drop into the column to the point where the density of the liquid exactly matches the density of the float. The location of the sample, and of the float above and below it is then accurately measured, and the sample density is calculated by interpolation. The temperature of the density gradient column has to be controlled very accurately for

good results. The density of the sample of polyolefin reflects its molecular structure, and also the process used in preparing the sample, so that to be meaningful and the method of sample preparation must be standardized. Density is widely used to classify polyethylenes, and many properties of polyethylene vary with density. It has little importance on other polyolefins, except simply to show their weight.

3.6.5 Solution Viscosity (ASTM D1601-61)

This is the viscosity of the dilute solution of the resin in solvent. Decalin and tetralin are commonly used at a temperature high enough to assure complete solution (130 C is commonly used). There are three ways of reporting this result. One is viscosity ratio and relative viscosity. This is the ratio of solution viscosity to the viscosity of the pure solvent. The second is the logarithmic viscosity number or inherent viscosity. This is the natural logarithm of the relative viscosity divided by the concentration in grams per 100 ml of solution. The third is limiting viscosity number or intrinsic viscosity, which is the zero concentration intercept of the plot of the logarithmic viscosity number against concentration. This number is used as a means of estimating molecular weight, and in conjunction with melt index, may be used to estimate molecular weight distribution.

3.6.6 Environmental Stress Cracking Resistance (ASTM D 1693)

This is sometimes called the bent strip test. A short strip of material is nicked on one side and bent into a U-shape. The ends of the U are held in a channel. a group of 10 strips is placed in one channel, and the assembly is placed in a stress cracking agent (Igepal CO 630 is standard) at a temperature of 50 C. The samples are observed periodically until they show cracks. The value reported is the time required for half the stripes to crack.

This test is the measure of the resistance of the material to crack by the stress crack agent. It is interpreted as an indication of general chemical resistance and general durability of the resin. Since service failure in polyolefins parts frequently occurs at well below the normal strength of the resin because of the contact with some hostile environment, modifications of this test using different environments are very common.

3.6.7 Tests of Physical Strength

Polyofins are tested by a variety of strength tests, which are identical with those used for other plastics and also for many other materials, and should be understood by most readers without explanation. These will simply be listed with appropriate references:

Flexural Stiffness ASTM D767-58T

Brittleness temperature ASTM D746-59T

Izod impact ASTM D256-56

Shore hardness ASTM D1706-63

Tensile properties (tensile strength, yield point, elongation) ASTM D638-61T, Appendix

Tensile Impact ASTM D 1822-61T

3.7 Tests on Films

The production of transparent film is such a large part of the polyolefin plastics business that some of the tests used on films should be mentioned.

3.7.1 Haze (ASTM D1003-61)

This represents the portion of a transmitted beam of light scattered by a piece of film and into a light trap which would absorb all of the beam in the absence of film. The light that is scattered so that it is not absorbed is caught and measured by an integrating sphere photometer. This measurement is compared to light of the whole beam and reported as percent haze. It is reported a milkiness or cloudiness in the film.

3.7.2 Gloss (ASTM D523-62T)

This is the measure of the amount of light reflected from the film when a light beam is directed at a film at an

angle. Gloss may be measure at an angle of 60, 20, and 80 degree by standard procedures, and 45 degree is commonly used although not standard. A photo cell measures the beam reflected from the film, and the result is reported in comparison with an arbitrary standard. That is to say, it is not a percent of anything but merely a level of an arbitrary scale. Gloss represents the visual shininess or sparkle of the film.

3.7.3 Transparency (ASTM D1746-62T)

This measures the scattering of an extremely narrow slit beam of light by the film. It differs from haze mainly in the dimensions of the light and its method of measurement. It is reported as the percentage of the incident light that is not scattered, absorbed, or reflected. Since the slit is extremely narrow the values depends on the position of the film, so the film is rotated during the measurement and the transmission at different film position is recorded. Maximum and minimum values are usually reported.

This is the measure of how clearly images can be seen through the film. Evidently very cloudy film cannot have high transparency, but clear film may differ considerably in how much it fuzzes up an image seen through it, and this is what we measure here.

3.7.4 Dart Drop Impact (ASTM D1709-62T)

A sample of film is clamped firmly in a circular holder held horizontally, and a small dart with a spherical head is dropped on the film from a standard height. The darts are arranged so that the weights can readily be added to it or taken from it. Drops with varying weights are made until the weight is found which has an equal chance of breaking or not breaking the film.

This is a measure of the ability of the film to withstand the impact loads it will meet in service, such as in packaging application. {Refer to 5 and 13}.

CHAPTER 4

THE MANUFACTURE OF POLYOLEFIN PLASTICS

4.1 Polyolefin Plastics Production

The development of any polyolefin plastic must necessarily be preceded by the development of an adequate supply of olefin monomer, at a price which will make the polymer attractive. In this sense the polyolefin plastic is just one end result of the development of the petrochemical industry.

At present most ethylene is produced from petroleum or from natural gas. The development of this industry has reached the state where any refinery stream from light gas to heavy naphtha can be used as feed stock for an ethylene plant. Which feed stock is used depends on the value of the stream at a particular location. Ethylene can even be made directly from crude oil. This makes it possible to build an ethylene plant at a location away from an oil refinery. Ethylene plants have increased in size and efficiency, making them a very attractive investment at the present time. This has naturally attracted new producers into the field and encouraged the old ones to expand, resulting in an adequate supply of ethylene at a cost which will probably decrease for sometime even in the face of general cost increases. This will improve the competitive position of polyolefins in comparison with that of products not based on

ethylene. Most ethylene plants produce some polypropylene as a byproduct, and many can be operated in such a way as to control the ratios of two products.

Ethylene and polypropylene are produced feedstocks consisting of a wide variety of hydrocarbons, saturated and unsaturated. This feed stock is thermally cracked, usually with the assistance of catalysts, to give a mixture of the desired olefins and both lighter and heavier materials. These are separated by distillation to produce pure olefins, while the unwanted products may be recycled or used for other purposes, depending on the most economic path.

4.2 High Pressure Process

The high pressure process, originally developed by ICI, is still the way in which the largest tonnage of polyolefin is made. This process is capable of making polyethylene ranging from hard, high density material through soft, rubbery copolymers. For economic reasons, however, its use is generally limited to polyethylenes in the low and middle density ranges, and to copolymers with polar comonomers such as vinyl acetate or the acrylic esters.

The process is carried out at pressures of from 15,000-50,000 psi and at temperatures from 200-250 degree F. Under these conditions ethylene is above its critical temperatures, so it remain in gaseous state, however it is

compressed to density that makes it behave like lubricating oil.

4.2.1 Types of Equipment

The process is carried out in two general types of equipment, long tubes and stirred autoclaves. The tubes are generally between 3/4 inch and 1 1/2 inches in diameter, and several hundred feet long. The autoclaves differ greatly in design among manufacturers, ranging from cylinders about the same length and diameter to cylinders 12 to 15 times as long as their diameters. The stirrer motors are sometimes included inside the pressure shell to avoid the problems associated with maintaining a packing on a movable shaft at these pressures. Details of the reactor geometry influence the properties of the resin produced.

The largest producers of high pressure polyethylene use both tubular reactors and stirred autoclaves, because certain grades of polyethylene are more readily made on one or the other. However, some manufacturers make a complete line resins using only one kind of reactor.

The polymerization of ethylene in a high pressure reactor is extremely rapid, producing a complete polymer molecule in a fraction of a second. This means that a small reactor has a very large output. Ethylene polymerization is highly exothermic, so the production of the polymer is limited to

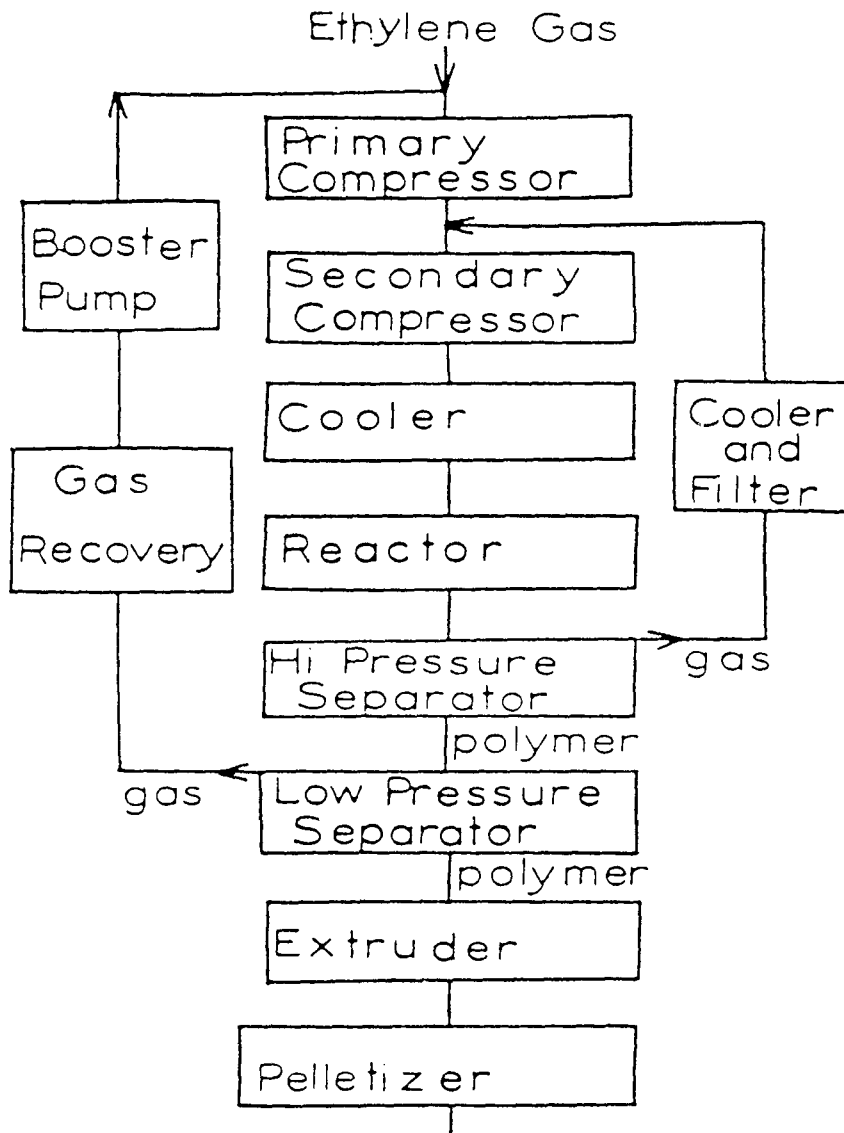


Figure 5 A Simplified Flow Sheet of The High-Pressure Polyethylene Process.

the amount of heat that can be handled. Because of the high rate of reaction, it is not usually possible to remove any significant proportion of the heat by heat transfer to the walls of the reactor. This means only as much polymer can be produced at a pass as will heat up the reacting mass to the maximum temperature that can be tolerated in the production of the particular resin being made. This generally limits the conversion to 10-15% of the gas by weight by pass. At one time a process was operated which used water as a heat control medium in the reactor, but the problems associated with separation of water and polymer make it unattractive. Tubular reactors, because of their greater ratio of surface area to volume can transfer a larger portion of the heat of reaction than an autoclave reactor and can therefore get more conversion per pass.

After passing through the reactor, the gas is separated from the polymer, cooled, compressed, and recycled through the reactor, while the polymer is extruded through a die, pelletized, and cooled.

4.2.2 Initiator Handling

The reaction initiator, generally a peroxide, is highly inflammable, temperature sensitive, and in some cases can be detonated by shock. refrigerated storage is commonly required, and it is generally practiced to use the initiator

in relatively dilute solution in an inert solvent to make it more stable. This also facilitates the accurate metering of the relatively small amounts used and permits ready dispersion in the reaction mix.

Initiator solution is pumped directly into the reactor in the exact amounts needed to maintain the reaction at the conditions desired.

Initiator injection points vary with the reactor design. In the case of tubular reactors or long autoclaves there may be several injection points throughout the length of the reactor. The location of the injection points serves to control molecular weight distribution in the resulting polymer.

4.2.3 Requirements for a Reactor

The highly exothermic propagation reaction is very rapid, and this requires excellent mixing in an autoclave or high gas velocity in a tube, to prevent the formation of hot spots from the excessive initiator concentrations. Hot spots can produce an explosive reaction known as "decomp", which results in a very sudden rise in pressure and the temperature, which is capable of destroying the reactor unless properly vented. Reactors are generally built with one or more large openings to a vent stack, which are closed

by rupture discs which release the contents of the reactor out the vent in case excessive pressures are built up. Because of the extremely rapid built up of pressure in "decomp", these have to be very quick acting to be effective, so especially designed disks must be used.

4.2.4 Reactor Control

Chain transfer agents are also added to the reactor to control polymer properties. The primary control of polymer chain length is reactor temperature and pressure. Temperature and pressure, however, also influence other properties, such as chain branching. The chain transfer agent gives control of the chain length independent of pressure and temperature, and also makes possible the combination of properties not possible without it.

Chain transfer agents are generally added to the reaction gas prior to the final compressor but may also be injected directly into the reactor.

Termination occurs by coupling or disproportionation of free radicals in the reactor and is controlled by reactor temperature; the higher the temperature the more frequent the terminations and therefore the shorter molecules.

4.2.5 Separation

After leaving the reactor the mixture of the polymer and unreacted ethylene goes to a separator, where the pressure is dropped to something between 1500 and 3000 pounds. The gas expands greatly and separates from the polymer rapidly. The gas is then filtered and returned to the suction of the secondary compressor.

The polymer with some dissolved gas goes to a low pressure separator, at essentially atmospheric pressure, where the remainder of the gas is released. This gas may be purified, recompressed, and returned to the system, or it may leave the system for some other use.

The polymer is removed from the bottom of the separator by a screw extruder and palletized in any one of the ways that will be described later.

Additives may be put into the polymer by injection into final separator, or into the screw extruder, or by subsequent blending or compounding operations.

4.2.6 Advantages and Limitations.

The wide range of temperatures and pressures over which this process can be operated, the wide differences in reactor design is possible, and the possibilities inherent to the

use of different initiators, chain transfer agents, and other reaction modifiers, make it possible to produce a wide variety of different polymers by this process. When the possibilities of copolymerization are added to this, it can be seen that this is an extraordinary versatile process.

4.2.7 Safety Considerations in High Pressure Process

Since its inception the high pressure process in making polyethylene has been plagued by disastrous explosions. This is not, as often assumed, due to the rupture of the high pressure reactors. Some of the very first explosions at ICI were due to this cause, but reactor design and venting have rendered pressure surges in the reactors harmless.

The main present danger lies in the fact that at pressures of 15,000 psi or over, a very large amount of gas can escape from a very small leak in a short time. Ethylene gas produces explosive mixtures with air over a very wide concentration range. The usual hazard is that an un noticed gas accumulates a large amount of an explosive mixture of ethylene and air around the plant and that this is then accidentally ignited.

The high pressure polyethylene manufacturers have operated very closely to develop safety standards for these plants. These include all welded piping, except where it is absolutely necessary to be able to break a line, and special

flanges there; high volume forced ventilation of all areas in which a leak could develop; the use of automatic alarms to detect gas in all danger areas, and stringent precautions to eliminate all possible sources of ignition in the danger areas.

In addition to this, personal is often protected by the use of remote control of the high pressure equipment, and the use of reinforced concrete block hose type control rooms.

While this process must always remain in an inherently hazardous one, the lessons learned from previous accidents have been carefully acted upon, and in the future it should be no more hazardous than other large scale chemical process using highly inflammable materials.

4.3 Low Pressure Process

While there are great many differences in detail between the low pressure processes for making the various olefins. There are also several different types of processes for each polyolefin based on different catalyst systems, but all have strong basic similarities, so will be handled together, and the differences noted as necessary. A general flow sheet for a low pressure process is shown in fig.

In the low pressure processes for olefin polymerization the reaction takes place at active locations on the surface of a

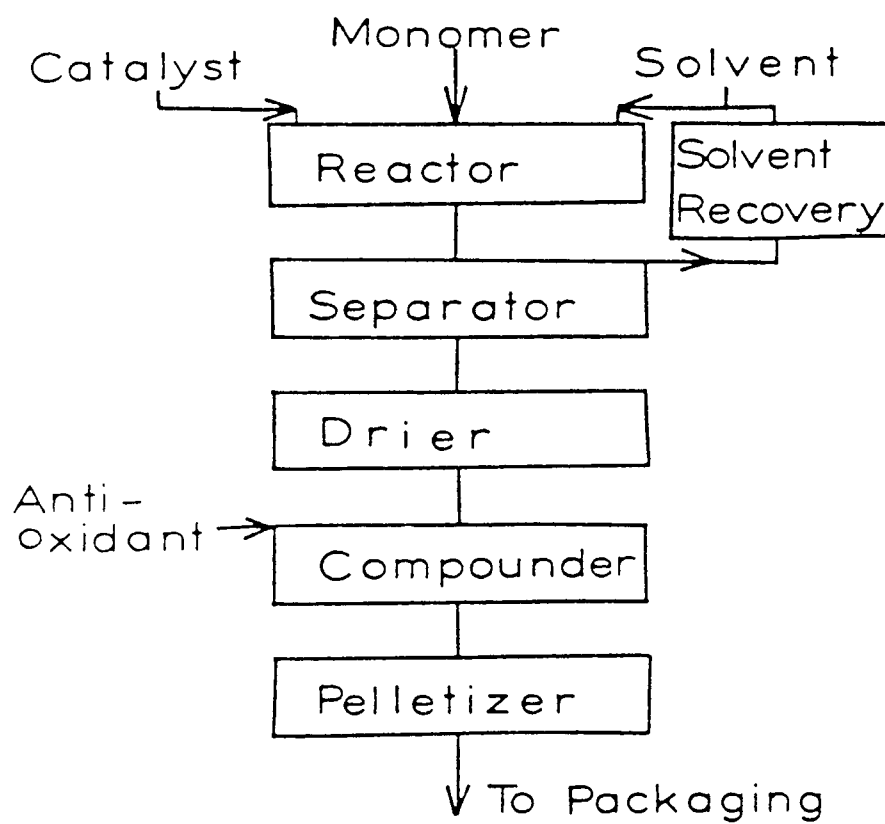


Figure 6 Simplified Flow Sheet of The Low-Pressure Process For Polymerizing of Polyolefins.

solid catalyst. The solid catalyst may be silica, or silica aluminum impregnated with small amount of metal oxide.

In the Phillips process the metal oxide is chromium oxide, in the Standard Oil of Indiana it is molybdenum oxide. In both of these processes other or nonmetals may be used in one form or another to promote or modify the action of the catalyst in some way. Also the catalyst must undergo a pretreatment or activation process before it will work. The exact details of this activation process are often of more importance than the chemical composition of the catalyst.

In the Ziegler or Zeigler-Natta process the catalyst is a complex formed by the reaction of an aluminum alkyl with a group IV metal halide, a typical example being aluminum triisobutyl and titanium tetrachloride. In these catalysts too, the exact method of preparation, crystal form etc. are very important.

In all of these processes the catalyst production technology is is the most important feature of the process. The catalyst preparation and activation techniques determine not simply the activity or efficiency of the catalyst, but the properties of the resin as well.

Phillips and Standard Oil of Indiana catalysts must be prepared and activated before contacting the reacting

mixture. Zeigler catalysts can be made by putting the separate components into the reactor, but are usually made separately.

4.3.1 Catalyst Handling

Catalyst handling is also extremely critical. The metal oxide catalysts are not dangerous to handle, but once they are activated they must be protected from oxygen and from the slightest trace of moisture or other catalyst poisons which will make them completely useless on contact.

The Zeigler catalysts are in addition top being extremely sensitive to poisons, so highly reactive that they will burst into flames on exposure to air. A whole new technology of absolute desiccation and protection from the atmosphere has been developed to handle these materials.

The use of these catalysts also requires very stringent standards of olefin purity, for all the monomers used. The traces of moisture undetectable by any ordinary means will destroy the catalyst. Many other impurities in the olefin that will cause no trouble at all in free radical polymerization, or drastically reduce catalyst efficiency.

4.3.2 Advantages of this Process

In view of these difficulties, what makes this process desirable?

There are many factors. The main factor is that this process can make resins with properties almost attainable by free radical polymerization. In ethylene polymerization a practically branch free polymer can be made with higher density, stiffness and strength. Such polymers can also be made by high pressure process, but only at prohibitive costs. With the higher olefins the low pressure becomes the only one that can make polymers suitable for plastics applications. Free radical polymers of these materials are soft rubbery materials. It is because the solid catalyst is able to coordinate olefin in such a way as to control its position as it enters the polymer chain.

Another important advantage of the low pressure process is that it operates at low pressures. This saves the high pumping costs inherent to the high pressure process, and makes it possible to use reactors of light and comparatively inexpensive construction.

Another advantage is that the solid catalysts are extremely efficient. Unlike the free radical initiators they are not consumed in the reaction, so they can go on producing polymer indefinitely until they are poisoned by some impurity. Productivities in the 5000-6000 pounds per pound range can be obtained by regular production basis. This means that the catalyst costs are extremely low in this

process compared to free radical initiator costs, where a pound of initiator may make only a few hundred pounds of polymer. The oxide type catalysts are also quite inexpensive per pound compared to organic peroxides. The Zeigler type of catalyst is more expensive, but considering productivity is no more so than free radical initiator.

A further advantage of the low pressure process is that the rate of reaction is slow enough so that the heat of reaction can be removed from the reactor by conduction, making it possible to get substantially complete conversion of olefin to polymer at one pass, obviating the recycling required in the high pressure process, and the attendant need for a gas purification system.

The slow reaction rate has another advantage. A single polymer molecule will be growing for periods of an hour or more. This makes it very convenient to make a special kind of copolymer by this process. The high pressure process forms a complete molecule in a fraction of a second. The only way a polymer is made in this process is to mix the two monomers together in a reactor, and two monomers will enter the chain just by chance in any order. This is called a random copolymer.

Most low pressure copolymers are made in the same way, producing random copolymers. However, improved properties

are possible in some cases by making a block copolymer. To make such a copolymer the solid catalyst is exposed alternately to one monomer and the other. The slow rate of growth of molecule in the low pressure process makes it quite easy to, alternate monomers a number of times in the same molecule. This polymer will then consist of a chain segment formed entirely from one monomer, followed by chain segment formed entirely from other monomer and so on. Such a copolymer will have different properties from a random copolymer.

4.3.3 Alternative Methods of Operation

The low pressure process is usually carried out in the presence of an inert hydrocarbon solvent, although some solid catalyst can be used in pure gas, without solvent. The solvent acts as a heat control and transfer medium, a means of obtaining good dispersion of the catalyst, and a carrier for the polymer in the process.

Low pressure polymerization may be carried out under two very different sets of conditions, in one of which the polymer dissolves in the solvent, and in the other of which the polymer is insoluble in the solvent and builds up around the catalyst particles in the form of a porous granule.

Selection of solvent is one of the critical determinants of how the process will operate, the more active solvents of

course tending toward solution. Temperature and type of polymer are also important, high temperatures and soluble types of polymer giving solution type polymerization.

All of the catalyst systems may be used in both solution and particles for polymerization. Although traditionally there has been preference for one or the other with a particular catalyst system, the pressure to broaden the product line has resulted in use of both with all of the catalyst systems.

4.3.4 Catalyst Removal

Catalyst removal is one of the most difficult and expensive steps in low pressure olefin polymer production.

In the case of the highly reactive Zeigler catalysts the activity has to be destroyed before removal. The alkali metal promoted Standard of Indiana catalysts also need pretreatment. In either case, simple washing with water or alcohol will render the catalyst inactive.

Phillips type catalysts are not dangerously reactive in air, so can be removed without pretreatment. In the case of solution form polymer, the catalyst residue can be removed simply by filtration or centrifuging. In the case of particle form polymer, the polymer must first be dissolved in an active solvent.

The development of the modern superactive catalysts has made it possible in many cases to eliminate the catalyst removal step, because the small amount of catalyst can be left in polymer without effecting the value. This reduces the cost of the polymer considerably. Especially in the case of particle for polymerization, avoiding catalyst removal greatly reduces the cost of solvent recovery. A filterable linear polyethylene solution will not contain more than five or six percent polymer. This means that the twenty pounds of solvents have to be recovered from each pound of resin produced. A particle form slurry can be handled at a solids content of 30-35%, thus reducing solvent requirements to one tenth or less.

The polymer produced either by precipitation from solution or from drying a slurry consists of very fine particles that are not convenient to use in conventional plastics processing equipment. Recent developments, are making it possible to use this resin "fluff" directly, but at present it is necessary to put it into pellet or granular form.

4.3.5 Finishing Operations

For this purpose the dried resin fluff must be put through some sort of machines which will melt it and force the melt through a die, which forms a palette of appropriate size.

A wide variety of machines is used for this purpose. There are two general sorts of machines used: screw extruders, and intensive mixers. The screw extruders again fall into two classes: single screw machines and double screw machines.

4.3.6 Intensive Mixer

This machine consists of very heavy jacketed housing containing two lobed rotating shafts. The lobe on the shaft is of such a size that it has only a very narrow clearance from the housing, and it is set at an angle to the line of shaft. Polymer is put into this machine and pressed strongly into the space between the rotors and the housing, and it is set at an angle to the line of the shaft. Polymer is put into this machine and pressed strongly into the space between the rotors and housing by means of a hydraulic ram. The rapidly turning rotors then press it against the housing, and also transfer it back and forth between the rotors creating a great deal of frictional heat which rapidly melts the polymer and forms it into a dough-like mass.

The great power of these machines result in a complete fusion of the charge in few minutes. The mass is then dropped out of the machine by opening a door in the bottom, and fed into a hot melt extruder. This machine has had considerable development and refinement recently.

For plastic processing the double lobbed rotors have been replaced by four lobbed rotors which reduce the time required for melting. Other manufacturers have come into the field with machines of the similar but slightly different design. The intensive mixer has also been modified for continuous rather than batch operation.

In this form there are conveyor screws at the end of the rotor which carry the unmelted resin into the mixing space between the rotors at one end, and then remove molten resin from the mixing space at the other and force it out through an orifice. These machines do not produce enough pressure on the molten polymer to force it through a small opening pellet die, so the production of the continuous mixer is fed to a hot melt extruder for palletizing. The operation of the extruder however, is considerably simplified by having to contend with a succession of batch loads.

4.3.7 Double Screw Extruder

Double screw extruders are available in considerable variety. Basically they consist of two helical screws rotating in a long chamber with a cross section approximating a figure eight. The screws may rotate in the same direction, or in opposite directions, or they may intermesh in varying degrees. This means that the lands of one screws may penetrate into the grooves of the other screw

either fully or partially. The helical flights may also be interrupted and modified in various ways. For instance, sections of the helix may be replaced by lobed disks which interact with the walls of the chamber and similar disks on the other screw, in much the same way as the rotors of an intensive mixer. The screws may be of the same length, or one may be considerably longer than the other. In the latter case we have essentially a double screw extruder feeding into a single screw extruder, except that both are the part of the same machine. The types most commonly used in palletizing polyolefin plastics are counterrotating, partially penetrating, unequal length screws, and screws made up of combinations of spiral and lobbed segments, although other types are undoubtedly used to some extent.

4.4 Finishing Steps Common to Both Processes

4.4.1 Palletizing

The machines produce a plastic mass under sufficient pressure to force it through a die. The way in which this is converted into a pellet may vary a great deal. Very generally there are three palletizing methods.

4.4.1.1 Cube Cut Strip

The polymer may be forced through a slit die, cooled until solid, and the resulting strip fed into a rotary cutter, which chops the strip into nearly cubical pellets.

4.4.1.2 Cut Strand

In this method a die with a large number of small holes is used. These holes may be round, square, or even triangular. The polymer is extruded through the die, the strands are cooled and chopped into short pieces by a rotary blade cutter. This makes short cylinders or prisms.

4.4.1.3 Die Face Cut

In this method the same general type of die is used as in the previous method, but instead of drawing a strand from the die, the hot extrudate is cut off by a rapidly moving blade at the die face. This is generally done under water; it is called under water pelletizing. It is also possible to do something by extruding into air and arranging it so that the cutter throws the pellet into water as soon as it is cut, to prevent hot pellets sticking together. This method produces pellets of general shape of a distorted sphere. It is the most common method of pelletizing polyolefin plastics. This form of pellet is especially desirable in case the plastic is being transferred by air conveyor because the spherical shape produces less fines during transfer. The only disadvantage of this type of pellet is that in certain dry coloring operations it is more difficult to get good distribution of color, because of the smaller surface area and the generally smoother surface.

4.5 Blending and Compounding

Polyolefin resins are susceptible in thermal degradation, so they must have a heat stabilizer, generally called an antioxidant, incorporated into them. Depending on the end use, it may also be necessary to add other materials. It is also desirable to mix two kinds of resins to get properties impossible to attain in a directly reacted material, or to take advantage of the economics of process that does not conveniently make a resin of desired properties.

4.5.1 Dry Blending

The simplest and least expensive method of mixing materials into the resin is by a dry blender. Low pressure process fluff or pellets may be used as a starting material. The additive must be in a form that will not segregate from the resin when mixed with it and must not tend to coat on the walls of the mixer. Liquid additives are usually sprayed into the mixing resin in a fine spray. Powder additives such as pigments or dyes may be added directly to the mixer; however it is commonly desirable to precoat the resin with a small amount of oil or similar liquid to improve adhesion of the pigment, especially in the case of pellets.

In the case of additives that are required in very small amounts, it is often impossible to get enough distribution of material by direct addition, and even in cases where the amounts are larger, better mixtures are obtained by master

batch methods. In a master batch the additive is first hot melt blended into a portion of the base resin, or a compatible resin of slightly different properties, at a higher concentration than that in the final product. This can be done in many of the kinds of described under finishing operations. Intensive mixtures are very commonly used. When blending with pellets it is then possible to make the master batch with the same pellet size and shape as the base resin, so that when they are mixed together there is no tendency to segregate.

4.5.2 Equipment Used in Dry Blending

The most generally used equipment is the double cone blender. This is a vessel with two conical ends joined by a short cylindrical section. Trunions are fitted to the center section and mounted on bearings so that the entire vessel can be rotated end over end. These can be made in large sizes, so that if desired, a 100,000 pound batch can be mixed at one time. The blender is filled about half full of the materials to be blended and rotated until they are well mixed.

The twin shell blender is also used a good deal. It consists of two cylinders that intersect in the form of a vee. It is also mounted on trunions in such a way as to rotate the vee end over end. If continuous rather than batch blending is desired, a succession of vees can be joined together and

entire assembly rotated, with components being fed continuous into one end and mix removed continuously at the other.

For small batches a cylindrical vessel, such as a 50 gallon drum may be mounted so that it is at an angle to the shaft and rotated.

Rotary blenders consisting of a cylinder fitted with baffles, and rotated on the axis of the cylinder are used. The baffles then carry a portion of the contents up as they rotate, and dump it down into the remainder when they near the top of the rotation, producing a mix action. This is generally similar to the action of a cement mixer.

A special sort of dry blender is called an intensive dry mixer. This must be distinguished from the intensive melt mixer, such as the Banbury which was described earlier. In the intensive dry mixer there are very rapidly rotating blades which strike the particles of the mix and impinge them violently against the walls of the mixer. Due to tough nature of polyolefin plastics, this produces little reduction in particle size but serves to imbed small additive particles into the pellets so that they are firmly bound and will not separate in later handling.

Dry blends are often quite satisfactory for use in plastics processing equipment, but in some cases it is necessary to produce a more uniform mixture or to modify the properties of the compound by more drastic mixing.

4.5.3 Hot Melt Mixing

The best possible plastic blends are made by means of hot melt mixers. The intensive hot melt mixer is the most widely used for this purpose. In case of the batch type, weighed amounts of resin or resins and additives are added to each batch and fluxed. In the continuous ones, belt, screw or vibratory feeders are used to meter the correct proportions of the material into one end, and the mixture is discharged at the other. These hot melt mixers then be pelletized.

Single screw or multiple screw extruders may also be used. For compounding services these are generally designed so as to give a more intensive mixing action than similar machines used for pelletizing

4.5.4 Transferring pellets of Resin Fluff

Raw resins and finished product pellets are ordinarily moved from place to place by air conveyors. These consist of relatively large diameter pipes designed with very gradual turns, through which a high velocity air stream is blown. The plastic pellets or fluff are dropped into this air stream, either in a continuous flow or in small portions by

means of a star feeder. They are then swept through the pipe by the air stream to the destination. If they are being blown into a large holding tank, the air stream may simply blow into the tank and exit from the top, dropping the pellets into the tank. If the destination is too small a container for this, or if it is desired to recirculate the air to the separate fines from the air stream before discharge, then the stream pass into a cyclone separator, which drops the pellets to the container, and the air continuous to the next step.

Lobe type blowers are usually used for large systems because they can produce large volumes of air at relatively high pressures, but centrifugal blowers may be adequate on a small line. Fluff transfer lines operate at lower pressure drop than pellet lines, so can be served by centrifugal blowers. Entry air must be filtered to prevent product contamination; this is done by bag filters, but screen filters are also used. The air intake must be protected to prevent entry of moisture in bad weather.

The piping is usually aluminum and should have internal treatment to prevent coating of the interior with polymer. Many polyolefin plastics, when air transferred through a completely smooth surfaced pipe, will smear out a little polymer on the surface each time a pellet impinges on the wall. Theses little smears gradually build up to a

continuous coating which, from time to time, will slough off sections producing what is called "snake skins". These can be very troublesome in blocking transfer equipment. If the interior of the pipe is roughened in just the right way, the development of the snake skins can be prevented. This generally increases the abrasion of of the pellets slightly, but the material worn off is in the form of fines, which cause less trouble than the snake skins. Fluff can be transferred in smooth lines, for it causes no snake skin problems.

4.5.6 Fines Removal

An excessive amount of fine material mixed in with pellets is likely to cause problems in the processing plant. Therefore, the pellets that have been air transferred a good deal must be separated from the resulting fines. This is usually accomplished by means of cyclone separators carefully designed to provide particle size separation; these will take pellets out of the air stream, while maintaining the fines in suspension. The fines are then removed from the air stream by bag filters, and the air is either recompressed to pick up the pellets again or allowed to escape.

Pellets may be transferred in this way to distances upto about a half a mile in the continuous pipe. If longer runs are desired it is necessary to have intermediate pumping

stations, otherwise the pressure drop is so great that the resulting air expansion produces exit velocities so high as to cause fines production.

4.5.7 Switching of Flow

Flow of material is switched from one branch of a pipeline to another by means of special butterfly valves with resilient seats. The design of these is quite critical because they must close reliably in the presence of relatively large plastic particles which would jam an ordinary valve and prevent its closing. Since different types of resins are continuously handled by the same line, perfect closing of the valve is essential to cross contamination. The valves may be manually operated, but in most plants they are automatically controlled from a central switch board, which not only operates every valve in the system but also indicates the position of every valve in the plant at all the times. This is very important in preventing mistransfer of the material. {Refer to 5 and 10}.

CHAPTER 5

BLOW MOLDING OF POLYOLEFIN PLASTICS

5.1 Introduction

5.1.1 What is Blow Molding ?

Blow molding is the process used to produce hollow objects from thermoplastic. The most widely used blow molding objects are bottles, jars, jugs, cans and containers of all kinds for the food, beverage, cosmetic, medical, pharmaceutical and home product industries (1 oz. to 1 gal..). Larger blown containers (up to 55 gal..) are often used for packaging chemicals, lubricants, and bulk materials. A common feature of all blow molded article is "re-entrant" curves, for example, a bottle having an opening much smaller than the body.

The basic process has two fundamental phases. First, a perform (or parison) of hot plastic resin in some what tubular shape is created. Second, a pressurized gas, usually air, is used to expand the hot perform and press it against a female mold cavity. The pressure is held until the plastic cools. This action identifies another common feature of blow molded articles. Part dimensional detail is better controlled on the outside than on the inside, where material wall thickness can alter the internal shape.

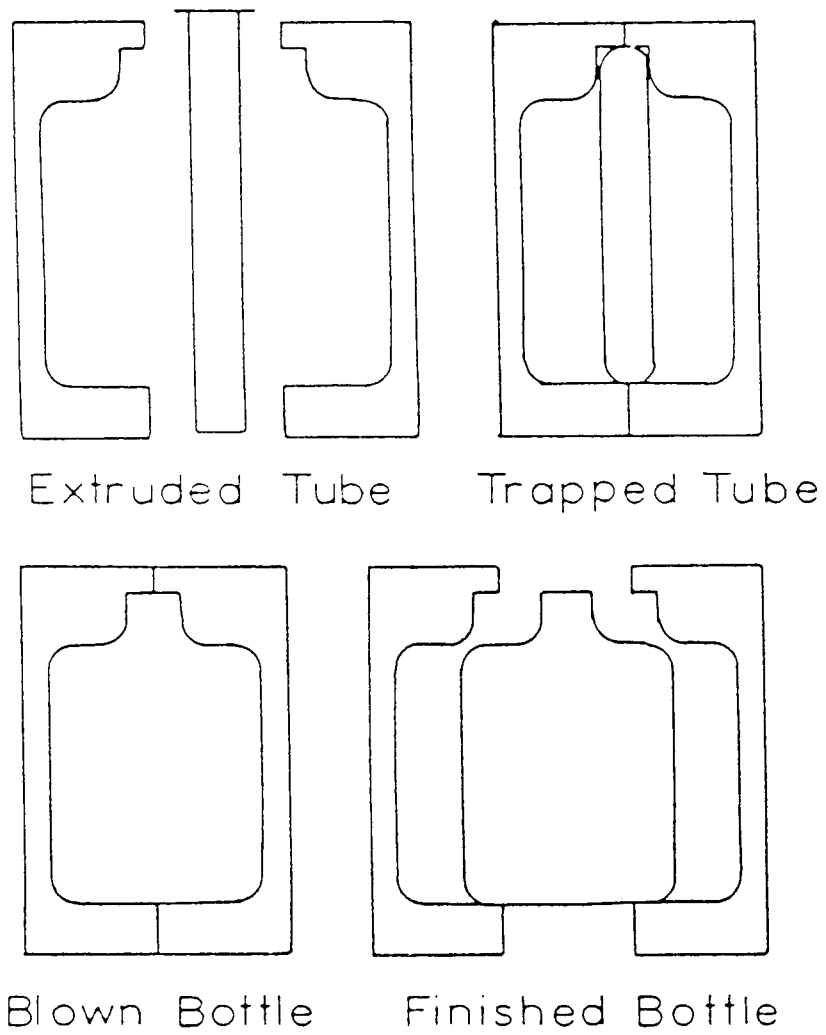


Figure 7 Principal Steps in Blow Molding.

Today, blow molding encompasses two fundamental process approaches based on the method used to create the preform or parison. These are injection blow molding, which uses an injection blow molded "test-tube" shaped preform and extrusion blow molding which uses an extruded tube parison. Several special processes, however, have elements of both, for example, most multilayer blow molded articles are produced on extrusion-based machinery, but injection based machinery is also used.

5.1.2 Blow Molding Markets

In recent years the blow molding has become one of the major processing methods of plastic industry. The most prevailing blow molding grade plastic raw material is high density polyethylene (HDPE). It comprises about 69% of all materials that are blow molded. Most of milk jugs are made from this polymer, other Polyolefins (LDPE, HMW-HDPE, PP) are also widely processed via blow molding.

Of the 8.2 billion pounds of HDPE processed domestically in 1988 roughly 37% (3 billion pounds) went into blow molding. About 25% of total molding poundage goes into milk bottles. That is tremendous market, but consumption for household chemical containers (bleach bottles, detergent bottles, etc.) is even larger: 33%. About 76% of the total resin usage goes into bottles and the other 24% is in industrial item gas tanks, bulk goods drum, seats, toys and the large

items. The rate of growth is faster in the industrial products area, but total consumption is lower.

5.1.3 Methods of Blow Molding

Three methods are generally used for blow molding:

1. Extrusion Blow Molding
2. Injection Blow molding
3. Multilayer Blow Molding

5.2 Extrusion Blow Molding

Three quarters of all blow molded products are made by extrusion-blow molding. The extrusion process is defined as making a product (extrudate) by forcing material through an orifice or die.

The extrusion blow molding process consists of five steps :

1. Extrusion of a plastic parison (hollow plastic tube)
2. Closing of two molded halves on the parison, clamping the mold and cutting the parison.

3. Blowing the parison against the cooled walls of mold cavity, calibrating the opening, and holding it under air pressure (80 to 125 psi) during the cooling time.
4. Opening the mold and removing the blown part
5. Finishing the part by trimming off the flash.

A basic blow molding machine comprises of:

1. Extruder
2. Extrusion head
3. Press section containing the mold
4. Calibration station
5. Parison separation device
6. Electrical control station

This fundamental unit is called a "blow and drop" machine. Expanded equipment includes in-machine cooling trimming or deflashing and oriented product discharge from the machine.

Plastic pellets are fed into the hopper mounted to extruder. A motor-driven screw, rotating up to 100 R.P.M. in a heated barrel, moves the material towards the blow molding or extrusion head or through the die.

Most extruders used in the blow molding are single-screw, either smooth barrel or grooved-barrel. Smooth barrel extruders have non-linear output characteristics when screw

speed is increased or back pressure is exerted by the blow molding heads or their tooling. Grooved-barrel extruders are pressure-insensitive; their output is linear with increased back pressure and weight deviations are controlled in the finished products.

Melt temperatures also remains stable because of the consistent feed provided by the mostly rectangular cross-section grooves that are located in the feed zone and have a 3 & 4 l/d relationship with cylinder barrel.

Extrusion blow molding is divided into two basic categories:

1. Continuous Extrusion
2. Intermittent Extrusion

5.2.1. Continuous Extrusion

In the case of continuous extrusion blow molding a stationary extruder plasticizes and pushes molten polymer through the head to form a continuous parison. Because the parison does not stop moving it is necessary to transfer the parison from die head to the mold either by means of arm or by moving the mold to parison.

The process has three sub-categories :

1. Rising Mold Method

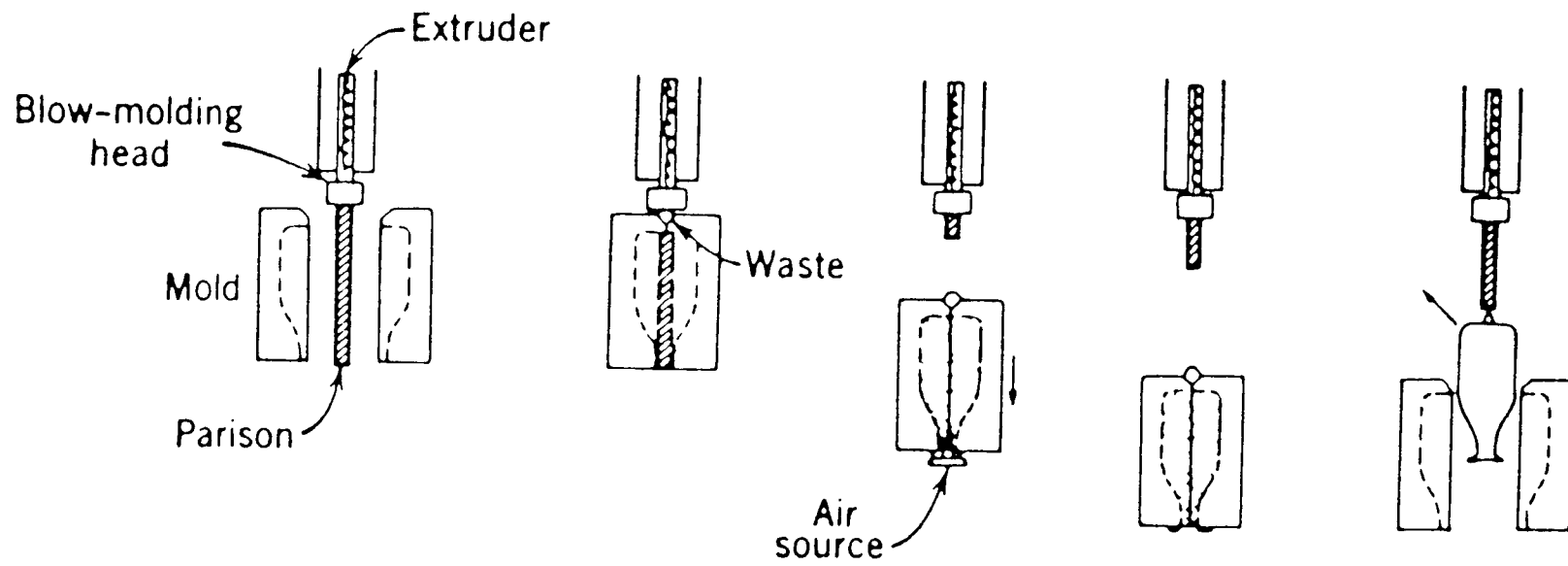


Figure 8 Continuous Extrusion with Rising Mold

2. The Rotary Method
3. The Shuttle Method

5.2.1.1 The Rising Mold Method

In the rising mold method, the parison is continuously extruded above the mold cavity. When it is at proper length, the mold rises quickly to capture the parison and returns down ward to the blow station. After blowing the bottle, the mold opens, the part is removed and the process repeats.

5.2.1.2. Rotary Method

In rotary method up to twenty clamping stations are mounted to either a vertical or horizontal wheel. As the wheel rotates past the extruder, simultaneously a parison is captured, bottles are molded and cooled and the cooled bottle is removed. This method can provide a high production yields; however, a disadvantage is the complexity and setup of the multiple mold clamps. It is usually not suited for short production runs.

5.2.1.3 The Shuttle Method

In the shuttle method a blowing station is located on one or both sides of the extruders quickly shuttle to a point under the extrusion head, capture and cut the parison and return to the blowing station with dual sided machines, the clamps shuttle on an alternating basis for increased production output, multiple extrusion heads are used. A symmetrical or

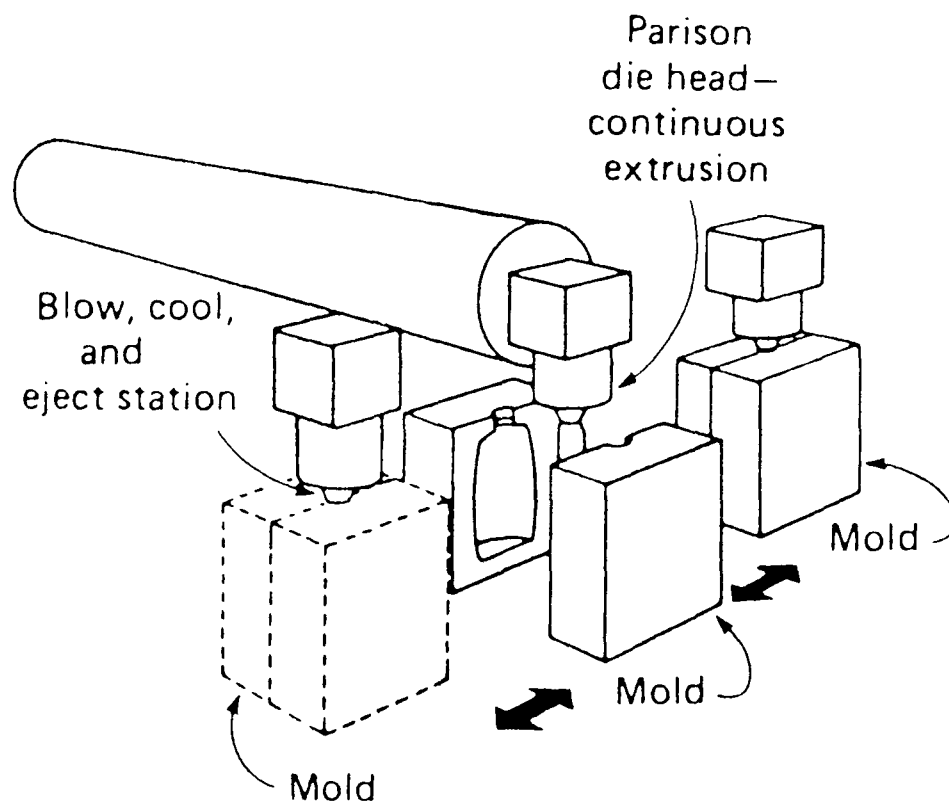


Figure 9 Shuttle Continuous Extrusion Blow Molding Machine

asymmetrical tube (parison) is formed by the die and the pin in the extrusion head. An asymmetrical parison is developed by shaping or ovalizing the tooling in the head.

Die and pin move often relative to each other during the extrusion process. This is caused by parison programming. Both methods, tooling ovalization and parison programming, are engaged for the production of blow molded products with uniform wall thickness distribution.

Continuous extrusion is used with shuttle type and wheel type machines. Since the parison is extruded continuously, an open mold is positioned periodically around the parison. With the parison at its proper length, the mold is closed and properly clamped and the mold is cut.

Objects without openings are often needle blown. Single stage shuttle machines have the mold positioned at the left or right of the extrusion head; double station machines have molds to the left and right of the head.

A blow molding machines productivity is governed by its cycle time, 80% of which is the cooling time. This long period is required for cooling of the hot plastic material prior to demolding, to prevent both post-warpage and dimensional distortion of the finished part.

For fast mold platen movements, proportional hydraulic circuitry has become standard on many machines. Rapid, controlled movements reduce unproductive periods. Timed mold closing slow down immediately preceding final mold closing will improve finished product quality.

Most blow molding machines are shuttle type, producing bottles and containers up to the capacity of 5-gal., at production rates of about 4000 units per hour. Production rates can be increased by the use of multi-parison heads (up to four parisons) and multicavity molds. Output can be further increased by combining vertical or horizontal rotary wheel systems (with as many as 24 mold cavities) with high output extruders.

As the wheel rotates, the molds mounted on it close on a continuously extruded parison. Production rates of up to 7200 units/hour can be attained.

The continuous extrusion process is used for bottles or parts 4.1 or less in volume; however with the ultra high molecular weight polyethylene resins providing superior melt strength the process could be used for some large industrial parts as well.

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5.2.2. Intermittent Extrusion

Intermittent extrusion is the second basic extrusion blow molding category. In this process the parison is quickly extruded after the bottle is removed from the mold. The mold clamping mechanism does not need to transfer to a blowing station. Blow molding cooling and part removal all take place under the extrusion head, which also allows the clamping system to be more simple and rugged. The stop/start aspect of the extrusion method makes this process more suitable for polyolefin and other materials that are not heat sensitive.

Intermittent extrusion machines are built in three versions:

1. Reciprocating Screw Systems
2. Ram Accumulator-type Systems
3. Accumulator Head Systems

5.2.2.1. Reciprocating Screw Systems

Reciprocating Screw Extruders move their rotating screws backwards as the material is plasticized and extruded forward into the extruder barrel. The extrudate is prevented from escaping the extrusion head, since the die is kept closed. After a specific volume of resin has been extruded, the die is opened, the screw is pushed forward hydraulically and a parison is ejected into an opened mold positioned under the blow molding head. The mold is closed, clamped,

and the die is sealed. Blowing and calibration (if required) take place through the die head.

Containers as large as 2.5 gal. capacity can be produced on reciprocating screw machines, which are available with up to 12 heads and molds for production rates of about 5000 units/hour.

5.2.2.2. Ram Accumulator System

Ram accumulator extruders are modified type of reciprocating screw systems. A cylinder with a floating piston is mounted alongside the extruder barrel. At the start of a cycle, the die in the extrusion head, or a valve between the die and the extrusion head mount is closed. The cylinder is charged with material by the rotating extruder screw. After a predetermined amount of resin has been pumped into the cylinder, the die or valve is switched open and the material is ejected through the die and the pin. This type of equipment is used for the production of blow molded parts weighing between 5 and 50 pounds.

5.2.2.3. Accumulator Head System

Accumulator head extruders are the most common types used for large containers and industrial parts: the largest machine in operation produces eight 248-lb, 530-gal-capacity HDPE fuel storage tanks/hour. Because large parts have heavy

walls, cooling times are longer and production rates generally lower.

Accumulator heads, attached to the end of an extruder barrel are designed to store and eject a measured amount of plastic material. Material ejection rate is approximately 1.1 to 6.6 lb/sec, depending on head size, parison programming requirement and material melt strength.

The mandrel or the diverter is the most important component in the accumulator head. It is responsible for the successful processing of high molecular or ultra high molecular weight PE, without affecting the chemical and physical properties of the final product.

The mandrel is equipped with a mechanical melt flow distributor whose computer designed channels accommodate the material flow characteristics as determined by rheological data. As the melt passes the device, a breakup and overlapping of the melt streams is accomplished, which contributes to the homogeneity of the material flow and temperature distribution.

Parison deformation during ejection and knitting lines previously visible in the products are eliminated. Material flow channels (in many cases resembling a double cardioid curve) and the melt flow distributor have a positive impact

on the wall thickness distribution of the finished container and on the time required for color changeover.

As the accumulator head is gradually filled and chemical settles the thermal degradation during dwell time must be avoided. Configuration of storage area and accuracy of the temperature control circuitry influence the formation of temperature gradients. Design of accumulator head is of prime importance for efficient processing of engineering resins.

5.2.3 Cooling and Trimming

Modern molding machines use built in stations for post molding cooling. Articles are transferred out of the mold into post cooling devices that basically consist of a cooling mold i.e a mold without pinch offs.

Cooling is accomplished via liquid cooling in the shell of the mold, and CO₂ refrigerated air or N₂ cooling inside the container. Advantages are seen in shorter cycle times and control of the part distortion inherent in parts with asymmetrical configuration and thick walls (0.3 in. for atypical gasoline tank).

After leaving the cooling station, container are accepted by trim or punching devices for flash removal: the need to regrind and reprocess the flash and the possibility that its

removal may expose seams which in turn can contribute to container's cracking and splitting upon impact.

5.2.4 Controls

Most blow molding machines are computer controlled. Data storage, diagnostics, monitoring functions, and all operator communications with the machine often are via an operator panel with CRT.

Graphics provides many ways of displaying, monitoring, and analyzing process parameters. Curves and corresponding values appear in different colors. Process deviations are indicated and may be printed. Digital measurements of the platen seeds, position control of the platens, and axially and radially integrated parison control systems are available features. Movement of blow pins, stretch pins, molds, etc. are controlled via proportional hydraulics and electronic circuitry. Blow molding machines are available with SPC systems and software that collects predetermined and preset process and machine parameters. Deviation from average are recorded, and lower and upper control limits calculated.

If the machine parameter drifts out of its window, it can be traced, a flag may be raised or an alarm sounded for process correction.

5.2.25 Commercial Information

There are approximately 8000 blow molding machines operating in approximately 1330 plants in North America. It is estimated that about 300 machines are added each year.

Continuous blow molding machines for producing containers up to 1-gal. capacity cost about \$ 260,000. The cost rises to about \$ 1.5 million for an accumulator head machine with options, suitable for producing 20-gal. automotive fuel tanks.

{The following figure has been taken from the book "Handbook of Plastics Materials and Technology" by Irvin I. Rubin.}

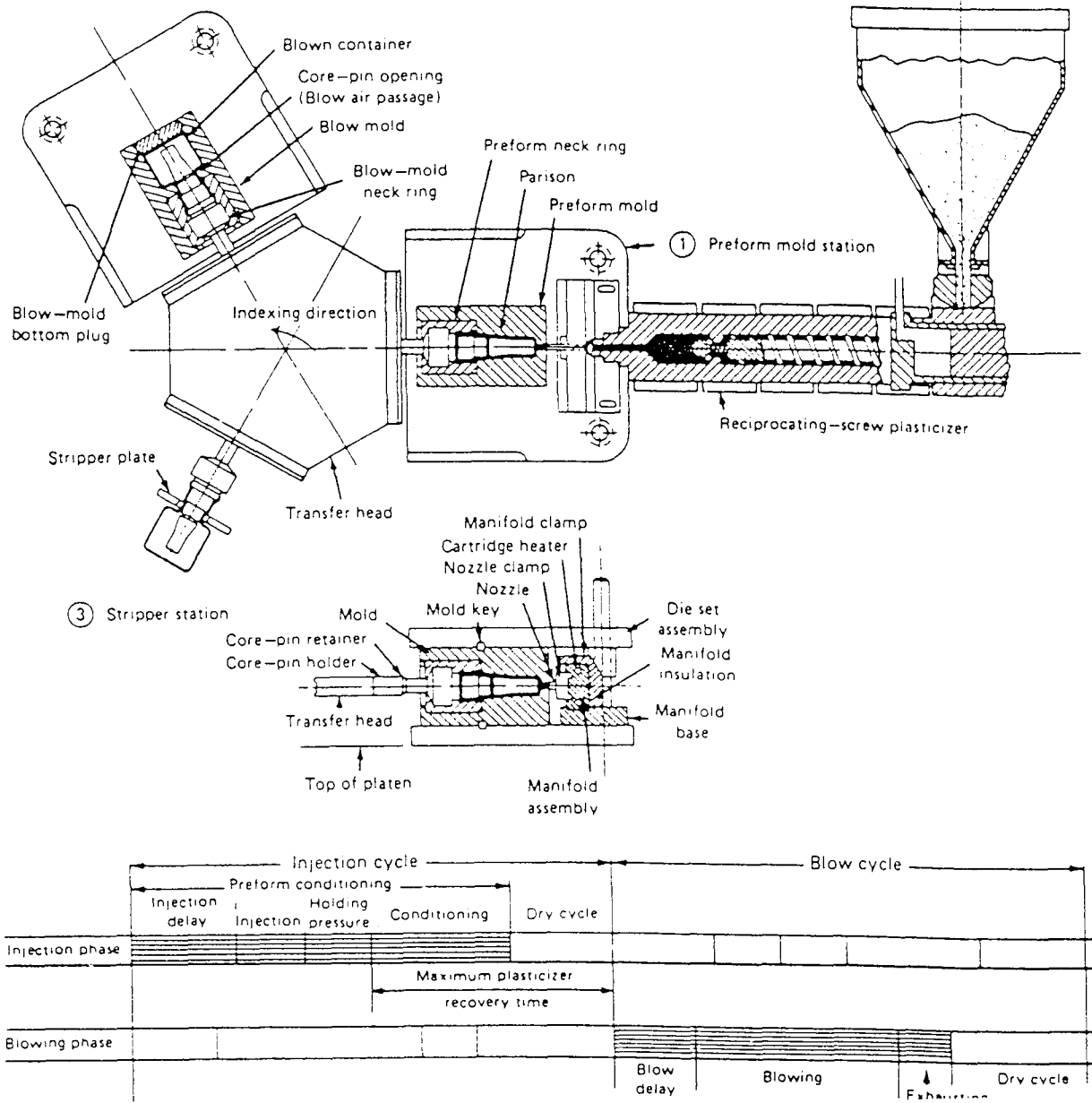


Figure 11 Process Description of Injection Blow Molding Machine

5.3 Injection Blow Molding

Injection blow molding combines injection molding with blow molding. The injection molding phase consists of injection molding a thermoplastic material into a hollow, tube shaped article called a preform. The preform is transferred on a metal shank, called the core rod, into a blow mold. In the blow mold the clamp tonnage is established to withstand the gas pressure that is used to blow the preform from the core rod to its predetermine shape. The air or other gas enters through the specially designed core rod to force the core rod to open and to blow the thermoplastic material, which is below its melt temperature, into the shape defined by the mold. Thus the term injection blow molding.

The earliest injection blow molding is normally credited to W.H. Kopitke, who was awarded patents in 1943 while he was with the Fernplas Company. The early injection blow molding systems were actually modified injection molding machines with specialized tooling mounted between the platens of the injection molding press. The most referenced press was the system developed by Piotrowsky others such as Moslo and Farkus, offered variations and improvements.

The injection blow molding systems of today basically employ the Gussoni horizontal indexing system that was patented in Italy in 1961. Wheaton also is credited with developing this system, but did not file any patents at that time. They had

acquired the rights to a Swiss process called Novaplast in the early 1950s and developed their injection blow molding process and machines, including tooling.

The injection blow molding process use in the plastics industry today on standard three station injection blow molding systems.

An important difference between the three station and four station indexing heads is the dry cycle time each achieves. Dry cycle time comprises the opening of the molds or clamp, the index time (to accomplish 120 vs. 90 degree movement) and actual close time. Because no processing takes place during the dry cycle time, it should be as short as possible while permitting the machine to function smoothly and consistently. The open index, and close time should be as close to 1.5 seconds as possible. Several companies including Ferguson and CAMCO, offer standard indexing heads that achieve this speed. The use of proportional hydraulics reduces shock to the machine from clamp closing and opening, thus reducing tool wear and damage and need for machine maintenance.

The fourth station has the advantage of requiring movement over shorter distances. It acts as a safety station where the core rods can be checked for preforms or bottles never stripped off, prior to the indexing to the injection station

to once again pick up the plastic material. This station can also be used to condition the outside and inside of the core rods to ensure they are at the correct temperature prior to entering the injection station. This is necessary with some of the latest engineering thermoplastic materials, including polyethylene terephthalate (PET).

As in any injection molding machine, the function of the plastifier is to convey, mix, melt, and inject the homogeneous melt into the injection mold. Normally the plastifier is of the horizontal reciprocating screw type. However the Jomer predominantly utilizes a nonreciprocating vertical screw type. The vertical screw can be used with most materials, especially where low shear and low melt temperatures are required. However the vertical screw is normally not preferred for high torque materials. It also has definite disadvantages with materials that must be dried. The mounting of the hopper drier poses structural and safety problems, and the drier mounting arrangement may result in poor drying. Shot control is not as consistent as on a horizontal reciprocating plastifier, and nozzle leakage has been an industry problem. Precise shot control on either type of plasatifier continues to be an area of improvement. Future machines may well have all electric devices for the plastifier units.

The injection station is the critical station in the injection blow molding process. The axiom "If you make a good preform, you will blow a good bottle" is quite true. The preform design is the first critical stage, and proper preform design is both an art and a science. No text book can cover all the factors for preform design at this time. Computer aided design (CAD) is being used, however it will take some time to incorporate the "hands on" aspect of preform operation into computer preform programs.

At the injection station, the molten homogeneous plastic material enters the injection mold by a gate. It fills the void between the female portion of the injection mold and the male core rod. Once the skin of the preform or parison, which is in contact with the female portion of the mold, has solidified sufficiently to allow the core rod to lift the parison out without fracturing the skin or causing a sag, the injection clamp opens and the dry cycle portion of the total cycle begins. Normal injection pressure is 1500 to 6000 psi. Thus the injection station mold clamp must have sufficient hydraulic clam tonnage to prevent the mold from opening due to the injection pressure necessary to fill void.

The injection clamp tonnage required to keep the injection molds closed is calculated as follows:

Projected flat area of preform, sq.in.	Injection pressure, psi	Total no. of cavities	Min.inj.
-----			= clamp
	2000 psi		force tons

Normally, a minimum 10% safety factor is added to the result.

At the blow mold station, the core rod lays the preinjected parison in the bottom half of the blow mold, this action is the part of the dry cycle. The blow clamp then brings the top half of the blow mold together with the bottom half and clamp tonnage is build up, normally by hydraulic pressure. The blow clamp required tonnage is calculated in the same way as the injection clamp tonnage, except that the projected area is the maximum area of the desired shape. The air pressure in the injection blow molding normally does not exceed 180 psi, for PET, and can be as low as 8 psi for polypropylene. The formula is:

Projected flat area of final molded shape, sq.in.	Blow pressure, psi	Total no. # of cavities	Min.inj.
-----			= clamp
	2000 psi		force tons

Once again, a minimum safety factor of 10% is added to the result.

At the stripper station the blown product is removed from the core rod. This is normally accomplished by a hydraulic cylinder with a Tempsonic control to activate the stripper bar. Some companies prefer an air cylinder stripper. The stripping is accomplished by a plate with U-shaped cutouts that just clear the threads or finish of the blown item. As the cylinder activates, the U-shaped bar pulls against the shoulder of the blown item to strip it from the core rod. In some machines, prior to stripping a gas flame is passed over and beneath the container to oxidize the surface of secondary decorating. This feature is usually custom designed by the using company rather than supplied by the machine builder.

5.3.2. Injection Blow Molding Application

Injection blow molding is typically used for bottles or parts that are 500 mL or smaller in size. Larger parts can be molded, but small equipment size and reduced cavitation will usually limit the economical feasibility of such parts. On the other hand, for the large quantities of small bottles, injection blow molding is usually low cost alternative.

Injection blow molding equipment can process a wider variety of resins. For some resins such as polystyrene, the process is the only alternative. general-purpose polystyrene is often used for low cost pill bottles.

The process is scrap free with no flash to trim or recycle. No pinch off scar is created where the flash would have been once attached.

The injection mold neck provides far more accurate neck and finish dimensions than is possible with extrusion blow molding. This permits special shapes with intricate internal and external contours. The finish or open end of the part does not need to be round or flat, which offers an entire realm of design possibilities.

Because the preform is accurately injection molded, part weight and, in turn, bottle volume are far more consistent.

5.3.3. Injection Blow Molding Advantage

Injection blow molding offers a number of important advantages:

It produces scrap-free, close tolerance, completely finished bottles that require no secondary operation.

It offers positive weight control in finished container (accurate to $- 0.1$ to $+ 0.1$ g.).

Neck shapes and finishes, internally and externally can be molded with an accuracy of $+,- 0.004$ inch.

{Following fig. from "Plast. Engg.Handbook" by B.L. Michael}

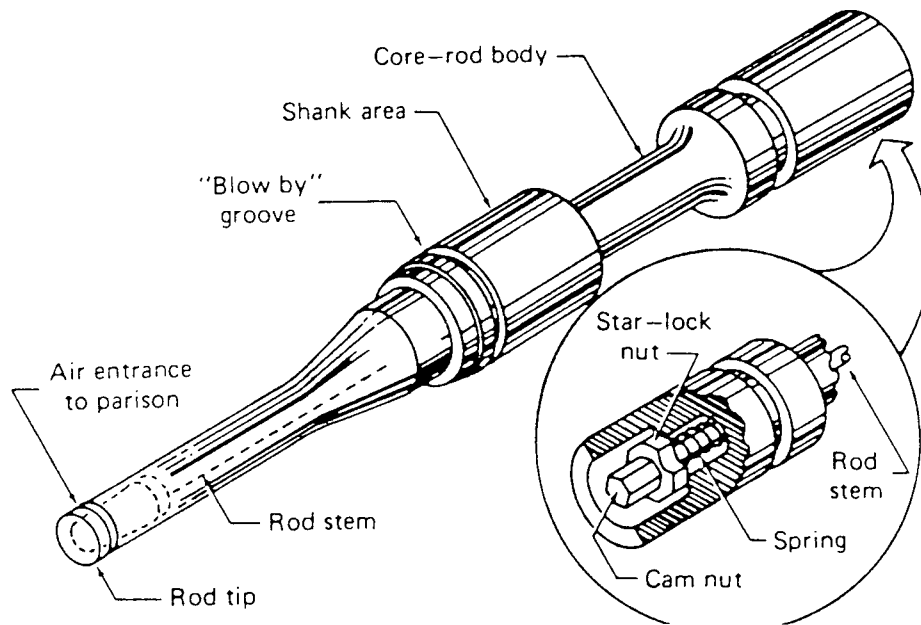


Figure 12 Typical Bottom Blow Core Rod Showing Its Principal Elements

Repeatable weights and bottle dimensions possible with the process allow for compatibility and ease of operation in conjunction with filling lines.

There is improved clarity and strength in a number of different materials due to the effect of some amount of biaxial orientation. Bottles are controlled and monitored at the ejection station allowing for automated line decorating and filling.

A minimum amount of operator supervision is required.

5.3.4. Injection Blow Molding Machines

There are some limitations to the process, related primarily to the sizes and shapes of the bottles that can be produced profitably on existing injection blow molding machines. There have been several types of injection blow molding machines available with different methods of transporting the core pins from one station to another, including the shuttle, two position rotary, axial movement, and rotary with three more stations. The three and four station rotary machine are preferred today. These units are divided into two basic categories: packaged blow molding assemblies that can be installed in some commercial injection molding machines; and complete injection blow molding, with the plasticator, hydraulic unit.

The exploded view of an injection blow mold has been taken from *Plastics Blow Molding Handbook* by L.C. Norman

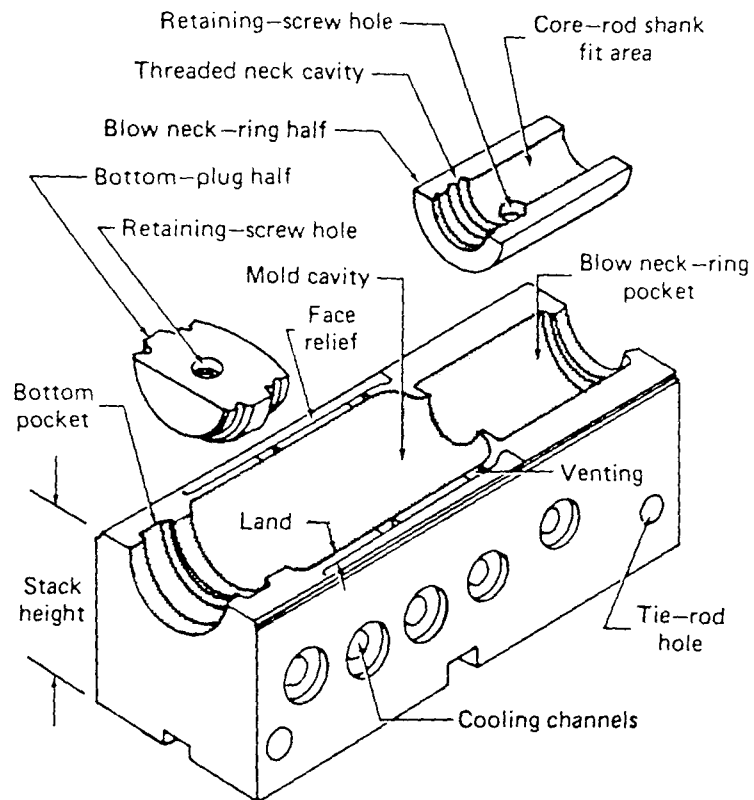


Figure 13 Exploded View of One-half of an Injection Blow
Mold

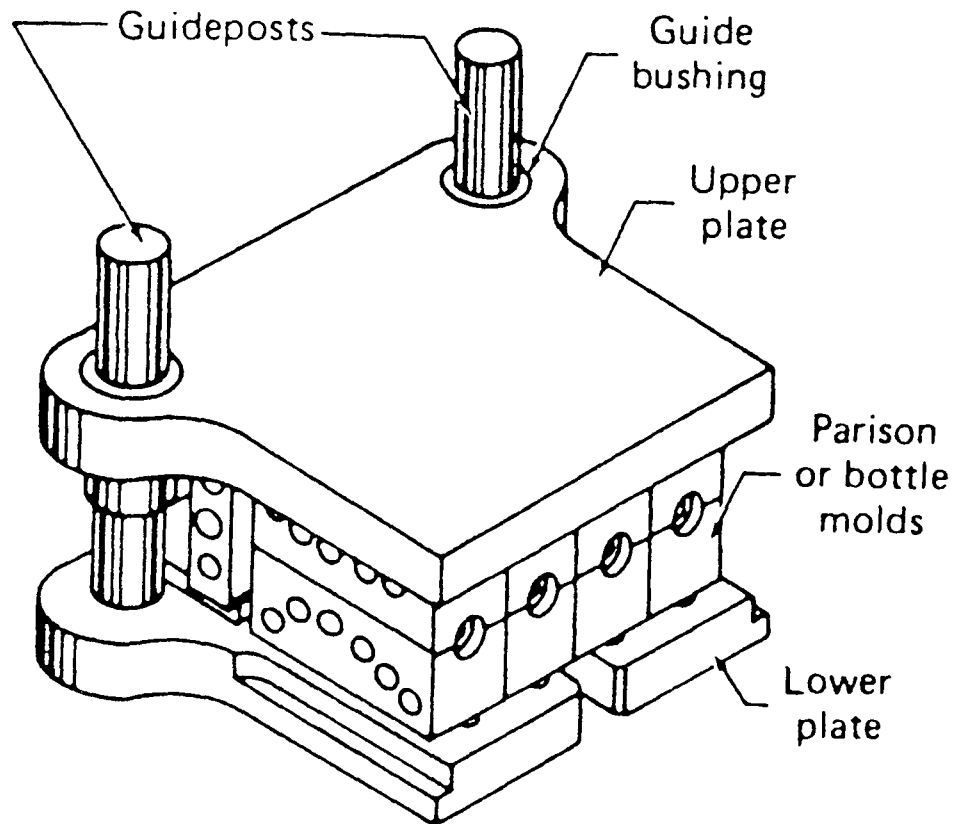


Figure 14 Die Set for Maintaining Position and Alignment of Injection Blow Mold Cavities.

controls, and other components integrated. These units are further broken down into two distinct types: those with a vertical nonreciprocating plasticator; and those with a horizontal reciprocating screw plasticator.

The vertical is considerably less complex than the horizontal type, requiring fewer parts, reduced power requirements, less floor space, and less complicated maintenance, while having the capability of delivering equal shot size at equal fill speeds but at reduced injection pressures, if desired. The reciprocating screw plasticator was developed primarily for injection molding. Although more complex in design than the vertical type, it has demonstrated reliability in operation.

Current machines include large standard production units, permitting larger containers to be produced at higher production rates, improvement of injection unit designs that result in easier processing of PVC and nitrile resins, and continuing development of additional stations. New materials developed specifically for the process have enabled injection-blow molders to move into other markets. PP copolymers that process easier, cleaner, and quicker have virtually replaced glass in cough/cold medicines as well as some mouth wash bottles.

Other new resins are the injection blow grade PVC homopolymers and poly carbonate. These crystal clear materials have been processed fairly easy on vertical screw machines, and on horizontal screw machines when equipped with continuous ram screw operation. New streamlined manifolds, plus improved nitrile and PVC resins have made it practical to run multiple cavity even though these materials are heat sensitive. One 8-cavity mold for PVC was run successfully and 12-cavity nitrile resin molds are currently in production. {Refer to 12}.

A number of companies are running up to 8 cavity PVC bottles. The material is modified to reduce its heat sensitivity. It is now apparent that, with larger machines, the higher clamping pressures and larger platen areas will permit economic production of containers upto 4 liters in size. The advantages of precision neck finishes and scrap elimination will tend to offset the higher tooling costs.

Future developments look to improvement in resin orientation due to machine developments (additional stations) and mold design inventions. Mold design techniques already have produced containers with offset neck finishes, necks of regular cross-sections, precision slots in container base, and reduction in overall wall thickness that decreases cycle time.

It is in the area of mold design developments that further penetrations is expected of the household chemical, toy, and especially food container market. Foods and their related merchandising have, by far, the largest volumes of all container sales. Key suppliers of three and or four station blow molding machines include Johnson Controls, Inc. and Jomar Corp. Costs for machines range from \$ 100,000 to \$ 300,000. For some applications, as many as 2.5 to 30 million bottles can be produced annually.

Another process somewhat related to injection blow molding is dip blow molding used for small containers. The process has the advantage of reducing some of the molded in stress. A core rod moves away, a predetermined amount of resin and packing it into neck finish area. As the core rod moves away, a predetermined amount of resin is permitted to remain on the rod. A hot knife cuts the hot plastic, separating the material on the rod from the melt pool in the couple. The core rod is then rotated to blow station for blow molding. Hesta is a supplier of this type of machinery.

5.4 Multilayer Blow Molding

5.4.1. Introduction

Multilayer blow molding refers to the products which contain several layers in their wall structures and to the technology to produce such articles. The layers can be of

the same material, colored material and not colored, recycled material and virgin, or of different materials.

The development of multi-layer molding technology is another step in taking advantage of the unique properties of the plastics. This process makes it possible to combine materials with various attributes to create a finished product most suitable for a particular application. Additionally, the various parts of the structure can be optimized for the best balance between properties and cost.

Although several layers have passed since the first use of multilayer blow molded containers - in the early 1970s, in Japan - multilayer extrusion really became the part of the blow molding scene with the introduction of the Gamma bottles produced by American Can Company in 1983. The bottles were used to package Heinze Ketchup and Lipton barbecue sauce.

Today the uses of multi-layer blow molded articles are numerous and diverse. Packaging of various types is the main end use of multilayer extruded products, with barrier properties being the main reason for the multilayer structure. This application is the result of the overall balance of the properties and the cost of the barrier materials used. {Refer to 14}

The multi-layered structure of coextruded products is created by combining layers in a die before their extrusion as a parison. The multilayer parison is extruded and blown into a product in much the same way as a monolithic blow molding parison. The main difference between single material extrusion blow molding and extrusion blow molding is in the extrusion system. In coextrusion each material incorporated into the structure is extruded from its own extruder. The extrusion die must be designed so that the different materials can be formed into the proper layered structure.

5.4.2 Multilayer Blow Molding Characteristics and Application

All materials, whether metal, glass, or paper, have certain strengths and weaknesses, advantages and disadvantages. Many times two or more materials can be layered and combined to overcome weaknesses economically. Examples are chromium plated steel, laminated automobile wind shields, and wax or polyethylene covered paperboard. Multilayer blow molding is a process in which the strengths of two or more resins are combined to package a product far better than any of the resins could individually.

A few important characteristics or requirements of many bottles are cost, strength, clarity, product compatibility, and gas barrier. Polyethylene or polypropylene, for example is relatively low in cost, approved for food contact and an

excellent barrier for of water vapor. It is also a poor barrier of oxygen. As such, the material is not suited for packaging many oxygen sensitive foods requiring long shelf lives. Poly(ethylene vinyl alcohol), on the other hand is a relatively high cost material that provides an excellent barrier, but is a sensitive to water, which can deteriorate its properties. A thin layer sandwiched between two layers of polyethylene or polypropylene can solve the problem.

All of the basic blow molding process methods have been used with multilayer blow molding. In case, additional plasticizers or extruders are needed for resin. The continuous coextrusion process has been used for bottles up to 5 L in size. The accumulator head process has been used for drums and tanks up to 500 L in size. The coinjection process has been used for small bottles 500 mL in size. Suppliers of multilayer blow molding equipment include: Johnson Controls Inc., Bekum, Battenfeld/Fischer, Wilmington, and Kautex for continuous extrusion based machines; Nissie for injection based machines; and IHI accumulator head based machines.

Related to coinjection process is a thermoform insert process. With this method, a coextruded sheet is thermoformed into an insert, which is placed on the core rod of an injection blow molder just prior to parison/preform molding. The hot resin from the injection step softens the

material in the insert, permitting it to be blow-molded in the next or blow station.

A common problem of multilayer materials is that the different layers will not stick to each other. An adhesive layer is often required to create the bond. As a result, three or more extruders are required. With the polyethylene (ethylene vinyl alcohol) example above, five layers are actually required: polyethylene, adhesive, poly(ethylene vinyl alcohol), adhesive, and polyethylene. {Refer to 12}

E.I du Pont de Nemours & Co. has developed a novel approach to gain some of the advantages of a coextruded blow-molded bottle without the cost and the complexity of multiple extruders and expensive scrap reclaim systems. Only minor modification of the basic equipment is required. A barrier resin is tailored for physical blending with a base resin in much the same way that colorant is blended with the resin. However, instead of producing a homogenized mix, the barrier resin is permitted to laminate in the base resin. Several random multiple layers of barrier resin of various lengths and sizes are created. Although no single layer completely covers the entire shape and surface of the bottle, barrier is created by the tortuous path the permeating gas must follow. A modified nylon material is the first to be used for this approach. Applications include fuel tanks and bottles for agricultural chemicals, thinners, and solvents.

CHAPTER 6

INJECTION MOLDING OF POLYOLEFIN PLASTICS

6.1 Introduction to Injection Molding

One of the most common processing methods for plastics is injection molding. Nowadays every home, every vehicle, every office, every factory contains a multitude of different types of articles which have been injection molded. These includes such things as electric drill casings, yogurt cartons, television housings, combs, syringes, paint brush handles, crash helmets, gearwheels, typewriters, facial panels, reflectors, telephones, brief cases - the list is endless.

The original injection molding machines were based on the pressure die casting techniques for metals. The first machine is reported to have been patented in United States in 1872, specifically for use with Celluloid. This was an important invention but probably before its time because in the following years very few developments in the injection molding processes were reported and it was not until the 1920's, in Germany, that a renewed interest was taken in account. The first German machines were very simple pieces of equipment and relied totally on manual operation. Levers were used to clamp the mold and inject the molten plastic with the result that the pressures which could be attained were not very high. Subsequent improvements lead to the use

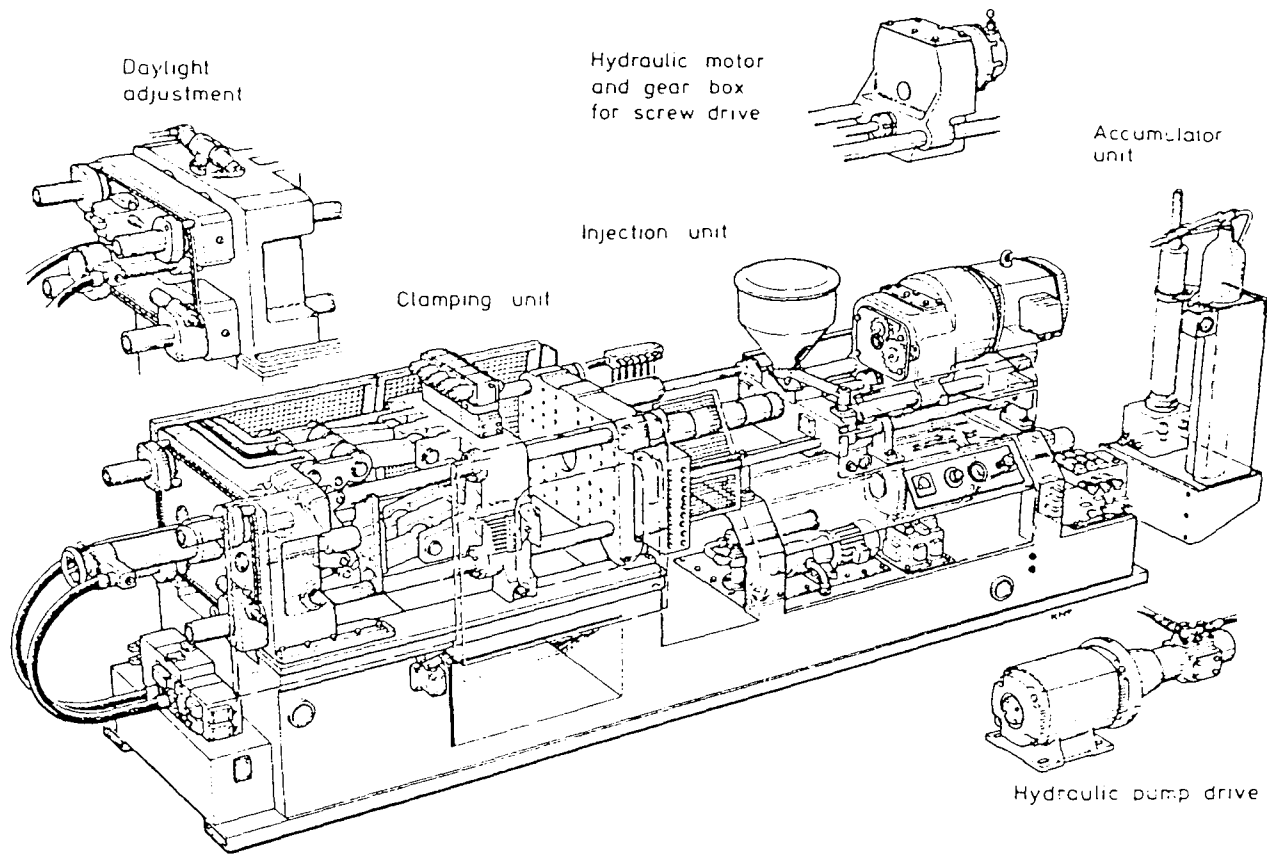


Figure 15 Injection Molding Machine

{The figures on the previous pages have been taken from "Handbook of Plastics and Material Technology" I.I. Rubin.} of pneumatic cylinders for clamping the injection which not only lifted some of the burden off the operator but also meant that higher pressures could be used.

The next major improvement in the injection molding , that is the introduction of hydraulically operated machines, did not occur until the late 1930s when a wide range of thermoplastics started to become available. However, the machines still tended to be hybrids based on die casting technology and design of injection molding machines for plastics was not taken really seriously until the 1950s when a new generation of equipment was developed. These machines catered more closely for the particular properties of polymer melts and modern machines are of the same basic design although of course the control systems are very much more sophisticated nowadays.

In principle, injection molding is a simple process. A thermoplastic, in the form of granules or powder, passes from a feed hopper into the barrel where it is heated so that it becomes soft. It is then forced through the nozzle into a relatively cold mold which is clamped tightly closed. When the plastic has had sufficient time to become solid the mold opens, the article is ejected and the cycle is repeated. The major advantages of the process include its versatility in molding a large number of products, the ease

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Today every home, every vehicle, every office, every factory contains a multitude of different types of articles which have been injection molded. These includes such things as electric drill casings, yogurt, cartons, crash helmets, gear wheels, typewriters, facial panels, reflectors, telephones, brief cases- the list is endless.

As in any injection molding machines, the function of the plastifier is to convey, mix, melt, and inject the homogeneous melt into the injection mold. Normally the plastifier is of the horizontal reciprocating screw type. However the Jomer predominantly utilizes a nonresiprocating vertical screw type.

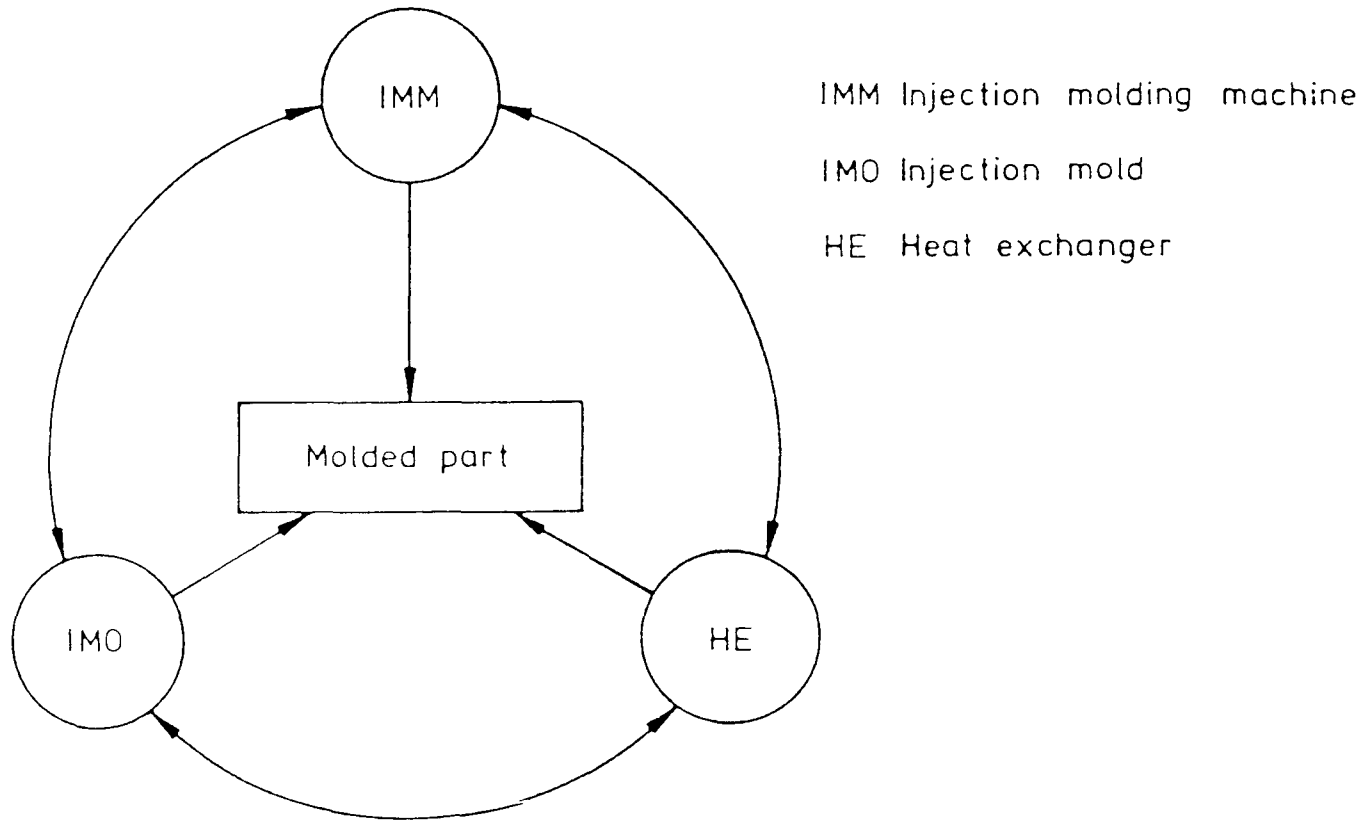


Figure 16 Injection Molding System

with which the automation can be introduced, the possibility of high production rates and the manufacture of articles with close tolerances. The basic injection molding concept can also be adapted for use with thermosetting materials.

6.1.1 Examples of Injection Molded Parts

Injection molded parts are pervasive in our lives and our economy. A few typical places where one finds them are personal items (from combs to full size cribs), packaging (bottle caps), automotive (grills), transportation (airplane trays), appliances (food processors), toys (chess sets), electrical (battery containers), electronic (circuit boards), medical (retractors), food (microwave dishes), disposables (cups), entertainment (CDs), and cosmetics (compacts).

If injection molding were stopped today, our manufacturing and economy would stop with it.

ADVANTAGES/DISADVANTAGES

6.1.2 Advantages of Injection Molding

- * Parts can be produced at high production rates.
- * Large-volume production is possible.
- * Relatively low labor cost per unit is obtainable.
- * The process is highly amenable to automation.
- * Part require little or no finishing
- * Many different surfaces, colors and finishes are available.

- * Good decoration is possible
- * For many shapes, this process is the most economical way to fabricate.
- * The same item can be molded in different materials without changing the machine or mold.
- * Very small parts can be fabricated in quantity; this would be almost impossible by any other method.
- * Minimal scrap losses result from regrinding and reusing of the thermoplastic runners, gates, and rejects.
- * Close dimensional tolerances can be maintained.
- * Parts can be molded with metallic and nonmetallic inserts.
- * Parts can be molded in a combination of plastic and fillers such as glass, asbestos, talc, and carbon.
- * Aside from die casting it is the commonly commercial process that can reuse its thermoplastic scrap immediately (regrind and remolded at the machine).
- * Compared to other materials (glass, aluminum , etc.), the amount of energy needed for manufacture is extremely low. From an energy point of view, the thermoplastic product can be reground after

use and remolded or burned, both of which further reduce its energy cost.

- * The inherent properties of the material give many disadvantages, such as high strength-to-weight ratios, corrosion resistance, strength, and clarity.

6.1.3 Disadvantages and Problems With Injection Molding

- * The plastic industry has very low profit margins
- * Three-shift operations are often necessary to compete.
- * Mold costs are high.
- * Molding machinery and auxiliary equipment costs are high.
- * Process control may be poor.
- * Machinery is not consistent in operation, and controls do not directly measure what is supposed to be controlled.

- * The possibility of poor workmanship is often present.
- * Quality is often difficult to determine immediately.
- * There is a lack of knowledge concerning the fundamentals of the process.
- * There is a lack of knowledge about the long term properties of the materials .
- * Plastics can not be made so that each pallet is same. One must deal with averages of molecular weights and molecular configurations; these not only vary from pallet to pallet but, on a larger scale, from batch to batch. This causes an unsteady and varying operational state, which contrasts with low molecular weight chemicals, such as salt, sucrose, naphthalene, etc, that can be manufactured identically in structure and properties.
- * To derive quantitative equations for flow and other properties needed in injection molding, one must know viscosity, temperature, and pressure. In a mold they are continually changing and not

measurable. When applied in practice, the assumptions made may lead at best to some very questionable results. Experience and qualitative calculations have yielded far superior results.

6.2 Basic Machine Operation

The injection molding machine must be installed with the proper electrical, water, and air connections. The machine hoppers must be filled with plastic material either manually or with automatic material handling systems. The mold must be properly clamped to the movable and stationary platens with its electrical and water connections properly made. Assuming all systems have been checked out for stationary operation, the machine is ready to cycle.

In the starting position, the clamp is open, the electrical power system is providing power to the hydraulic system, the electrical sequence system is turned on, and the injection barrel heater band system is turned on and upto temperature.

Normally, plastic material would be melted and ready for injection into the mold prior to closing of the clamp. Melting occurs by turning the plasticizer screw, which pumps and shear the plastic material while the heater bands add heat. This combination of shearing and heat melts the

plastic. After a preset amount of plastic has been melted, the plasticating screw is stopped.

The clamp then comes forward and builds tonnage. When the proper tonnage is obtained, the injection cycle can take place. The hydraulic system directs oil to the injection cylinders, pushing the melted plastic into the mold. Normally the injection cycle continues for a preset time period. When an injection process has ended, the plastication process begins, with melted plastic again being prepared for injection into mold.

If a rotary shut-off valve is used, the clamp can open during the plasticizing process. If not, the clamp opens after the plasticating cycle. As the clamp opens, ejection takes place. The ejection of the molded part can occur by ejector pins in the mold being actuated mechanically or hydraulically by the machine, while some parts can be blown off with air. Once the machine is open, the next cycle can take place.

6.3 Clamping Concepts

The injection molding machine clamp is used to close the mold, hold it closed during the injection and curing of molded material, and open the mold for the removal of the formed part.

There are three different types of clamp designs:

1. Straight hydraulic clamp
2. Linkage or toggle clamp
3. Hydromechanical clamp

6.3.1 Straight Hydraulic Clamp

This design uses hydraulic fluid and pressure to open and close the clamp and to develop the force required to hold the mold closed during the injection of the plastic.

The basic concept is to direct hydraulic fluid to the booster tube to move the clamp ram forward. Oil fills the main area by flowing through tank to the prefill to the main area, pulling fluid from the tank into this chamber. Once the clamp is closed, the prefill clamp is closed, trapping the oil in the main cylinder area. High pressure fluid is put into this area, compressing this volume of oil and thus raising the pressure in this area. The maximum pressure is controlled by a pressure control valve, which closely controls the clamp tonnage (the maximum hydraulic pressure times the area is pushed against).

{The figure attached is from "Handbook of Plastics and Material Technology by I.I Rubin.}

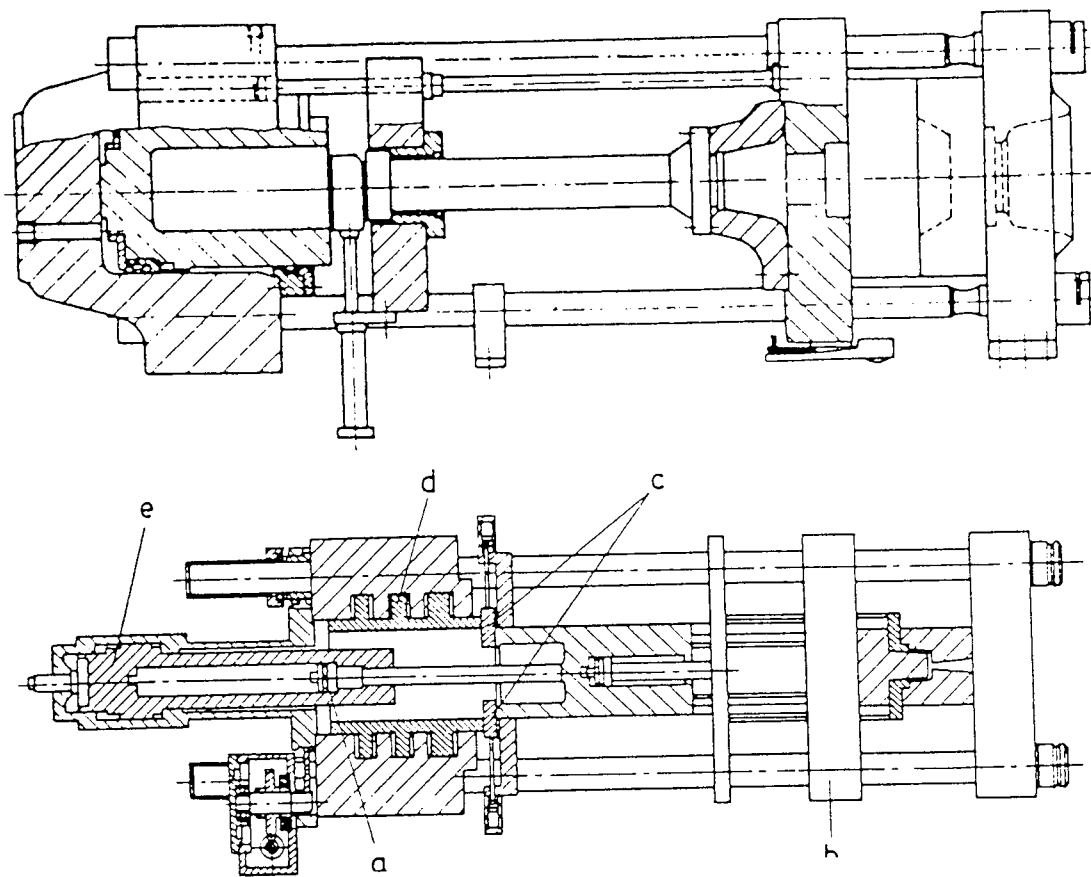


Figure 17 Clamping Unit with Central Hydraulic Cylinder and
Mechanical Lock.

To open the clamp, hydraulic fluid is directed to the pull back side of the cylinder while the prefill valve is open, with fluid from the main cylinder being returned to the tank. The of the major advantages of the straight hydraulic clamp is its very precise control of the clamp tonnage.

6.3.2 Linkage or Toggle Clamp

This concept uses the mechanical advantage of a linkage to develop the force required to hold the mold closed during the plastic injection portion of the cycle. Normally the linkage design is done in such a way that slowdowns are built in. The advantage of a toggle clamp is that the less hydraulic fluid is required to open and close the clamp. A disadvantage is that the clamp tonnage is not precisely known.

A small hydraulic cylinder is used to close the clamp. This cylinder travels at a constant speed with the slowdown for mold close built into the linkage. The mechanical advantage of the linkage is extremely high, so a relatively small closing cylinder can develop high tonnage.

6.3.3 Hydromechanical Clamp

This design uses a mechanical means for high speed close and open. A short stroke cylinder is used to develop tonnage identical to the straight hydraulic design. This concept is

said to offer the advantage of toggle clamps for high speed close and open, and the advantage of a of a straight hydraulic for precise control of the clamp tonnage. The hydromechanical design normally has a high-speed clamp close and open devise which is usually a hydraulic cylinder or actuator. The closing and opening mode occurs with relatively low force. Once the clamp is closed, a blocking action takes place allowing a large diameter hydraulic cylinder to to build tonnage similar to straight hydraulic design. When the clamp is to be opened, the blocking member is removed, and the clamp opens rapidly. The blocking action is normally a mechanical device, and the tonnage action is done by hydraulics; hence the name hydromechanical.

6.4 Plasticizing Units

The evolution of plasticizing units occurred in the following order:

1. Plunger
2. Two-stage plunger
3. Plasticizing screw (non-reciprocating)
4. Reciprocating Screw

6.4.1 Single Stage Plunger

The first single plunger units were heated with hot oil and eventually with electrical heating bands. A torpedo section in the rear zone spread the plastic feed material out into a thin section as the plunger moved forward. This {Fig. :- "Handbook of Plastics" by I.I. Rubin}

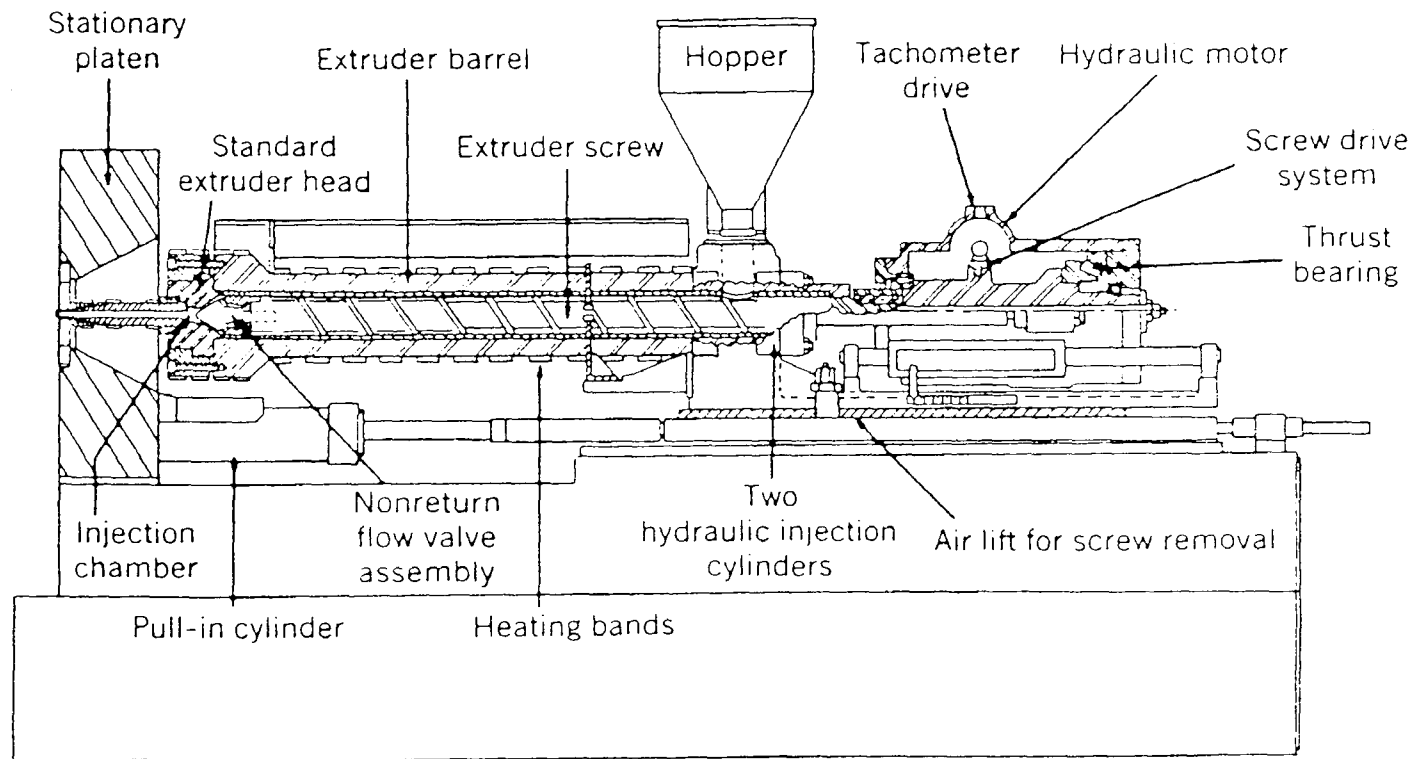


Figure 18 Schematic Drawing of Injection end of Reciprocating Screw machine

thin section of material is then entered the center section where most of the plasticizing took place. On later designs the center section consisted of a series of small holes drilled parallel to the horizontal center line of the plasticizing chamber. In the front section of the plasticizing chamber torpedo was reduced in diameter, and the cross-section of the melt was reduced to better plasticize any unmelt coming out of the center section. The front section had to be of sufficient length to ensure a constant temperature throughout the melt as it was forced out of the plasticizing chamber and into the mold. of the problems experienced with these units were leakage between the center section and front end, color change, pressure drop through the chamber, scored plunger, poor shot control, and difficulty in running heat-sensitive materials. As the designs improved the mechanical slide type of feeders which substantially improved the shot size control. Pressure switches and contours were added to the electrical and hydraulic cylinders to permit packaging material between the plunger and torpedo and to allow prepositioning of the plunger to be past the feed opening before the next shot. These two features increased the maximum shot size on a unit and also reduced the cycle time.

6.4.2 Two Stage Plunger

With development of two stage plunger units cycle times were reduced, injection rates (cu in/sec) were increased, and the clamp tonnage requirements were reduced.

The first two stage units consisted of a stuffer unit for plasticizing and an injection unit. The stuffer unit was the conventional single plunger unit set piggyback over the injection unit. Material was stuffed through the plasticizing chamber, and the melt from the plasticizing unit was channeled down in front of the injection plunger, causing the injection plunger to be pushed to the back of the injection shot chamber. Shot size was controlled by the use of an adjustable positive stop and limit switches, which controlled the position of the injection plunger when the required amount of melt was in front of the injection plunger. A rotary valve was placed in melt channel between the stuffer unit and injection chamber and the injection unit and nozzle tip. In one position the valve directed melt from the stuffer unit into the injection shot chamber. When the melt was to be forced into the mold, the valve was shifted, connecting the injection shot chamber to the nozzle tip and closing of the passage to the stuffer unit. These units were a great improvement over the single-stage units, but they still had problems with color changes and running heat-sensitive material.

6.4.3 Two Stage With Fixed Screw

The two stage plunger units were then replaced by a two-stage unit with a fixed screw for the plasticizing unit. The injection shot unit was essentially the same as used with the plunger plasticizer. These units could run any type of material, and with design improvement on the injection plunger configuration and washing action obtained as the first melt for each shot entered the shot chamber, color-change problems were greatly reduced.

6.4.4 Reciprocating Screw

One of the most significant breakthroughs in plastic occurred with development of the concept of reciprocating screw injection units. These units allowed high melting rates of plastic materials, close tolerance on shot size, and ability to control temperature of melt and perform reliably. By reducing L/D of the barrel and the screw, these units can run thermoset materials including rubber and BMC (Bulk Molding Compound). Longer L/D units (24:1 to 30:1) are used for hard-to-melt materials and vented machine application.

6.5 The Machine Hydraulics

The hydraulic system on the injection molding machine provides the power to close the clamp, build and hold tonnage, turn the screw to plastic material, inject the

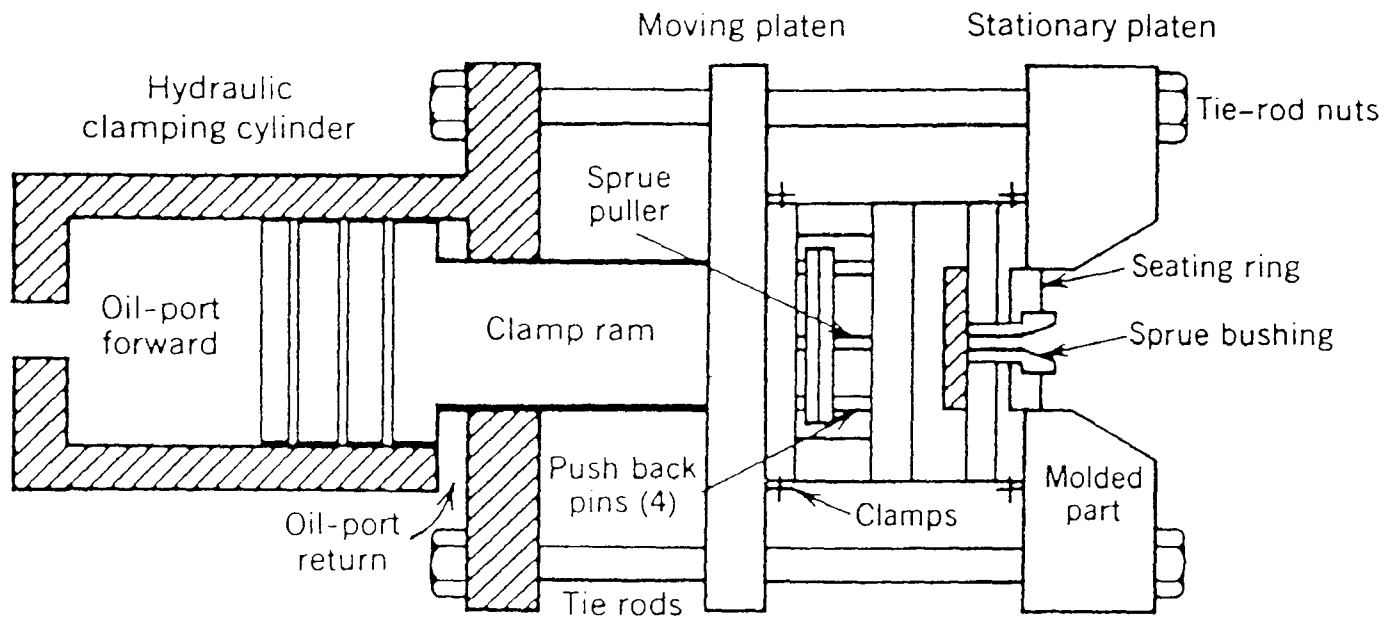


Figure 19 Molding Process for Reciprocating Screw Machine with Hydraulic Clamp.

{Fig:-"Plastic Engineering Handbook" by B.L.Micheal}

plastic material into the mold, and so on. A number of hydraulic components are required to provide this power, including pumps, valves, hydraulic motors, hydraulic fittings, hydraulic tubing, and hydraulic reservoirs.

6.5.1 Reservoirs

The reservoir or tank provides hydraulic oil to the system for use in powering the machine. The reservoir must be sized to ensure that an adequate supply of oil is available to the system and also allow sufficient capacity for the system to return oil to the reservoir.

Suction lines should be placed near the bottom of the reservoir to ensure an ample oil supply. Return lines from system should discharge beneath the oil level to avoid spraying into the air and foaming, and some type of antisiphon device should be used to stop the back flow of the oil through the return lines in case of line breakage or the removal of a component for service. A standard guideline for sizing a reservoir is that it be three times the pump output in one minute, but all system requirements should be carefully considered before the final reservoir size is determined.

6.5.2 Suction Strainers

A suction strainer should be placed before the inlet to the pump to be sure that particles of the sufficient size to

damage the pump will be removed. One should consult the pump manufacturer when determining what size strainer to use. It is important that both the flow capacity and the maximum removable particle size be correct.

6.5.3 Pump

The hydraulic pump receives oil from the tank at low pressure and increases the pressure to that required by the system. The pump provides the hydraulic flow and pressure to the system.

Several different types of the hydraulic pumps are used. The most common is the fixed displacement type pump, which provides an almost constant output at various pressures. Various designs are available to provide this constant output, the most common being:

1. Vane
2. Piston
3. Gear

Variable volume and pressure compensated pumps are being used more frequently in an attempt to conserve energy. These pumps are capable of varying the output to meet a particular flow requirement, or will put out only enough flow to develop a particular pressure requirement.

6.5.4 Directional Valves

Directional valves are used to direct the hydraulic oil coming from the pump to where it is needed. Spool, check, and cartridge valves are commonly used for this control.

The spool type directional valve is commonly used on injection molding machines. Spool valves can be either two-position or three-position. In two position valve, a solenoid is energized for one position, and normally a spring will return the spool to the second position when the solenoid is de-energized. The three position valve is obtained by adding a second solenoid.

Small valves can be directly operated by the solenoid; on larger valves solenoid operated pilot valves direct pilot flow to the main spool for shifting.

A check valve is a single one-direction valve that allows flow in one direction.

An extension of the check valve that is beginning to find greater use in the cartridge valve. It is essentially a check valve that is powered open normally by a small spool directional valve. Cartridge valves are grouped to provide the same directional flow capability as spool valves.

6.5.5 Servos and Proportional Valves

With the advent of more advanced microprocessor control systems with process control, greater use is being made of proportional valves and servo valves. The valves can be used to control flow and pressure. The main difference in performance between the proportional and servo valves is speed of response, with the servo being much faster than a proportional valve.

6.5.6 Injection Screw Drive Hydraulic

The most common drive unit for the injection end plasticating screw is the hydraulic motor. It receives pressurized fluid from hydraulic pumps and in turn converts this energy to the hydraulic motor drive shaft in the form of torque and rpm.

The most common type of injection system uses a direct drive hydraulic motor. This motor is directly coupled to the screw; thus the hydraulic motor torque and speed are also the plasticating screw's torque and speed. A second type of injection unit uses a gear box in conjunction with a hydraulic motor. In this way a smaller hydraulic motor can be used operating at high speed and increasing the torque. With the gear box, it is also possible to use a variable speed electric motor to provide power to the screw.

6.5.7 Barrel Temperature Control Systems

A important part of melting the plastic material is the heat that is added to the material from heater bands placed around the injection unit barrel. Grouped in zones in the screw, these heater bands are controlled by pyro meters that receive temperature information from thermocouples located in the injection unit barrel and turn the heater bands on or off, depending on where the indicating temperature is in relation to the pyrometer set point. On the larger microprocessor systems, the temperature control capability is built into the software, eliminating the needs for separate pyrometers.

6.5.8 Maintenance and Services

Most injection molding machines will run reliably if they are properly serviced and maintained. It is important that a scheduled maintenance program be established. Common problems on machines are lack of lubrication, in-sufficient cooling water, failure to change filters and strainers, and general house keeping.

6.6 Injection Molding Polyethylene Lids

Injection molded polyethylene lids are used in a wide variety of closure applications. Many products such as, margarine, cream cheese, whipped topping, ice cream, and

sandwich spreads, are packaged in plastic containers that have polyethylene lids for primary closures. Many other products such as, coffee, peanuts, and shortenings, are packed in the material cans that are used after they are opened to store the unused portion of the contents. Most of these cans are sold with polyethylene overcaps that snap into place and furnish good closure for the cans after removal of the metal tops. The characteristics demanded in polyethylene lids vary widely. Economy is always important, and in nearly every application, it is desirable that the lids are flat and that they cover. Some applications demand some degree of clarity so that printed matter on metal lid can be read through the overcap before the can is sold. Some required resistance to environmental stress cracking, so that the material that may be in contact with them will not cause them to split. Some require still other characteristics. In addition, the polyethylene lid business has undergone significant technological advancement in past years with most of the emphasis on the processability or production rate. Extremely fast recycling machines, stack molds, and larger tonnage presses all have contributed to an increase in the molder's productivity. Also, more sophisticated machine controls make present injection molding machines very sensitive to process and material change and or variation.

Consequently, molding polyethylene lids for their many uses is an exacting process that requires good selection of molding machines, mold design, part design, plastic formulation, molding conditions, and other factors such as variation in processes.

6.6.1 Molding Conditions

When condition for the molding polyethylene, the objective should be to inject fairly hot material into a cold mold while subjecting the molded part as little strain as possible. This is usually accomplished by using higher injection pressures to ensure quick filling of the mold and by using very short plunger forward times.

6.6.2 Melt Temperature

Usually high melt temperatures are used to permit the plastic to be injected quickly into the mold with minimum strain, because high melt temperatures give maximum clarity minimum sunburst and minimum warpage in the molder.

On the other hand if the melt temperature is too low, molding will be too difficult, requiring extra high pressures and longer plunger forward times. Due to this difficulty The lids produced are very poor in clarity and having sunburst and warpage.

The range of the melt temperature generally varies from 325 to 550 degrees, depending on the machine used, the mold size and construction, and the plastic formulation. Large machines with large hold ups in the cylinder usually operates between 325 to 475 degrees, whereas small machine with little hold up generally operates between 425 to 5590 degrees.

In a machine operating near its plasticating limits, an indicated temperature of 480 degrees may be required to maintain the melt temperature of 450 degrees Fahrenheit.

6.6.3 Mold Temperature

The optimum mold temperature for the lid production seems to be about 40 to 50 degrees F. Temperature in this range permit short cycles and produce lid with good clarity. On the other hand if the temperature is below 40 degrees, it can make mold filling a difficult task. It should be noted that the very clear lids can be produced in the case of higher mold temperature results in slow lid cooling.

6.6.4 Cycle Time

The two most important factors in the molding cycle are plunger forward time and clamp time.

The plunger forward time should be about 0.1 to 0.3 seconds larger than the actual mold filling time. If it is

significantly longer than this, the area around the gates will be packed, and thus will shrink less than the area around the outer edge of the lids, so that warpage could result. The plunger forward time is generally determined by setting all temperatures for molding, decreasing the plunger forward time in small increments until a short shot results and then increasing the time about 0.1 to 0.3 seconds. The clamp time should be absolute minimum setting at which the lid is produced with acceptable flatness, toe-in, and shrinkage can be produced. The clamp time, which must be set after the plunger forward time is fixed, must sufficiently exceed the plunger-forward time to allow the molten plastic to solidify in the cavities. Since toe-in is desirable but the warpage is not, the clamp time must be set for each mold to give the satisfaction.

6.6.5 Injection Pressure and Injection Speed

The injection pressure and the injection speed should be maximum in order to fill the cavities as rapidly as possible but keeping the proper shot-size control.

6.6.6 Shot Size

The shot size must be exact amount of plastic needed to fill the mold cavities if it is possible. So proper adjustment of the shot size is required. On some small molding machines, and even on some large ones equipped with screw plasticators, shot-size control is sufficiently precise to

make this possible. With precise shot size control, the adjustment describe for cycle time, injection pressure, and injection speed should be satisfactory.

On many large machines, it is very difficult to maintain the high precision of shot size control. One shot might be short and other one packed without changing machine settings. If necessary, keep a cushion of the molten plastic in the injection machine to better the rim action, but the cushion should be as small as possible.

Sometimes a cushion of molten plastic in the machine may cause excessive packaging of the cavities, resulting in warped lids. If this situation arises then it will be necessary depart from the previously described adjustments of cycle time, injection pressure and injection speed. The procedure is to reduce the injection pressure first, then if necessary, to reduce the injection speed. Every effort should be made to keep the rate of molten plastic into the mold as high as possible so that no appreciable solidification of the material will occur until after the mold is filled.

6.6.7 Screw Speed

In order to get rid of the delay cycle, maximum screw speed is usually used. Fast screw speeds generate frictional heat in the plastic and help to produce the homogeneous melt. If

temperature becomes too high and the material degradation results, the screw speed should be reduced. The heat generated in the plastic by rotation of the screw is a function of the square of the screw speed , therefore a small reduction in the screw speed can result in an appreciable reduction in the heat generated. If screw speed tends towards high side then it is very dangerous for design. {Refer to 8,12,13 and 14}.

CHAPTER 7

EXTRUSION OF POLYOLEFIN PLASTICS

7.1 Introduction to Extrusion

Extrusion is the process of forcing material through an opening. Many different materials are processed by extrusion; metals, foodstuffs, ceramics, and plastics. The machine on which the process is performed is an extruder. The extruder is indisputable the most important piece of machinery in the polymer processing industry. Many different types of extruders are used to extrude plastic, the main ones being the screw extruders, disk extruders, and reciprocating extruders.

Single screw extruders have only one screw; multiscrew extruders have two or more screws. Single screw extruders are most common type of extruders used in the plastic industry, and, accordingly, are the focus of this section.

In standard single screw extruders, the screw rotates but do not move axially. However, there are screw extruders designed to allow axial movement of the extruder screw in addition with rotational movement. These machines are called reciprocating screw extruders and are widely used in injection molding machines. The ability to move the screw axially allows the reciprocating screw extruder to operate

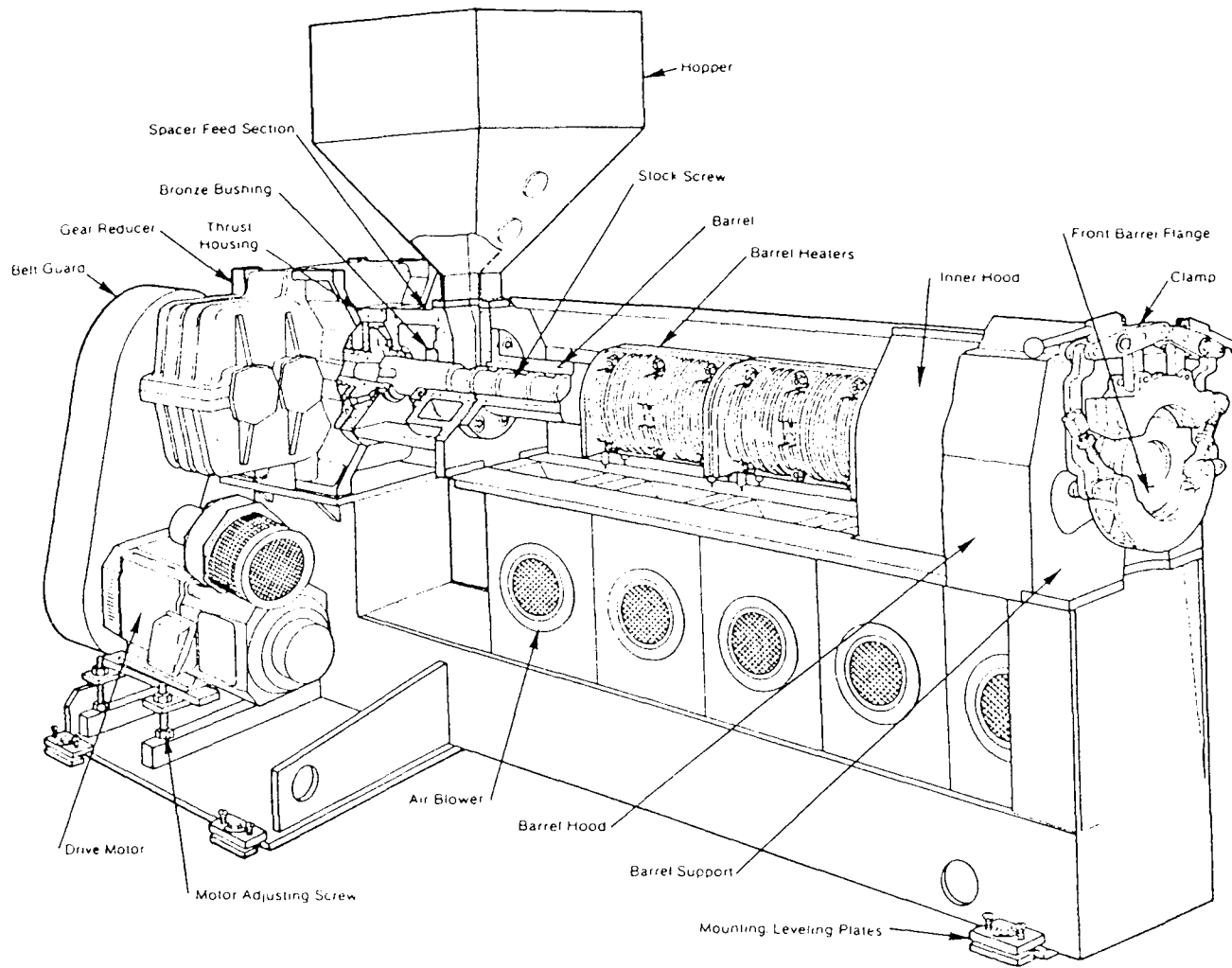


Figure 20 Cutaway View of Extruder

{Fig :- "Handbook of Plastics Materials and Tech., I.I Rubin} in cyclic fashion, which is necessary in the injection molding process. The standard single screw extruder operates in a continuous fashion, which is beneficial in the production of long lengths of product with constant cross sectional shape, such as tubing, film, and profiles.

The first machines for extrusion of plastic were built around 1935. They were primarily used to extrude rubber. Shortly after the introduction of the single-screw extruder, the twin screw extruder was developed in Italy in late 1930s. The early screw extruders were quite short with a length of diameter (L/D) ratio of about 5. They were generally heated with steam. Later machines became longer and electric heating began to replace steam heating. Modern single screw extruders range in length from 20 L/D to about 30 L/D, with some specialty machines being considerably longer than 30 L/D. Most modern extruders now use electric heating.

7.2 Extruder Types

7.2.1 Single Screw Extruders

Single Screw extruders frequently are specified for less complex compounding tasks because they are less costly than multi screw extruders.

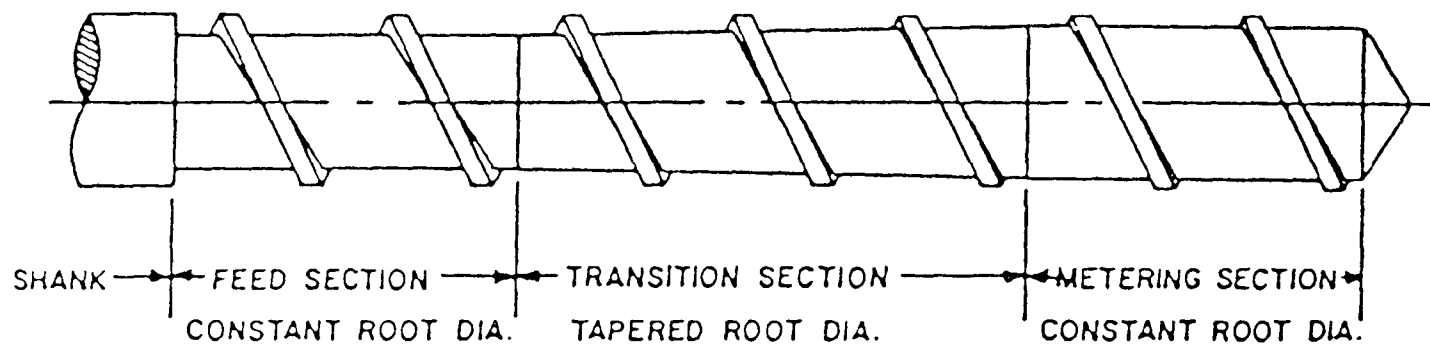


Figure 21 Typical Screw for a Single Screw Extruder

As a compounder, the single screw design often will use such mixing enhancements barriers, flutes, waves, pins, or cavities to overcome the inherent shortcomings in distributive and dispersive mixing.

Technically, a single screw device, the Kneader, represents a special category of compounding equipment where the screw rotates and axially oscillates. Each turn in the screw's spiral is interrupted by the gap. The resulting kneading flights are continuously wiped by stationary teeth in the machines barrel. The uniform shear is introduced at low pressures; making the process particularly well-suited for heat and shear sensitive polymers.

Another special single-shaft design is the Dickpack with its parallel flights.

7.2.2 Twin Screw Extruders

Twin screw extruders are used when processing needs exceed the capabilities of single-screw extruders. The twin screw mechanisms can be co rotating or counter rotating, intermeshing or non intermeshing. Co-rotating, intermeshing extruders are the most widely used for commercial processing. Next in significance are counter-rotating intermeshing; and counter rotating, non intermeshing machines. Each type has a different operating principal.

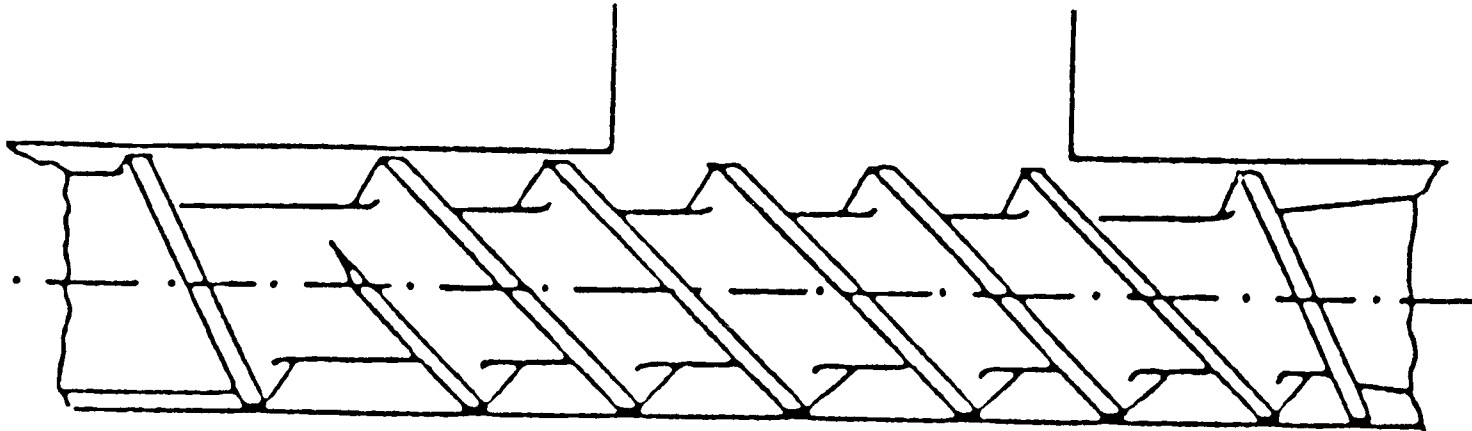


Figure 22 Two Stage Extruder Screw-extraction Section.

7.2.3 Co-rotating Intermeshing Extruders

Co-rotating, intermeshing rotators have the roots and flanks of one screw continuously wiped by the crest of the adjacent screw. The polymer follows a figure eight path as it moves along the screw, with polymer surfaces being constantly renewed. residence time (heat and shearing history) is short and well defined for each particle, facilitating good process control.

Screw diameter range from 0.6 to 15 inches. Throughput rates range from a few pounds per hour in a laboratory units to 100,000 lb/hr in the largest production size machines.

Length diameter ratios vary from 15:1 to 48:1, and screw speeds typically are at 300 RPM (but can be as high as 600 RPM).

7.2.4 Counter Rotating Inter Meshing Extruders

Typically the counter rotation is outward at the top and inward at the bottom. The material essentially moves as a unit volume in a closed chamber. Material in the wedge area undergoes a motion similar to that involved in the calendaring.

While the effect offers advantages for some processes, it can have a harmful influence on screw and barrel wear,

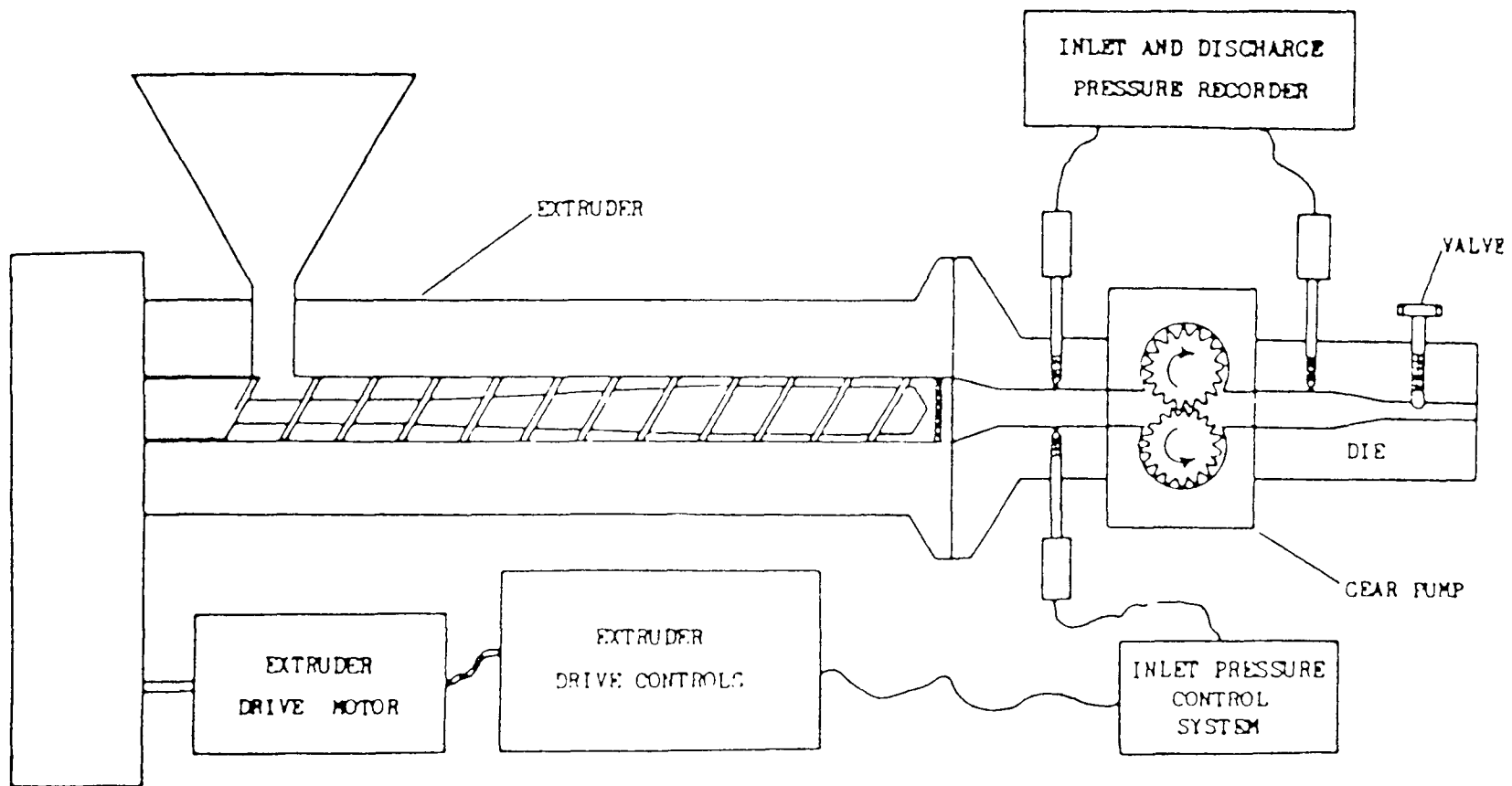


Figure 23 Extrusion Line with Melt Pump.

especially at higher barrel speeds and larger diameter units.

Having evolved from just pumping (extrusion process), this mechanism offers advantages to compounding with good feed intake and pumping control capabilities. Disk rings and spacers are added to interrupt the characteristics encapsulating flow.

Screw speed usually does not exceed 150 RPM. Sizes of 1.34 to 6.7 inches diameter are available, with L/D ratios from 16:1 to 42:1.

7.2.5 Counter Rotating Non-Intermeshing Extruders

There are two representative types: the continuous mixers uses a rotor design that combines the transport effect of a screw with the dispersive mixing capabilities of winged rotor, similar in design to Banbury (batch) mixer. This simple design controls shear rate by motor speed and a variable pressure discharge valve.

7.2.6 The Counter Rotating Tangential Extruder

The counter rotating tangential extruder essentially operates as two single screw extruder side by side. The screw pitch of both screws are opposed so that the drag flow from the two screws pumps the polymer in the same direction.

The area where the screws touch is open in the barrel, so that the leakage flow occurs from one screw to another. Thus the melting and mixing mechanisms is different from the single-screw models. The counter rotation direction is down between the two screws, facilitating good feeding. Furthermore, the large free surface area created by the two adjacent screws helps the process of devolatilization.

7.3 Extrusion Processes

Extrusion of thermoplastic materials can be accomplished through various means, depending upon the product being manufactured. Typically, the extrusion with polymeric materials (plastics) involves a continuous operation as opposed to making a product with an intermittent process as done in injection molding. The various products made by extrusion include pipe tubing, coating of wire, plastic bottles (blow molding), plastic films and sheets, various plastic bags (blown film), coatings for paper and foil, fibres, filaments, yarns, tapes, plastic plates, and cups (thermoformed sheets), and wide array of profiles.

Extrusion is accomplished by melting the material and forcing the melt through a forming die. The polymer material is fed through the extruder through a feed opening and can be introduced to the extruder in pellet (or cube) form or alternately as a powder, a granulate, or, in some processes a melt. Extruders used in rubber extrusion and with some

adhesive must accept a strip as the feed form. The extruders that are fed a melt are used pumping to pressurize and to force the material through the die system or to aids in such parameters as cooling in the melt from a melting extruder. The typical extruder is required to take a solid feed material and to melt, homogenize and pump the melt through the die system with acceptable output uniformity. The output consistency of the dimensions of the finished product.

The extruded melt is continuously shaped and cooled by downstream equipment placed after the extruder. The sizing cooling equipment can be comprised of cooling rolls, water tanks, vacuum sizing fixtures, air cooling tables, pulling devices, cutting equipment, coiling or winding equipment, and so on.

The extruders used to produce these products are overwhelmingly of the single screw variety, with several other types of machines used in some situations. These single screw extruders are simply comprised of a flighted screw that rotates with in a heated cylinder (barrel). The screw is rotated by a drive motor through a gear reducer. Alternate extruders to the single screw include multiscrew machines (usually twin screw), rotary extruders (screwless), and ram extruders. The twin screw and also the less popular quad screw extruders are comprised of multiple screws within

a heated barrel and are most popular for making rigid PVC (polyvinyl chloride) powders into pipe and various profiles (window profiles, house siding profiles, etc). The melting performance of this material lends itself to the low shear pumping seen with these types of extruders. Most polymers require more energy to thoroughly melt and homogenize them than a typical twin screw extruder can effectively produce. When a twin screw extruder is designed to develop shear levels comparable to those of single screw extruders, the performance is not improved over the single screw machines, and economics and operational advantages favor the single screw extruders, the performance is not improved over the single screw machines, and the economics and operational advantage favor the single screw extruder. That is why twin screw extruders have not widely penetrated the single screw marketplace. Here special mixing twin screw machines have been developed, which do a good job and are very expensive, these compounding twin screw extruders typically can deliver high output levels (2000-10,000 pounds/hour and greater) and are not economically practical for the extrusion of every day products as described above.

Rotary extruders have been in use for the last ten to fifteen years but have seen limited use due to their sealing problems against melt leakages and their low pressure generating capabilities. These machines are made up of

heated disks that rotate with polymer between plates where shear is developed and melting takes place. Some pressure can be developed, but nowhere near the typical 2000 to 10,000 psi levels of single screw or twin screw extruders. The possibility of melt leakage leads to concern for contamination due to degrading polymer because the system is not totally self cleaning.

Some large rotary units are being used for pelletizing or compounding applications, and a few smaller units are being used for products such as polypropylene sheet; but the single screw extruder still is and will remain the workhorse in polymer extrusion for the foreseeable future.

There are some materials in the flouropolymer area and some materials such as ultra-high molecular weight polyethylene that will not process acceptably on the screw extruders mentioned above. For these materials, a ram extruder is employed. This device is a non steady state machine that discharges its volume by using a ram or a plunger to extrude the melted material. The polymer is melted by conducted heat through the barrel in which the ram travels. This extruder is not a substantial influence on today's extrusion markets.

7.4 Single Screw Functional Description

Because the single screw extruder is by far the predominant machine used in polymer extrusion, its operation is mainly

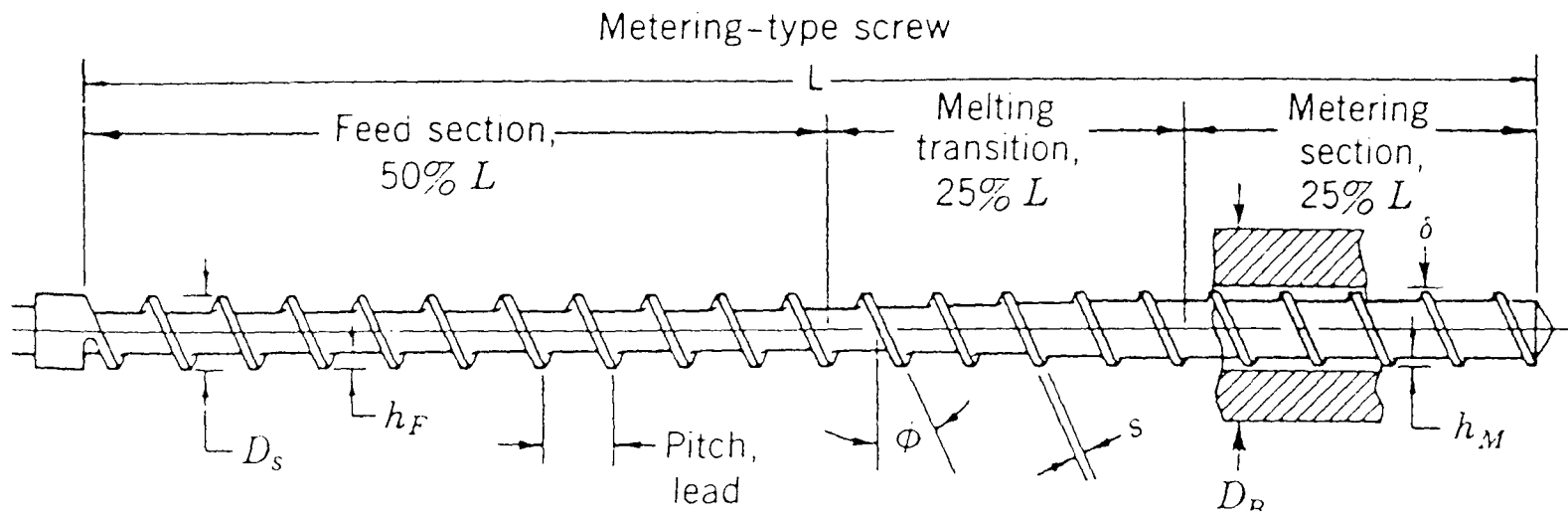


Figure 24 Injection Screw

described, with comments regarding alternative extrusion means added as appropriate. The conveying is forced by the rotation of the screw via a drive motor and gear reducer. The material usually must be melted (plasticated) along the path through the extruder screw although some processes introduce the feed material already in melt form so the extruder need only convey it. The melting of the polymer is aided by heaters that tightly encapsulate the barrel's outside diameter and are separated on the barrel onto zones. These zones can be set at different temperatures as appropriate for the particular process involved. The screw must develop enough pumping efficiency to force the material through the die system. The pressure developed can be substantial for high restrictive die systems and can reach 8000 to 12,000 psi. Typically the die pressure levels encountered are in the 1000 to 5000 psi range.

There are six major functions performed in screw extruders: solid conveying, melting or plasticating, melt conveying or pumping, mixing, devolatilization, and forming. Devolatilization is not performed on all extruders, only on those especially designed to extract volatiles from the polymer. These devolatilization extruders are usually referred to as vented extrudates. Two other functions that are not performed on all extruders are solids conveying and melting. Some extruders, called melt-fed extruders, are charged with

molten polymer; their only function is to mix, pump, and force the material through the die. In most extruders, called plasticating extruders, the machine is fed with solid material and, therefore, solids conveying and melting are important functions to be performed.

7.4.1 Solid Conveying

Solids are extruded in two, regions: the feed hopper and the screw extruder. The solids conveying in the feed hopper is generally a gravity flow of particulates polymers; the material moves down the feed hopper by its own weight. Unfortunately, this does not always work without problems. Some materials have poor bulk flow characteristics and may get stuck in feed hopper. This problem is called arching or bridging. It is likely to occur when the particle shape is irregular, when the particle size is small, and when the internal friction of the bulk material is high. Highly compressible bulk materials are also quite susceptible to solids conveying instabilities. Feed hoppers can be designed to avoid bridging if the bulk material flow properties are known. The most important property is the internal shear strength of the flow material as a function of the normal stress: this functional relationship is referred to as yield locus (YL). For non-cohesive or free-flowing materials the shear strength is a unique function of normal stress and also of consolidation time. These concepts and their application to feed hopper design have been described in

detail by Jenike. Theoretical and experimental work on gravity solids conveying in feed hoppers and the design criteria for feed hoppers are reviewed in a recent book on polymer extrusion.

If a solid conveying problem does not occur in the feed hopper there are several measures that can be taken into account to eliminate the problem. In many cases, a vibrating pad, will be attached to the hopper to prevent the material from settling and consolidating. In other cases, a crammer feed is employed to force to bulk material from the feed hopper into the extruder.

7.4.2 Drag Induced Solid Conveying

Once the bulk polymer falls down into the screw channel the transport mechanism changes from gravity induced solids conveying to drag induced solids conveying. The polymer moves forward as a result of the rotation of the screw in the stationary barrel. The frictional forces acting on the polymer particles are responsible for the flow of the polymer. The loose particles are compacted rather quickly into a solid bed. The compacting occurs because polymeric particles are conveyed against a certain pressure. The pressure increases along the solids conveying zone causes the compaction of the solid bed. Once the solid bed is sufficiently compacted, it moves in plug flow. Thus all, elements of solids bed is sufficiently compacted, it moves

in plug flow. Thus, all elements of solid bed at any cross section move at the same velocity; there is no internal deformation in the solid bed.

There are two main frictional forces acting on the solid bed; one at the barrel surface and one at the screw surface. It is important to realize that the frictional force at the barrel surface is the driving force for the solid bed and the frictional force at the screw surface is the retarding force on the solid bed.

7.4.3 Melting

The solid conveying zone ends when the temperature in the solid bed reaches the polymer melting point and the thin film of the molten polymer starts to form. Melting will start because of the heat conducted from the barrel heaters and the heat generated by friction along the screw and the barrel surface. The frictional heat generation is generally quite substantial. It is often possible to initiate melting without applying any external heat from the barrel heaters, using only the frictional heat generation.

The melting process occurs primarily at the interface of the upper melt film and the solid bed. This is result of the generally large velocity difference between the solid bed and the barrel surface. The large relative velocity, combined with small thickness of the melt film, causes a

substantial amount of viscous heat generation in the upper melt film. There might or might not be melt film between the film between the screw surface and the solid bed. Even if there is a melt film, the melting at the lower interface will be quite small compared to the melting at the upper interface. This is because the general velocity between the solid bed and the screw surface is small. Thus, there will be a little viscous heat generation in the lower melt film and, therefore, little melting.

The two major sources of heat for melting are the viscous heat generation in the melt film and the heat conducted from the barrel heaters. Under normal operating conditions, the contribution of the viscous heat generation will increase with the screw speed and polymer melt velocity. It is important to realize that an increase in the barrel temperature does not always improve melting. Higher barrel temperatures will increase the heat conduction from the barrel heaters but will reduce the viscous heat generation in the upper melt film. The latter occurs because the temperature in the melt film will rise, prompting the viscosity of the material in the film to drop. As a result, the viscous heat generation in the melt film will decline. Thus, polymers whose melt viscosity is very sensitive to temperature are likely to exhibit reduced melting performance with increased barrel temperatures. Generally speaking, amorphous polymers have a rather strong

temperature sensitivity to viscosity, particularly materials such as PVC, ABS, PMMA, and PS. The melt viscosity of the semi-crystalline polymers tend to be rather insensitive to temperature.

The melting rate depends strongly on the thickness of the melt film. The melt film thickness at the trailing flight flank is primarily determined by the radial clearance between the flight and barrel. The smaller the clearance, the thinner the overall melt film and higher the melting rate.

7.4.4 Melt Conveying

The melt conveying zone of the extruder starts where the melting zone ends: at the point where all solid polymeric particles have melted. The melt conveying portion of the extruder acts as a simple pump. Forward motion occurs as a result of the rotation of the screw and the helical configuration of the screw flight. If the pressure is constant along the melt conveying zone, the output of the extruder equals the drag flow through the screw channel.

It is interesting to note that the drag flow rate is independent of the polymer melt viscosity.. Thus, if the density is the same, the drag flow rate for olive oil will be same as for the polyethylene melt, polypropylene melt, etc. In many cases, the actual extruder output will be

reasonably close to the drag flow rate. Accordingly, the drag flow rate can be used as an approximate prediction of the actual extruder output. In most actual extrusion operations, the pressure will not be constant along the melt conveying zone; there will be a pressure gradient, either positive or negative. If the extruder has to pump against a high die head pressure, the pressure gradient will generally be positive. In this case, the actual extruder output will be less than the drag flow rate. If there is significant pressure development in the solid conveying or melt zone of the extruder, the pressure gradient in the melt conveying zone will be negative. In such a situation the actual extruder output will be greater than the drag flow rate.

7.5 Die Forming

In this functional zone, the polymer is shaped and for this reason the die forming zone can be considered the most functional zone. The die-forming zone is always a pressure consuming zone. The pressure built up in the preceding functional zones is used up in the die forming zone. The die-head pressure is the pressure required to force the polymer melt through the die. The pressure is not determined by the extruder but by the extruder die. The variables that effect the die head pressure are:

- * The geometry of the flow channel in the die.

- * The flow properties of the polymer melt.

- * The temperature distribution in the polymer melt.

- * The flow rate through the die.

When these variables remain the same, the die head pressure will be same whether a single-screw extruder or a double-screw extruder is used. The main function of the extruder is to supply homogeneous polymer melt to the die at the required rate and die-head pressure. The rate and the die-head pressure should be steady, and the polymer melt should be homogeneous in terms of the temperature and the consistency. Die design is the one aspect of extrusion engineering that has remained more an art than a science. The obvious reason is that it is quite difficult to determine the optimum flow channel geometry from engineering calculations.

Description of the flow of the polymer melt through the die requires knowledge of the visco-elastic behavior of the polymer melt. The polymer melt can no longer be considered as purely viscous fluid because elastic effects in die region are very important. Unfortunately, there are no constitutive equations that adequately describe the flow behavior of the melt over a wide range of flow conditions.

Thus, a simple die flow analysis is generally very approximate; more accurate die flow analyses make use of the finite element method (FEM).

The objective of an extrusion die is to distribute the polymer melt in the flow channel in such a manner that the material exits from the die with a uniform velocity. The actual distribution will be determined by the flow properties of the polymer, the flow channel geometry, the flow rate through the die, and the temperature field in the die. If the die flow geometry is optimized for one polymer for one set of conditions, a simple change in flow rate or in temperature can make the geometry non-optimum. Except for circular dies, it is impossible to obtain a flow channel geometry that can be used, such as, for a wide range of polymers and for a wide range of operating conditions. For this reason, one generally incorporates adjustment capabilities into the die by which the distribution can be changed externally while the extruder is running. The flow distribution is changed in two ways: by changing the flow channel geometry via choker bars, restriction bars, valves, and so on, or by changing the local die temperature. Such adjustment capabilities complicate the mechanical design of

the die but enhance its flexibility and controllability. Some general rules that are useful in die design are:

- * There should be no dead spots in the flow channel.
- * There should be steady increase in velocity along the flow channel.
- * Assembly and disassembly should be easy.
- * Land length should be about 10 times land clearance
- * Avoid abrupt changes in flow channel geometry
- * Use small approach angles

In die design, problems often occur because the product designer has little or no appreciation for the implications of the product design details on the ease, or rather, the difficulty of extrusion. In many cases, small design changes can drastically improve the extrudability of the product. Some basic guidelines in profile design to minimize extrusion problems are:

- * Use generous internal and external radii on all corners; the smallest possible radius is about 0.02 in. (0.5 mm).

- * Maintain uniform wall thickness

- * Avoid very thick walls

- * Make interior walls thinner than exterior walls for cooling.

- * Minimize the use of hollow sections

7.6 Calibration

In extruding of large products or using polymers with relatively little melt strength, the extrudate emerging from the extruder die is often led into a sizing die. The actual dimensions of the extrudate are, to a large extent, determined by the sizing device, which is generally referred to as a calibrator. Its use is required if the emerging extrudate has insufficient melt strength to maintain the required shape. The calibrator is in close contact with the polymer melt and cools the extrudate. When the extrudate leaves the calibrator it has sufficient strength to be pulled through a hauled-off device, such as a catapuller.

In a vacuum calibrator, a vacuum is applied to ensure good contact between the calibrator and the extrudate and to prevent the collapse of the extrudate. The use of a vacuum calibrator is generally easier to maintain at a constant level than the use of positive air pressure within the extrudate. The latter tends to vary with the length of the extrudate is difficult to maintain when the extrudate has to be cut into discrete lengths.

Calibrators are useful when good, accurate shape control is important. When the requirements for the shape control are less stringent, the extrudate shape is often maintain by support bracket placed downstream of the extrusion die. In fact, the extrudate shape can be modified substantially by support brackets. These can be useful because they allow the shape of the extrudate to be modified without changing the die but only by changing the shape of the support brackets.

7.6 Polyolefin Film Production

Most low density polyethylene film is made by the blown film process. It is also possible to make film from other polyolefins in this way.

7.6.1 Blown Film Extrusion

Blown film extrusion is a continuous process where the molten tube is simultaneously axially drawn and radially expanded from an annular slit die. The hot tube is cooled by an annulus of high speed air from an air ring on the outside; some times it is cooled from on the inside of the tube as well. Although some processes use a horizontal configuration or are vertically downward, most are configured vertically.

The cooling occurs on the expanding tube, which usually is 1.2 to 4 times the die diameter. At a point above where the polymer is cooled below its melting range, the tube is squeezed by two opposing flat surfaces to collapse the bulb before it enters the primary nip rolls at the top of the tower structure. The cooled collapsed lay flat tube is transported on idler rolls down the tower by the secondary tension controlled nip and then wound on to cores to make

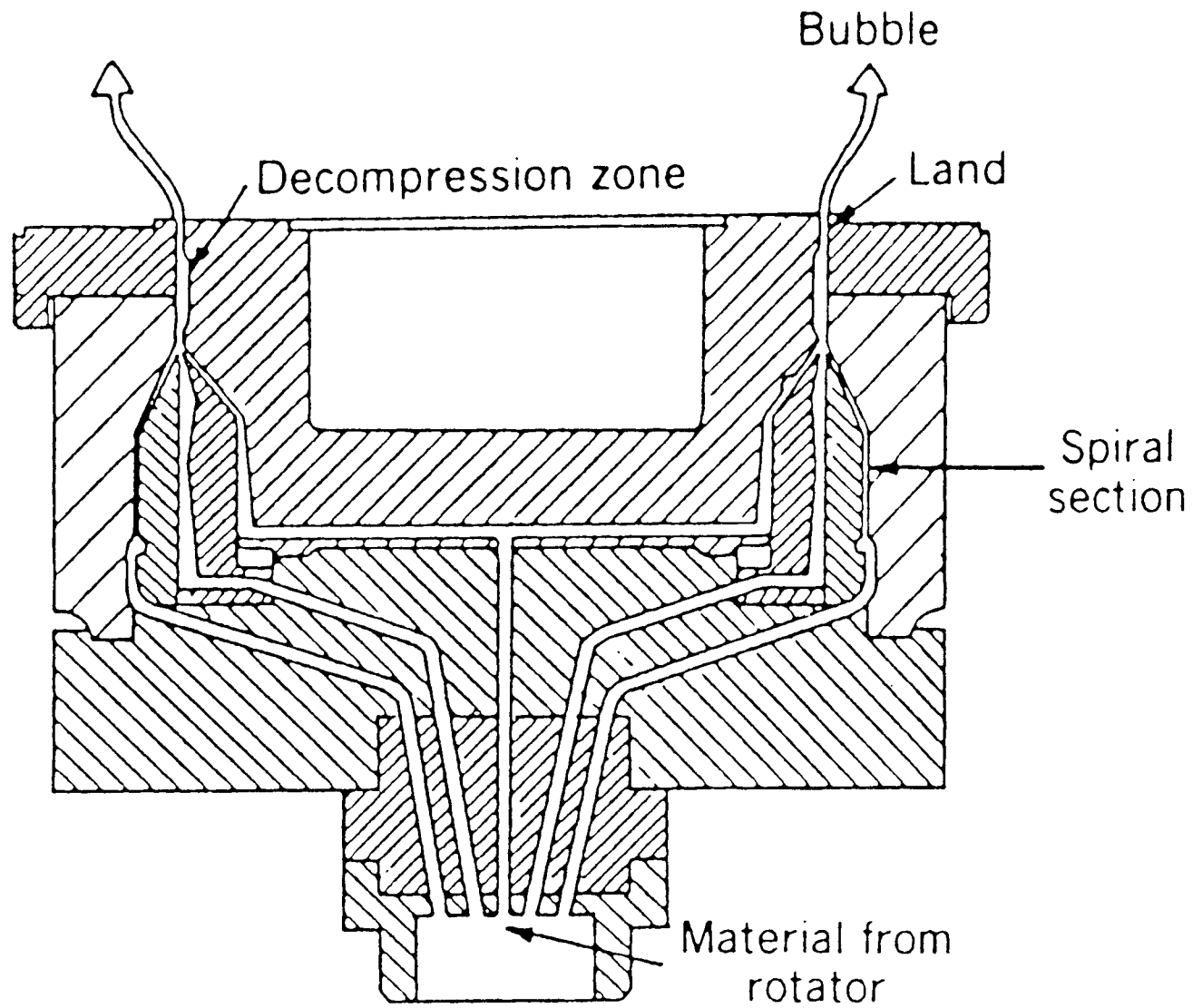


Figure 25 Multimanifold Blown Film Die

film roll stock. The tube also can be sent to an in line sealing machine to make bags.

Polyolefins (LDPE, LLDPE, HDPE) are the most frequently used polymers, although ethylene copolymers, FPVC, nylon, TPUS, elastomers, nitriles, PETG, and polycarbonate are sometimes used to make blown film. Homopolymer (polypropylene) needs a special water or mandrel quench process.

Major markets are bags for trash, lawn clean-up, and kitchen. Blown film is also used in T-shirt grocery sacks, and dry cleaning and baked goods bags. A large amount of film is used in agricultural and construction applications such as ground cover for mulch and fumigation and for water and wind barriers. Coextruded blown film in 3 to 5 layer structure is used for sack food, cereal, meat, and other food packaging.

7.6.2 Process

Melted polymers supplied by extruders is formed into a very thin wall, upward following annulus by the die and exist into an annular air stream supplied by the air cooling ring. Air also is fed through a hole in the die to inflate the tube and expand it into the desired diameter.

Once the process is stabilized, the inside air is stagnant and no more inflation is needed (unless internal cooling is

also used). The balance of the polymer flow and cooling air stream flow maintains the proper position of the maximum expansion zone of the bubble above the die. Because the film is unsupported in the cooling air stream, resins most frequently used are more viscose, and melt temperatures are kept low to maintain melt strength.

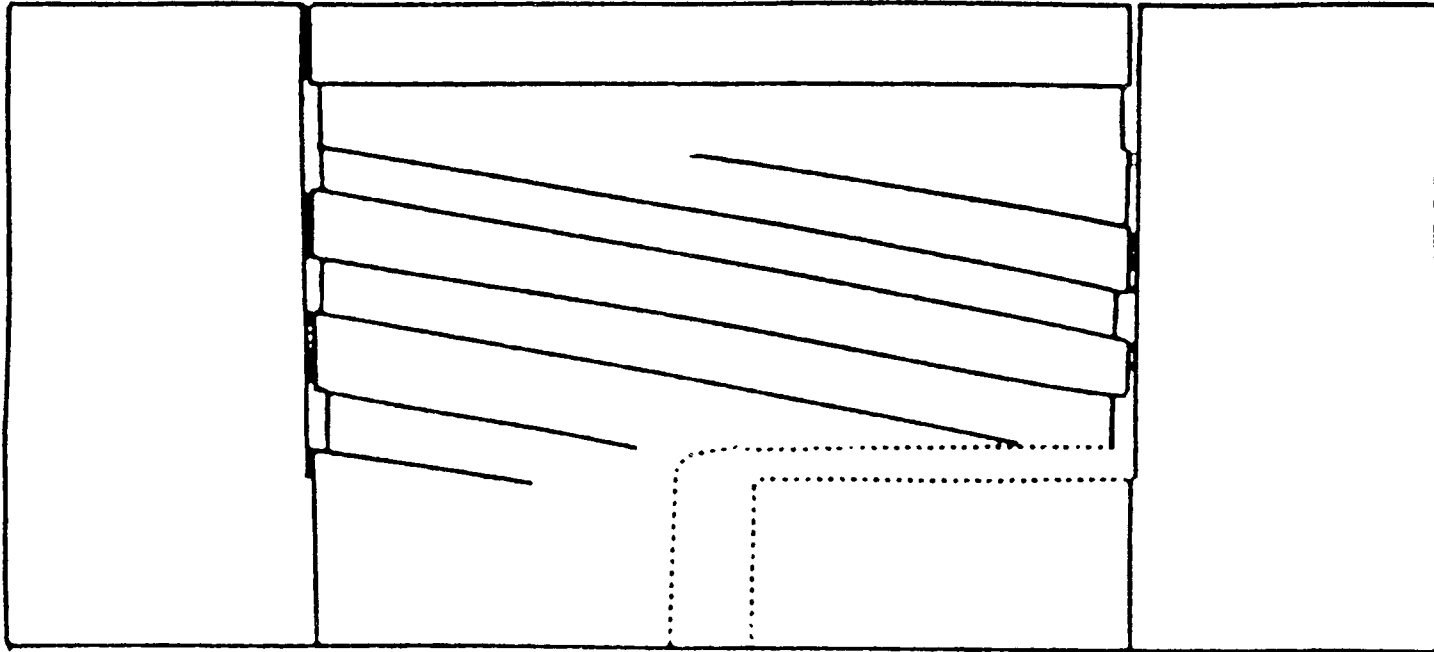
These factors coupled with the need to form the polymer to a uniform flow, very thin walled annulus, create higher extrusion pressure than what is encountered in the processes.

7.7 Equipment and Parameters in Blown Film Extrusion

The size of the tubular film is usually described by its lay-flat width. This is the width of a roll of double thickness film. A tube with diameter D gives a lay-flat width of $\pi \times D/2$ or $1.57D$. Primarily the width is controlled by the amount of air in the bubble. During start up, after the desired width is obtained, the air line C is closed. Then there is trapped bubble of air over which the molten plastic is extruded, sized, and cooled. This air is under a very slight pressure. If too much air is in the bubble, some is let out by cutting a hole in the tube.

7.7.1 Air Ring

A very important piece of equipment is the air ring E which is used for forced and controlled cooling of the molten



Inlet
Channel in core

Figure 26 Internal Channel Blown Film Die

tube. The ring directs a large volume of air upward over the surface of the bubble which removes the heat put into the resins by the extruder. This forced air cooling air allows the film to freeze faster and thus more feet per minute of film can be made. An air ring is carefully baffled to supply the same air flow at all points around the circular opening.

7.7.2 Blow Up

The diameter of the bubble is larger than that of the die opening. This is called blow up and characteristic of the process. The amount of blow up is calculated as the blow up ratio. It is equal to the film with a bubble diameter of eight inches made from a 4 inch die has a blow up ratio of 2. The blow up ratio is commonly in the range of 1.5 to 2.5. This means a single die can be used for as range of films widths, but to make all widths several dies are needed. Dies range in diameter from less than four inches to greater than four feet.

7.7.3 Thickness.

Drawdown is the another characteristics of the process. Die openings are typically of about 0.025 inch and film ranges in thickness from 0.00025 to 0.010 inch. Thus the melt is reduced in the thickness. The combination of drawing and blow up results in drawdown. By tradition, the product is called a film if its thickness is 0.01 inch or less and a

sheet or sheeting if its thickness is greater than 0.01 inch.

Much of the polyethylene film we use has a thickness of 0.00125 inch, and often the thickness of film is expressed in mils rather than inches. One mil equals one thousandth ($1/1000$ or 0.001) of an inch. Thus, this common film has a thickness of 1.25 mils (1-1/4 mils) and may be called mil and quarter film. The word gage is often used to refer to film thickness.

7.7.4 Thickness Uniformity

An important aspect of extruding blown film is to make it a uniform thickness around the tube. Several things must be done right. The die must be adjusted to produce a uniform flow of resin. Die temperature must be uniform and constant. Hot and cold spots will make adjustment and uniform flow impossible. The melt must have consistent behavior in drawdown and blow up to obtain uniformity of thickness. This no doubt depends on the uniformity of the melt viscosity, elasticity and temperature. To make control of the drawing and the melt processes still more difficult we must remember the resin is being cooled. It is very important that the same rate of cooling be used around the tube. If it is not, the thickness will not be uniform, causing difficulty in the subsequent processing.

We should note another characteristic of the process. The material from the given spot of the die moves along the same line to a given location on the roll of the film. Thus, a thin or thick spot continuously stacks on itself. A thick spot piling up will give the roll a thick section called a gage band. The roll has a poor appearance and handles improperly even though the variation in a single thickness of film would cause no problem.

7.7.5 Rotating Die

As uniformity of thickness is difficult to achieve, an innovation was developed to hide the problem. The die and cooling ring were made to rotate to distribute variation in thickness around the bubble and back and forth across the roll. Thus a thick spot does not accumulate, gage bands vanish and the roll appears uniform. Best of all the film is satisfactory and useful.

7.8 Operating Conditions

Blown film extrusion is carried out at as low temperature as possible. The extruder, resin, and screw are chosen to give low melt temperature which can be extruded at high rates. Melt temperatures for making the film from polyethylene are close to 350 degree F. As only air cooling is used, cooling is quite slow, and higher melt temperatures mean slower cooling. To speed up cooling, refrigerated air is sometimes used. It follows that the thick film cools slower than the

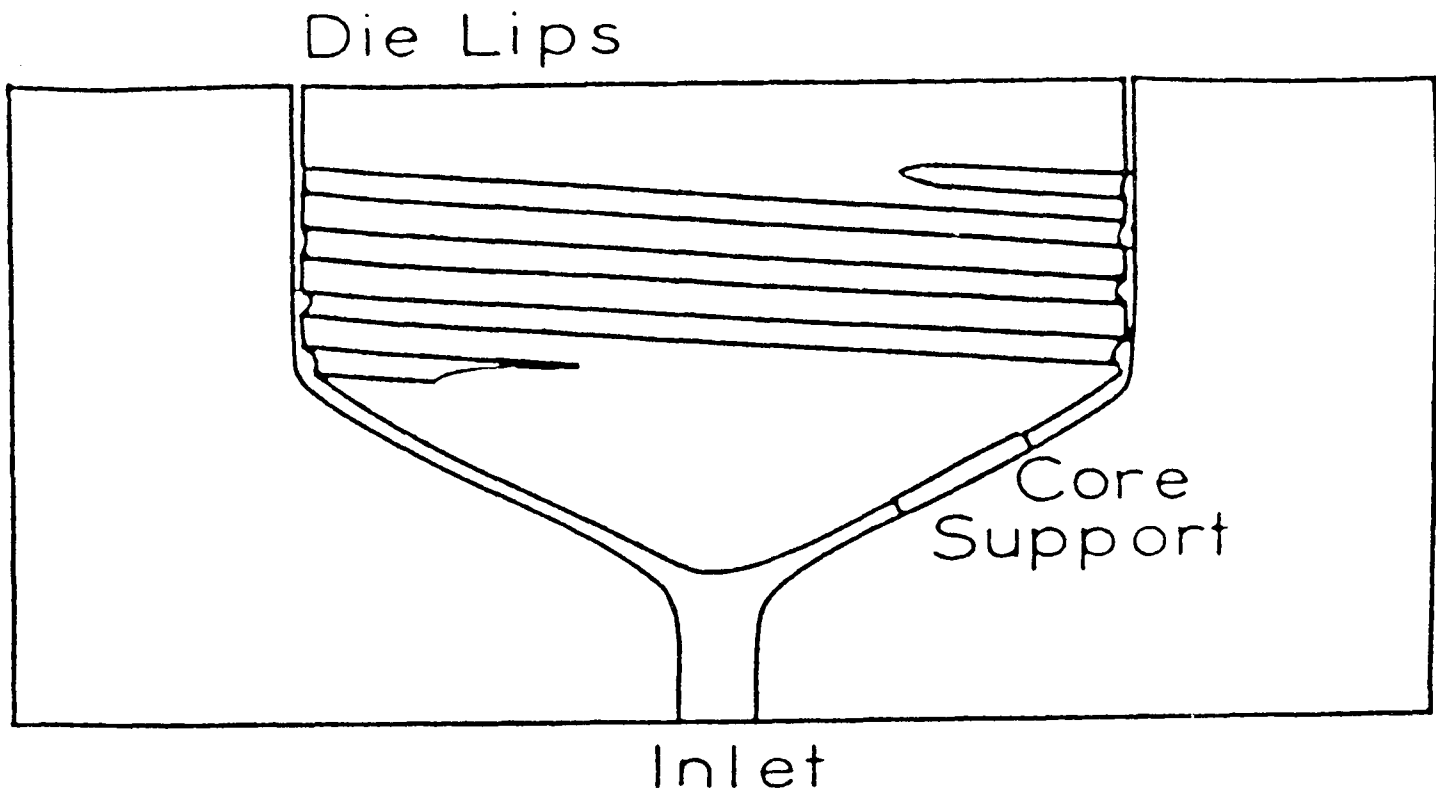


Figure 27 Spider-type Blown Film Die

thin film. Blown film is often made at take off rates of 50 to 100 feet per minute. Some thin film is made at 300 feet per minute.

7.8.1 Slip and Block

Films are made for many uses and form resins formulated for specific uses. Two properties of film which depend up on the amounts of the special additives are called slip and block. Slip is related to the eases of sliding a film over itself. This can be important in a bagging machine as to how a stack of bags behaves. Block has to do with the behavior of the film in a roll. A "blocked" roll of film forms a solid block of plastic and film can not be unwound. If this happens, different operating conditions or a block-resistant grade of resin should be used.

7.8.2 Windup

The winding of the roll of film is done with sophisticated equipment. Usually a dual winder is used which will automatically change from one roll to next when it is filled to the desired size. The winder controls how tight the film is wound onto the roll. Film which is too loose on the roll will slide around and cause handling difficulties. The roll should have an even edge and be smooth. Special features of the winding equipment provide for this.

Many plastic bags are made with gussets and the blown film process lends itself to making gusseted film from which such bags are made. Both edges are folded inside making the new edges four layers thick. When such a gusseted tube is wound on the roll, the roll is narrower than the full lay flat width. The edges have four layers and the center two. Thus the roll has a soft center. Bags are made by heat sealing across the tube with four layers sealed together at the edges. For its apparent width, the suggested bag is wide opening bag. The gusset is made in the bubble by pushing the film in and forming the gusset a short distance below the pull rolls.

7.8.3 Sitting

The blown film process also is used to make a single thickness film by slitting the tube after it goes through the pull rolls. The simplest method is to slit just one edge and to wind it up as a folded film of two layers. Some construction film is made this way. When it is unwound it is also folded to give a double lay-flat width of film. Slitting may be done at several points across the film to make two or more narrower rolls. Film may be separated by layers and wound independently.

7.8.4 Optical Properties

Much of the blown film is used for packaging and some of it is expected to add to the beauty and sales appeal of

the package. In this case, the optical properties of the film are important. Films with high clarity and gloss may be required. These properties are measured in a laboratory with instruments. Be carefully looking at a piece of film it is possible to see many things right or wrong with it. Some of the imperfections which can be seen are called gel, fish eyes, apple sauce, and chicken tracks.

7.8.5 Treating

Much of the film used for packaging is printed for decoration and advertising, but most films unless treated cannot be printed as ink will not stick to it. If film is not printed, it usually passes through a treater before it is wound onto a roll. A treater is an electrical discharge apparatus which changes the chemical nature of the surface of the film so that it will accept the ink.

7.8.6 Impact Resistant

Blown film is noted for its impact resistance or toughness. In a laboratory, this is often measured by a dart drop test by dropping a blunt dart onto a film held in a frame. Failure takes place when the dart breaks the film. In a practical test, a bag may be filled with sand or resins granules and then dropped. If the bag is not damaged, the film is considered tough and satisfactory.

The toughness of blown film develops during the drawdown and blow-up process. They give the melt a two way, or biaxial stretch. To a degree, this process gives alignment of polymer molecules. Drawdown gives "machine direction" orientation and blow up gives transverse orientation. Most extrusion processes involve only drawdown and thus only machine direction orientation. As a result, many extruded products differ in strength, stiffness, or toughness in their machine and transverse directions. The transverse direction where there was no stretch is the weak direction. The good toughness of the blown film may be looked upon as a film not having a weak direction.

7.8.7 Heat Shrinkable Film

The blown film process can be used to make heat shrinkable film which is used in packaging a group of products. A package wrapped in the film is heated for a moment, and the film shrinks around the contents, holding them together.

The shrinking comes from forces frozen into the film when it is being made. The film becomes solid before it was through shrinking and the forces which are causing the film to shrink are frozen in. The tendency to shrink did not disappear. It reappeared when shrinkage again was possible. This is particularly important here since a low melt temperature was used, and thus, the elastic forces are high

and the memory is long. Drawing and blowup takes place with an elastic melt.

7.8.8 Orientation

It is important to discuss the word orientation, as it has several; meanings. Orientation is used to refer to the drawing of either a solid or a molten plastic. We have already discussed the later process. The drawing of a solid makes a thinner product and increases its strength 100 to 500 percent. Such an orientation of the solid is used in making fibres. Some films are oriented by cold drawing. The products are called oriented films and they are considerably stronger than extruded films. Orientation of film is a very specialized process. The melt orientation of the blown film process results in only a slight (10-20 percent) increase in strength. Hence, the product is not considered an oriented film. {Refer to 2,3 and 13}.

CHAPTER 8

OTHER IMPORTANT PROCESSING TECHNIQUES OF POLYOLEFIN PLASTICS

8.1 Materials Handling

The modern polyolefin processing plant receives its resin in bulk by rail car or truck, unloads the material by air conveyor into large silos, and distributes the resin to individual processing machines pneumatically. Transfer systems may be actuated by compressed air or vacuum. Very commonly both are used; resin is blown into the bins by compressed air and distributed to the using machine by suction devices, which are actuated by a hopper level sensor at the machine, which draw the resin when the level descends below a preset point. This means that the machine operator does nothing about resin handling but does make the proper piping connections and see that the automatic equipment operates properly.

Automatic handling equipment not only saves labor involved in resin handling but also helps prevent resin contamination and assures that it arrives at the machine at a uniform temperature.

8.2 Coloring and Compounding

There has been an increase in the amount of coloring and compounding of polyolefins done at the resin consuming facility in recent years. This is likely to increase further as plants expand.

Injection molders commonly color polyolefins by blending dry pigments with resin pellets. They also blend linear and high pressure polyethylene pellets to obtain materials immediately between the two in flexibility.

In the extrusion field there is more of a tendency to use master batch for this purpose. A master batch is a polyolefin compound containing a high concentration of color or additive; it is mixed with natural resin in the proper proportions before use to give the final mix the desired additive concentration.

In addition to colors, masterbatches may be used in both molding and extrusion to add slip and antiknock to film resins, ultraviolet absorbers to film and non filament resins, carbon black to pipe resins, butyl rubber or other elastomers to improve the impact strength of the resins, and glass fibres to improve the strength and heat resistance of moldings, as well as other materials for special uses.

The cost of master batch and the blending operation is generally lower than the cost of purchasing a premixed compound from resin manufacturer. This is not, however, the principal incentive for on-plant compounding. The real advantage is the ability to buy and store in a bulk small number of base resins; these may be modified as needed in accordance with a particular order, instead of having to maintain an inventory of a large number of special compounds.

8.2.1 Mixing

On-plant mixing of dry color is usually done in a tumble blender, which may be merely a fibre drum mounted on an axle that may turn end for end or at an angle. Cement mixers may also be used, or, of course, blenders similar to those used at the resin manufacturers plants.

When dry color quality better than that obtained by tumble blending is needed, an intensive dry mixer may be used, as at the manufacturing plant.

8.2.2 Pigment Dispersant

Dry coloring is facilitated by precoating the polymer pellets with mineral oil or other viscous liquids which would stick the pigments to the pellets. This reduces dusting, allows the use of higher pigment loadings, which would not segregate from the pellets handling, and shortens

the needed mixing cycle. Of course, care must be taken to avoid a dispersant that will damage resin quality, and to avoid excessive use that will result in the dispersant bleeding to the surface of the finished product. Dispersants may also, in some cases, cause pigment agglomeration.

8.2.3 Masterbatch Blending

In addition to the types of blenders used for dry color blending, masterbatch is very commonly blended by continuously feeding a stream of masterbatch and a stream of raw resin to processing equipment. Available equipment can maintain the proportions of the two streams accurately, even when the overall rate changes must be made to accommodate the process. Belt feeders that actually perform a continuous weighing are very accurate but expensive. Screw feeders are very satisfactory in most cases and piston feeders which feed measured volumes are also good, where the materials are being fed do not vary appreciably in bulk density. These devices do not actually weigh out product; hence, in order to get proportions by weight, the output must be weighed over a range of conditions to obtain a calibration curve.

8.3 Extruded Heavy Sheeting

Sheeting from 30-250 mils thick is made on equipment somewhat like that used for chill cast film. The die opening as are, of course, wider, and this makes impractical the control of thickness by changing the die opening only.

Sheeting dies therefore have a variable restriction in the slot between the manifold and the die lips, which may be moved to obtain uniform flow across the die. This is called a choker bar. The die lips themselves are usually set at a constant opening near the desired sheet thickness. Instead of the single chill roll, sheeting is usually taken from the die to a vertical stack of three or five temperature controlled polished rolls. The hot sheet from the die goes either between the two top or the two bottom rolls. The distance between these rolls is adjusted to exactly that required to produce the sheet thickness. This is, of course, slightly wider than sheet thickness because there is shrinkage on cooling. Roll and extruder speeds are adjusted so that the sheet contacts both rolls, but without accumulating a "bank" of excess material that cannot be pass through the nip. In this way both sides of the sheet get a polished surface from contact with the rolls, and variations in sheet thickness are ironed out by the rolls. Excess material will cause a rough or rippled surface on the sheet.

The sheet is then led down the stack or up, depending on whether it was introduced at top or bottom, passing between the second roll and the third, and around the third.

If there are five rolls it makes a similar "S" pass over these. The nips after the initial one generally are not closed enough to put appreciable pressure on the sheet. The

rolls in the stack are generally at a temperature below the melting point of the polymer, but not cold enough to stiffen the sheet too much because, especially on the heavy sheet, it must be kept warm enough to follow the rolls without buckling. When the sheet leaves the stack it is set up but still warm, and is carried along a roller conveyor where it is cooled by air jets, or in some cases, by water spray. When fully cool it may be rolled up if flexible enough, or cut into sheets and stack if it is too stiff to roll. All polyolefins may be made into sheet in this way.

8.4 Extrusion Coating and Laminating

Polyolefins are very widely used as extrusion coating and laminating materials. We are distinguishing between coating and laminating by considering a coating as a layer of polyolefin placed over the surface of another material, while laminating with the polyolefin melt consists of placing the polyolefin between two layers of other material.

Polyolefin extrusion coatings are widely used on paper and paperboard as a means of waterproofing, and are also used on aluminum foil, cellophane, and other materials as a convenient heat sealing medium.

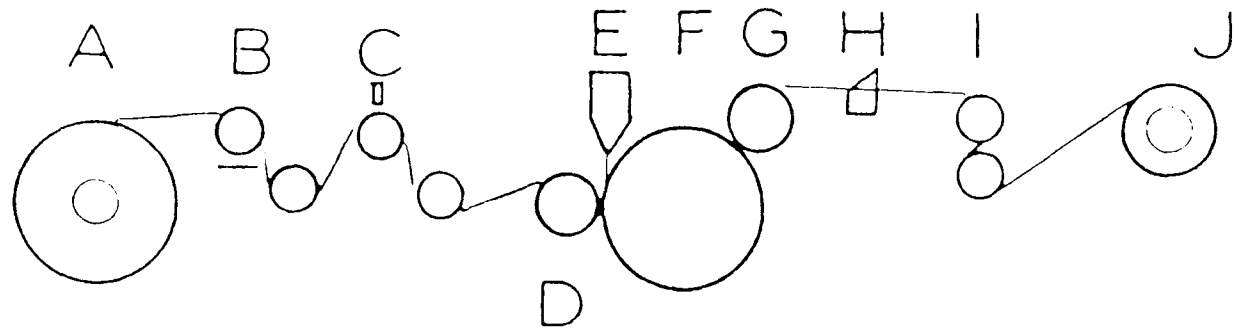


Figure 28 Polyolefin Extrusion Coating.

8.4.1 Extrusion Coating Equipment

The equipment used for extrusion coating closely resembles that used in the chill roll casting method of making film. Addition of a letoff mechanism for the substrate used, a pressure roll to press substrate and coating to the chill roll, and some slight modification to the die, are all that is different.

Substrate treatment or primary stations are commonly found on extrusion coating machines. These treat the substrate in order to improve adhesion of the coating or other closing properties. There are many kinds of these, only a few of which will be mentioned. Flame fibres which might penetrate the coating consist simply of playing a gas flame against the surface of the substrate. Corona treating of the glass substrate is identical to the corona treatment of polyolefin film for printing. It is used to improve coating adhesion. Priming is practiced to improve adhesion of the coating. This designates the application of some liquid, usually some residue on evaporation to the substrate. A primary station generally also includes a drier to remove the liquid. Water is used as primer on some paper stock, and promotes adhesion simply by roughening the paper surface a little. Resin emulsions are commonly used; these may contain striven polymers, polyvinylidene chloride, or other polymers. In the case of polyvinylidene chloride the primer

not only promotes adhesion but also adds to the barrier properties of the structure. Organic solvent solutions of titanium esters are also used. In this case the priming station includes a drier to remove the solvent, followed by a steam chest to hydrolyze the ester.

Extrusion coating requires very high melt temperature in order to get good adhesion to the substrate in the absence of an effective primer. Therefore, the extruders used to prepare the melt are longer than those used for other purposes, often having an l/d ratio above 30/1. The screws used in these machines are also unique in having very long metering zones, often more than half the length of the screw, and these metering zones are shallow for the size of the screw. These extruder characteristics are needed because the high temperatures required cannot be achieved simply by frictional heating. When a polyolefin melt gets very hot its viscosity is so low that the shear developed by skew rotation is no longer high enough to produce much heat. The extruder must therefore have a lot of oil surface area to expose the melt to heat conduction to reach the high temperatures.

The extrusion coating die differs from the chill roll cast film die in that the shape of the face of the die may be modified in such a way as to allow the die lips to reach down close to the nip between the chill roll and pressure

roll. This is to prevent excessive cooling of the melt before it comes in contact with the substrate.

Coating dies also commonly have a feature rarely used on film dies. This is some device for adjusting the die width, commonly called decries. These may be rods placed inside the die lips, but are more commonly external covers over the die lip opening. The decries are used to adjust the coating width to a substrate width, which is very important to avoid waste of material. In some case the coating is made a little narrower than the substrate, and the coated material is then trimmed to remove the bare substrate. Since substrates are generally more expensive than the polyolefin coating, it is much more common to "overcoat", which means to make a coating wider than the substrate, and trim the excess coating.

The pressure roll has a resilient so that it can press against the chill roll without damaging it. Neoprene or silicone rubber are often used as roll facing, and there may also be a thin layer of Teflon tap over this, especially at the ends of the roll to prevent sticking of the melt coating.

While the chill roll used for film casting is almost always highly polished, other finishes are often used on coat lines. This is done for several reasons, the most important

being to control the frictional qualities of the coatings. Many coated substrates are converted, that is made into end use products on high speed machinery that requires the coating to slip over metal guides or, in some cases, against itself. Highly polished coating surfaces tend to stick or at least not slip reliably in these circumstances. A slight roughening of the surface can greatly improve the slip properties. If a glossy appearance is needed but with improved slip, a special roll finish called "mirror pocket" is used. As its name implies this finish contains minute depressions that are highly polished inside. The coating pressed against it therefore has very small shiny raised areas, which help it slip, but give the coating a glossy appearance. In many cases, of course, gloss is not needed, so various sand blasted or matte finishes are used. For decorative effects textured or embossed rolls are available.

The rest of the equipment is generally like that used for flat film. Trim scrap generated in coating operations can rarely be reused because of the contamination with the substrate, so it is generally burned.

When the polyolefin melt is to be used as an adhesive between two other materials, a let off for the second substrate must be provided because above the chill roll, which is arranged so that it may feed the substrate in over

the top of the chill roll. The other substrate comes in over the pressure roll in the normal manner for coating, and the olefin melt goes between the two substrates where they come together at the intersection of the chill roll and pressure roll. A lamination completely adhered across the whole width can be made in this way, but in some cases it is desired to have adhesion only in certain areas, leaving other parts free. This can readily be done by modifying the die to give bands of melt where the adhesion is needed, and leaving the rest of the free. This can readily be done by modifying the die to give bands of melt where the adhesion is needed, and leaving the rest of the width free . A similar effect can be obtained by pressure roll modified to press only certain areas. This permits a continuous olefin coating but only partial adhesion.

8.4.2 Coextruded Laminations

Composite films consisting of two or three layers of different polyolefins are often made by coextrusion. This is done on chill roll cast or water bath film equipment, but the product is more nearly related to the present idea, so it will be discussed here. In this process two extruders are used to feed a single die. The two melts are introduced into the opposite sides of the die for a layer construction, and flow through the die passages and the die lips together.

Rather astonishingly, there is no appreciable mixing of the two melts as they flow through the die. This is because the flow in the plastic melts are entirely laminar, due to their high viscosity, the melts then emerge from die lips as a single firmly bonded film. The relative thickness of the two layers is determined by the relative speed of the two extruders. Quality control of the relative thickness depends on finding some composite property to check, because the two layers are so firmly bound that they cannot be separated. In the popular low density polyethylene polypropylene laminates, for instance, yield strength is a function of the relative amounts of the resins and can be used for quality control. The difference in certain infra red absorption bands may be used for same purpose, and this has the advantage of being adaptable to continuous on line monitoring.

Three layers constructions can be made in the same way with one melt coming in between the other two. Some care must be taken in the configuration of the die passages to assure that three even layers start into the die, but once they are established they flow quite uniformly through the die. In experimental work this can be established readily by coloring the layers different colors.

It is necessary to select the grades of the resin, used, so that at the temperature and flow rate of the equipment, they

have similar flow resistance; otherwise, flow instability may appear and disrupt the layers.

8.4.3 The Use of the Masterbatches

Polyolefin coatings are frequently pigmented for appearance or for resistance to ultraviolet light damage. Pre colored resins may be used for this purpose, but generally a colored concentrate or masterbatch, which contains the desired pigment in high concentration in a polyolefin base, is added to regular coating resins. If the masterbatch is made with a suitable base resin, and has good dispersion of the pigment, then the resulting coating will be as uniformly colored as one made from precolored resin.

masterbatch is also used to introduce additives other than colors. For instance, it is often necessary to control the coefficient of friction of a coating by the addition of slip additives to the resin. These same additives may also be used to prevent sticking of the coating to the chill roll, where this is a problem. These additives may be obtained in masterbatch form and added to the resin as needed. Other sorts of additives like antioxidant, ultraviolet stabilizers, antistatic agents, and others, may also be added to the resin in masterbatch form.

{The following figure has been taken from Polyolefin Plastics by Theodore O.J. Kresser}

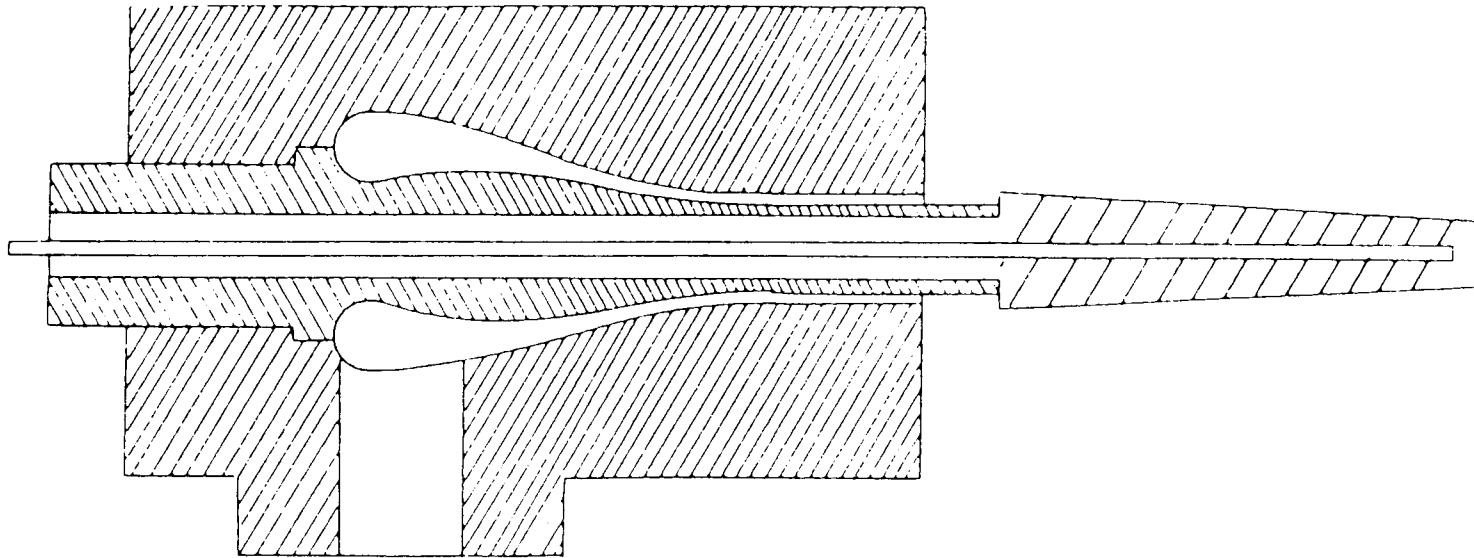


Figure 29 A Pipe Extrusion Die with an Extended Mandrel.

The use of masterbatch with a single base resin greatly reduces the inventory problems when a wide variety of different coating formulations is used in the plant.

8.5 Polyolefin Pipe Production

Polyethylene is the most widely used polyolefin for plastic pipe. Both low density and linear polyethylene, and the mixtures of the two are used. Polybutene-1 has limited use, especially in conjunction with linear polyethylene and polypropylene. Pipe is made from very high molecular weight linear polyethylene by proprietary methods. Crosslinked polyethylene pipe, and biaxially oriented polypropylene pipe have been described, but have not yet obtained appreciable commercial usage.

The methods used for the largest volume production of low density polyethylene, and low density linear blends will be described.

A die of this kind may be mounted across the front of an extruder, or it may be mounted with a right angle connection to the extruder, in which case it is called an offset die. Dies are usually designed with interchangeable cores and bushings, so that several pipe sizes may be made from the same basic die. The extended mandrel shown is optional.

The basic problem in pipe extrusion is supporting and maintaining the shape and dimension of the pipe just after it leaves the die and is still hot and soft. The main variation in pipe lines occur at this point. The extended mandrel shown is one common device for this purpose. The mandrel is water cooled, and in use water is generally flowed over the outside of the hot pipe while it is passing over the mandrel. If the system is operating properly the pipe will be self supporting when it leaves the end of the mandrel, and it may be further cooled by water spray or immersion in a water bath. The other most generally used method is the external vacuum sizing die. In this method a cylindrical die with internal dimensions the size of the outside of the desired pipe is equipped with small holes in an area a little in from one end, and a vacuum is drawn on these holes. The hot pipe is led into the die, and vacuum hold the surface of the pipe against the inside of the sizing die. The surface between the pipe and the sizing die is generally water lubricated, and the sizing die itself is water cooled. Here again the pipe should be self supporting when it leaves the die. Sometimes a combination of these two methods is used; the pipe comes from the end of the extended mandrel still warm and is led to the sizing die. This combination permits higher extrusion rates than either alone. There are also other methods but these are in less use.

Whatever the initial cooling method, final cooling is done by immersion in a long cooling tank, after which the pipe goes to the capstan which determines the line speed, and in either rolled up or cut into lengths depending on its size and stiffness.

8.5.1 Polyolefin Monofilament

Monofilament is essentially the same thing as textile fibre except larger in diameter, and is finds applications in many traditional textile uses like fishing line, furniture webbing, sewing thread, twine, marine cordage. However, the main monofilament manufacturers have been separate from strictly textile fibre manufacturers, and the equipment for monofilament production, while hybrid in nature, has tended towards the traditional plastics machinery. For this reason it will be treated very briefly here.

Monofilament is generally extruded through a conventional screw extruder of rather small size, 2.5 inch diameter being typical. The die consists of a series of small holes which may be arranged in a line, but more commonly in a circular pattern of several rows, because in this way more orifices may be placed in a small area. The holes are about three times the diameter of the desired monofilament size, and a die may have 60-80 holes. Pump type dies like those used in fibre extrusion may also be used for monofilament. In these dies a small positive displacement pump is located within

the die and assures a uniform flow of polymers, regardless of pressure fluctuations from the extruder.

The monofilaments are extruded downwards into a water tank and then go in a group to a set of pull rolls. These are called godets in this industry. This first set of godets determines the rate of draw from the die and also the strand diameter. From the first godets the filaments go to an oven or tank of hot liquid which is at the proper drawing temperature, and then to another set of godets which run motor rapidly than the first. Typically the first set will go at 9-12 times the speed of the first. This draws the fibre to develop the tensile strength and also bring it to the final diameter.

From the second godets there may be another oven and another set of godets running slightly slower, to set the monofilament and reduce shrinkage. After the last godets the films are separated and each one is wound on a separate spool.

The physical properties of the filament depends on the degree of stretching and the temperature of the stretching. Polypropylene and linear polyethylene typically draw at 350-400 F, while low density polyethylene may be drawn at 200-300 F.

8.6 Processing Powdered Polyolefins

There are several processing methods that start with finally powdered resin. Low density polyethylene is the most commonly used, although some linear is used in this way.

8.6.1 Rotational Molding

This is the most widely used powder processing method. A light weight split mold is used. A charge of powdered resin which is the weight desired in the finished piece is placed into the open mold, and the mold is clamped together. The closed mold is placed into a rotator, which turns it on two axes, so that powder tumbles evenly over all inside surfaces of the mold. The mold and rotator are placed in an oven which heats the mold until the polymer is melted and coated evenly over the inside of the mold. The mold is cooled then by air once a water spray and opened to remove the part. this process produces a hollow part without any opening, and can make parts of very uniform wall thickness. Molding cycles are rather long so as large number of molds is required for any considerable production. The process is not used for toys and some industrial items.

8.6.2 Powder Coating

Rugs are sometimes backed with polyolefins by spreading a layer of powder on the back of the rug and melting the polymer by radiant heat. Rugs backed in this way may be heat

formed and retain their contours, which is convenient for the processes like automotive carpeting.

Metal parts may be powder coated by heating the board above the polymer melting point, and dipping it into a fluidized bed of polymer powder. Powder will stick to the metal and coat it. A reheating is usually used to smooth and polish the coating. Additional layers of the coating may be added by reheating and redipping, but this deteriorates the first polymer layer, so is rarely advisable.

Powder may be applied to large metal areas by flame spraying. In this method a spraying gun is used which can blow plastic powder through the center of the flame. The flame is used to preheat the metal part to the melting point, powder is then blown through the flame, where it melts and sticks to the metal when it hits it. In this process generally a base layer of a rubbery polymer is put down first, followed by the polyolefins.

8.7 Foamed Polyolefins

Polyolefin foams are used as resilient gasketing materials, and as light weight insulation. Two general foaming methods are used, direct foaming by addition of gas or volatile liquid, and the use of a foaming agent which is solid when added but decomposes to release a gas when heated to final processing temperature.

The direct addition of gas is usually done in an extruder. The extruder barrel is equipped with inlets for gas near the front where the plastic mass is molten and pressure. High pressure gas, usually nitrogen is blown into the melt, but the pressure is high enough so that there is little expansion of gas. The extruder screw, opposite the entry points, is modified to promote good mixing between polymer and gas. The mixed mass is then extruded through a die, and expands from the pressure drop. While simple in principle this is difficult to practice and many ingenious devices have been invented to make it possible. This method can make a very low density foam and is usually made in sheet form to use as gasketing.

Volatile hydrocarbons can also be used in an extruder for the same purpose; however it is possible to use these simply by saturating the extruder feed with the volatile material.

Solid foaming agents are generally compounds that are released nitrogen on heating. Azodicarbonamide, which is sold under several trade names, is most commonly used for low density polyethylene. Linear polyethylene and polypropylene require a material for higher decomposition temperature, and is then extruded into final form, above the decomposition temperature of the foaming agent. Foamed polyethylene is used for wire coating. Azodicarbonamide and some other foaming agents have an added advantage that in

addition to producing nitrogen they are also free radical sources, so that they cross link the resin to some extent while foaming it, thereby increasing the abrasion resistance and softening point.

Foamed polyolefins may be injection molded as well as extruded. In this process the melt containing a foaming agent is kept under enough pressure to prevent expansion until the time of injection. Only enough melt to refill part of the mold is injected, and the expansion fills the mold. The material which contacts the mold walls is cooled so quickly that it does not expand much, resulting in a part with a solid skin and a foamed core.

8.8 Polyolefin Wire and Cable Coating

Wire insulation was one of the first uses of polyethylene and is still an important polyolefin market. The resin most commonly used is low density polyethylene. Some linear polyethylene and a considerable amount of copolymers of both linear and low density types are used.

As with many of these processing methods, melt is prepared in a screw and forced through a die. The die in this case is essentially a tube die, but the mandrel of the die has a hole through it to allow a wire to pass inside the polymer tube. There are two basic forms. In one form the die mandrel ends some distance before the opening of the die,

so that wire itself acts as mandrel. During the passage through the die lips. This type of die is used for the large wire and particularly for cable covering., because it allows plastic to be forced into outer windings of the cable, thus anchoring the coating and reinforcing the construction manually. In other version the die mandrel extends to die lips, so that a tube slightly larger than the wire is produced, and then is drawn down into good contact with the wire by stretching caused by the haul-off speed. In both types of die, a vacuum may be drawn around the wire to assure the absence of air bubbles at the plastic wire interface.

The wire line consists of a wire let off which should have good automatic tension control, a wire straightener to assure absence of any kinds of bends, and a wire heater. It is necessary to heat the wire in order to obtain good adhesion of plastic to the plastic to metal, and to preclude air containing separations which could produce internal corona discharge in service, which rapidly destroys the wire. The most common wire preheater provides for two metal contact rollers with some strength of wire in between them. A low voltage high amperage current is passed through the wire between the rollers, raising its temperature. Oven preheat may also be used, but this takes much more space.

From the heater the wires go directly to the die, where it is covered with plastic, and from there into a tank where tank for cooling. Thin coverings are generally plunged directly through the die, where it is covered with plastic, and from there into a water tank for cooling. Thin covers are generally plunged directly into the cold water, but heavy ones may be air cooled for a distance first, and may also be immersed first into the warm water, because sudden chilling of walls may produce voids.

The cooled wire is then run over capstan rolls, which determine the speed of the wire, and from there to a reel. The reel mechanism should have a good tension control to assure a uniformly wound reel.

8.8.2 Cross-linked Polyethylene

In order to improve the strength abrasion resistance, and heat resistance of the low density polyethylene wire insulation, it is cross linked. This is done by using a compound containing a peroxide shrinking agent, extruding it at a temperature below the decomposition point of the peroxide, and passing the coated wire through a vulcanization tube after it leaves the die.

A continuous vulcanization (CV) tube consists of steel tube, which may be hundred feet or more in length and is covered with thermal insulation. At each end of the tube there is a

pressure lock which permits the wire to go through, but allows a build up of pressure within the tube. High pressure steam is admitted into the tube to raise the temperature to a level above the point where the cross linking agent becomes active.

CV tubes may be either straight or catenary in form. Since the insulation is soft and readily deformed during the most of its path through the tube, it cannot be allowed to touch the tube or to be supported in any way while in the tube. This means that the wire must be supported before it enters and after it leaves the tube. Since electrical conductor wire, whether copper or aluminum, cannot withstand very great tension, the wire sags considerably while passing through the tube. This means that a tube must have a fairly large diameter to permit the sag without wall contact. For this reason many very long CV tubes are built in catenary shape, which follows the sag of the wire, and which functions just as with a smaller diameter tube. In this tube the coating is heated above the decomposition temperature of the peroxide, and the polyethylene is crosslinked. It is then cooled up and reeled up as before.

This process has broadened the use of polyethylene insulated wire to include power applications, where it had previously been excluded because of its low softening temperature.

8.9 Fabrication and conversion

Many of the processing methods that have been described produced articles that are ready for an end use; some of them however, produce an intermediate product that requires further operations before it is useful. These operations are called fabricating and converting. The products concerned are film and sheeting and to a laminated extent rods and tubes.

8.9.1 Thermoforming

Polyethylene sheeting is very often made into a finished product by thermoforming. This process consists of heating a sheet of polyolefin, usually clamped on a frame, until it has softened enough to stretch very readily, and then forcing the plastic web into conformity with a mold by suction, pressure, mechanical action, or a combination of these forces.

Thermoforming is, at this point, such a complicated family of techniques that we cannot do more than some of the methods used.

The film is usually heated by means of high intensity infra red heating elements, usually each on one side of the sheet. These are called sandwich heaters. Ovens, hot gas jets, or contact with heated surface may also be used.

Heavy sheeting is usually handled by the sheet, with a frame indexing between the heating forming station, carrying the sheet. Thin sheeting is handled in rolls, with only the edges of the web being clamped; passage through the oven and the molding stations may be continuous or intermittent. In intermittent motion, a length of sheet is first held in the heating station for the needed time, and then the heated portion will be moved to the molding station, bringing a new length between the heaters. Continuous operation may be obtained by using moving molds that synchronize their motion with that of the sheet. The molds may be carried on chain conveyors or on a rotating drum. There is no standard nomenclature for the forming methods but the following paragraph describes a few of them.

8.9.2 Vacuum Forming

In this method the heated sheet is positioned over a female mold, and the edges sealed to the mold. Vacuum is then drawn into the mold to pull the plastic into conformity with the mold. Simple vacuum forming is limited to fairly shallow draws, otherwise the bottom of the mold piece thins out considerably. If deeper parts are needed, a mechanical plunger is used to push the softened web down into the mold. This is called plug assist. The plug is always smaller than the mold, but may be shaped like it, just leaving a small

clearance all around, and sometimes the plug only goes in part way. In either case vacuum is drawn to pull the plastic and form it to the mold. The plug may also be perforated such that air can assist this process.

8.9.3 Drape Forming

This is essentially vacuum forming on male molds. The soft sheet is drawn down over the male mold and sealed to the base mold. Vacuum is then drawn through the holes in the low spots of the molds to conform the sheet closely to the mold. If a container is made in this way, the bottom will be thicker than the top, because the hot sheet first contacts the bottom of the mold where it is slightly cooled, before the stretching down the sides is completed. One of the main problems with this method, particularly when multiple molds are used, is called webbing. Webbing occurs because when the hot sheet is drawn down over an angle in the mold, it tends to mold and stick together rather than remain a single sheet. One of the ways in which this is remedied is to use a drape assist, which presses the plastic to the mold base around each individual mold.

8.9.4 Pressure Forming

This may be done with either male or female molds, and differs only in positive pressure is applied to the sheet instead of, or in addition to vacuum on the mold. The advantage is that much greater pressures are possible,

making it possible for thicker sheet, and making it possible to form at lower temperatures where the sheet is not so soft.

8.9.5 Matched Mold Forming

In this process the soft sheet is trapped between a male and female metal mold., which are designed to leave just the space needed for plastic. This permits the most accurate and the most rapid forming. In its final development it becomes sheet stamping, which will be described in more detail under future developments, because it is not at present used to its potential.

8.10 Film Conversion

Film conversion is also a complex of many techniques which may be classified into printing or decorating on the one hand and joining or sealing on the other hand. The principal end uses are packages.

8.11 Printing

Polyolefin film is printed in four different ways. By far the most common is the flexographic process. The printing plate in this method is made of flexible rubber or plastic and supported on a metal roller. An inking roller applies ink to the plate, and the film runs between the plate and a backing roller, picking up ink in the process. The low cost and easy interchangeability of the printing plates makes

this particularly suitable for printing bags or other packages where relatively frequent changes of plastic is necessary. This does not produce the highest quality of printing, but the process has undergone a great deal of development and produces printing that is quite acceptable for most packaging applications, and that may be done at relatively high speeds. It is not usual to print in line with the film extrusion process by this method.

The best quality of printing is done by the rotogravure process, where the design is etched onto a metal roller as a series of small dots. This method can produce subtle shadings and very fine detail at very high speeds. It is suitable for long runs of the same design, but the rollers are large and expensive, so that a large number of designs require a high expenditure and much storage area. It is sometimes used for the main decorative part of the package printing, where the design is identical for many packages, leaving only a small part to be done flexographically to identify a particular item .

Offset printing where the ink is transferred from a printing plate to a rubber roller, and from that to the plastic is less frequently used for the film, although it is used increasingly for items like bottle labeling.

Silk screen printing, where ink is forced through holes in a fine screen partially blocked to form the design, is used where a heavy coating of ink is needed. It is not very widely used on film, but is the most commonly used method of printing on bottles and other relatively heavy plastic objects.

8.12 Sealing and Joining

By far the most common method of sealing polyolefin film is heat sealing. This has a variety of forms, the oldest and still common being the hot bar sealer. In this form the two layers of the film to be sealed are placed on top of each other between a heated metal bar and a flexible support. The bar is brought down on the film long enough to heat them to the point where they fuse together under the pressure of the bar. The bar is then lifted and the sealed film is removed. A variation of this is in the impulse sealer, where the heated bar is replaced by an unheated or even cooled bar faced by a resistance wire or tape. As before, the assembly to be sealed is clamped between the bar and the flexible support. Then a short surge of electrical current is passed through the resistance wire, heating it enough to soften the plastic. The assembly then remains clamped until the seal cools somewhat. This method is preferably for heavy film or for oriented film where the hot bar method will cause distortion of the seal. In both of these methods a Teflon coated glass fibre tape is interposed between the material

being sealed and the sealing bar, to prevent sticking of the plastic to the bar.

Band sealers consist of two metal tapes which run over pulleys in such a way as to be parallel and close together for part of their travel. The material to be sealed is caught between the two bands and carried into a heated area where it is melted while the tapes are pressed together. Then there is a cooled area to set the seal between the two bands and carried into a heated area where it is melted while the tapes are pressed together. Then there is cooled area to set the seal before the sealed area reaches the exit end of the sealer. This makes a continuous seal and is useful for long seals.

Hot wire sealing is used in many high speed bag making machines. In this method a wire heated to a temperature where it will melt the plastic almost instantly is passed through the material to be sealed, cutting it and sealing the edges together. This makes the two seals at the same time, one each side of the cut. Side seal bags are made by this method simply by cutting the sealing the desired lengths from "J" and "U" tubing. Similar seals may be made by the hot knife method, where a heated knife is pressed against the film, cutting and sealing at the same time.

Flame sealing is used on heavy film or thicker wall constructions like collapsible tubes. The edges to be sealed are clamped together leaving a projecting edge. A flame or a high density infrared heater melts the edges, and they are clamped together by a cooled metal clamp to complete the seal.

This is by no means all of the heat sealing methods now in use, but it illustrates their variety. Bar and impulse seals are used on coated materials as well as unsupported film. In fact in some cases the principle purpose of the coating is to make this rapid method of sealing possible.

Available adhesives can make low strength seals between Polyolefin films that are satisfactory for the same purposes. These are the tacky pressure sensitive adhesives. They really never become hard and make a solid joint but are adequate just for holding film together.

Rigid Polyolefin molded parts are sometimes sealed together by ultrasonics. High frequency compression waves pass from a generator into one of the parts to be sealed together. The other part is supported on a rigid base. The ultrasonic waves produce fusion at the part interface without any great heat production. This means no part distortion and no delay for cooling, allowing fast production. The equipment is

expensive, part design must be right for the purpose, and the process has not had wide use. {Refer to 5, 12, 13 and 14}.

CHAPTER 9

POLYOLEFIN PLASTIC APPLICATIONS

9.1 Packaging

For quite a few years packaging has been the largest volume used for Polyolefins and it is one of the fastest growing industries. Polyolefins are used as film, as coatings, formed and molded containers and lids, tubes and bottles and closures.

9.1.1 Fresh Product

The first large scale civilian use of polyethylene film was in the packaging of the fresh vegetables. The moisture resistance of the film reduces moisture loss from the vegetables, thus decreasing weight loss in shipping and keeping the produce in good condition longer. The relatively high oxygen and carbon dioxide transmission of the film permits the vegetable to continue a low level of respiration in the package which is essential to retard spoilage. For some vegetables the barrier properties of the polyethylene film are too strong, so that the best storage conditions require some perforations in the bag. The use of polyethylene film for packaging produce is now so widespread that most of the vegetables or any vegetable counter will be packaged in polyethylene film.

9.1.2 Frozen Foods

Frozen vegetables are also very often packed in low density polyethylene bags. The low density polyethylene has a remarkable ability to remain tough and flexible even at low zero temperatures of food freezing. Ethylene-Vinyl Acetate copolymer show even better low temperatures flexibility and are beginning to be used in these applications. The plastic bags quite adequately serves as the sole container for the frozen food, and a large quantity is sold for this purpose, usually in the large size economy bag. In some cases the plastic bag is used inside the cartoon which serves mainly as a means of display.

Prepared frozen foods are often wrapped in the Polyolefin film sometimes in the form of multiple pouches, each of which contains a separate component of a dish or meal. This illuminates the need for a cluster of small separated containers, which are hard to package together and keep together until used.

9.1.3 Bakery Products

Bread and other bakery products are also mainly packaged in Polyolefin plastic film. Here too, low density polyethylene is most widely used, with some linear, mostly as blends with low density polyethylene, and some polypropylene, mostly as a component of the composite with low density polyethylene also being used. The low density polyethylene is the largest single item in the bakery products packaging , amounting to

about 60% of the total growing rapidly. Smaller amounts of low density polyethylene bags are used for other bakery products.

Polypropylene and linear polyethylene are used mainly for bread over wrap. When Polyolefin film manufacturers first tried to penetrate the bread wrap market, it was being served by wax paper and cellophane, which were applied on high speed wrapping machinery. It was therefore necessary to produce a film that could be used on the same wrapping machinery with a minimum modification. The main obstacle was that the low density polyethylene film was too limp to feed properly into the machines. Thus the market was first penetrated by the films made from blends of linear and low density polyethylene but these were not entirely successful. Polypropylene film was then introduced into the market but encountered the sealing problems. The next development step was the production of laminates of polypropylene and low density polyethylene. These were made with polypropylene sandwich between two low density polyethylene layers or with just one layer of each (linear polyethylene is also used in a manner similar to polypropylene). In these constructions the stiffness and resistant to "burn through" on sealing were contributed by the linear component, while easy heat sealing and tear resistance were given by the low density polyethylene. These constructions are still used as a good deal in a bread wrap and operate very well in a high speed

over-wrapped machinery. However, they are losing out through the low density polyethylene bags, mainly because consumers show a decided preference for the bag as opposed to the over wrap.

The advantages of the bag over the wrapping are its ability to be opened easily and its reclosable feature. Opening a wrapped loaf was sometimes difficult, for the film might not tear where expected, spilling the bread, etc. The bag is held close by a readily removable clip, which may be put back to reclose the bag. Once a wrapped loaf is opened, the wrapper no longer serves to keep the loaf together, while the bag remains intact, may be used to store the bread until it is gone.

As with the fresh vegetables polyethylene retards dying and keeps the bread fresh longer than other packaging methods do. The polyethylene bags are very resistant to breakage, practically eliminating the loss due to package failure.

9.1.4 Soft Goods

Soft goods packaging is another field taken over almost entirely by low density polyethylene bag packages. Soft goods encompass clothing, shirts, sweaters, sheets and blankets. These are now commonly packaged in an ingenious bag, which is essentially self closing when filled.

The bags are made by sealing and cutting across the tubing, making the side sealed bags. To fill the bag the inner flap is pulled out, the article inserted, and then outer flap is pulled, over the end of the article,. The pressure of the contents which must, of course, be a single compressible article, then halts the inner flap against the outer making a closer. Generally a strip of pressure sensitive tape is put across s the two flaps just for safety, but even without that, it is quite a secure closure.

The polyethylene bag is clear enough for the contents to be sealed. For them to be felt to some extent, tough enough withstand a rough handling, and serves to protect the contents against the soiling.

Cast polypropylene film is used to a considerable extent in the textile wrapping, and this use is growing rapidly. The superior clarity and sparkle are an advantage over polyethylene, and the stiffness results in a neater looking package. It is mainly as wrapping rather than as a bag, and polypropylene handles the better on wrapping machinery.

9.1.5 Garments Bags

Closely related to soft goods packaging but in a separate category is the laundry and dry cleaners 'shirt and garments bag'. Very thin low density polyethylene film is used for this purpose; the usual garment bag film is 0.3 mm thick.

This thickness can be used since the plastic is remarkably tough, and because the application only requires a single-short time use. The extreme thinness of the film makes it quite inexpensive. This is really the only application we will discuss where the cost becomes a major consideration in the use of plastic film. For this application the polyethylene film is the cheapest material that will do the job; in addition it is better, than paper because of its transparency, toughness and easy handling.

With many successful new plastic applications' garment bag production was made practically by a new way of dispensing the material. An extremely thin bag is too limp to be handled like a paper bag. This problem was solved by producing the bags in a continuous roll, with easily torn perforations between the bags. This roll is supported on a dispenser which hangs above a hook supported from the floor. The garment on the hanger is hung by the hook, and the bag is un-rolled from the roll and in some motion drawn over the garment. When the end of the bag reaches the top of the garment, the perforations above the bag seal are torn through a stroke of the hand separating the bag from the roll and leaving the open end of the next bag ready for use.

9.1.6 Shrink Wrap

Cotton over wrap is another and growing field for polyethylene film. In this application the primary package is a rigid paper-board carton and the polyethylene is wrapped over it to protect it from dirt and moisture, to give it gloss and often to hold it shut. This is done by wrapping a sheet of film over it and sealing the edges together on the bottom or ends, much in the same as other sheet wrapping materials are used. In recent years this method of wrapping has been changed to a great extent to shrink packaging, where a special shrinkable film is used. The package is usually placed between two sheets of film, and the edges are heat sealed all around, giving a rather loose fitting wrap. This is then run through a shrink tunnel, where hot air or infra red heaters heat the film to its shrink temperature, where it then shrinks up into a neat tight fitting wrap. In this application a certain amount of polypropylene in addition to low density polypropylene, is used. Shrink packaging is used in the overwrap field and to an increasing extent in produce wrapping, meat wrapping, and other types of wrapping.

9.1.7 Skin Packaging.

Polyolefin film and sheetings are also used in skin packaging , where the film is softened and drawn down by vacuum to conform to the contours of the object packaged. This is widely used for consumer packaging of hardware and

kitchenware items. Some of the polar copolymers and the ionomers are particularly well adapted to this application, because their toughness makes it possible to package objects with sharp corners or points, without danger of puncturing the film.

9.2 Polyolefin Coatings

9.2.1 Milk Cartons

The use of low density polyethylene on paper board to produce milk containers is one of the largest coating applications. This has almost completely replaced the wax paper carton because it is a much more durable container. In this as in many other coating applications, the polypropylene coating provides heat sealing barrier properties.

9.2.2 Pouches

As a heat seal coating on cellophane, low density polyethylene also provides needed water resistance. This material is used to form pouches for retail packaging of a wide variety of products, foods, candy, etc.

9.2.3 Skin Pack Meats

Low density polyethylene is coated on polyester or nylon film for packaging of fresh and processed meats. One example of nylon containing constructions is the skin pack packages

of processed meat , where the film is formed against the product for optimum display. Polyester film itself is not thermoplastic enough for any great amount of forming. The polyethylene on the inside seals the packages it also protects the outer ply from the moisture in the meat. These constructions in some cases have a thin vinylidene chloride layer in the center for added resistance to gas permeation.

9.2.4 Industrial Packaging

Low density polyethylene is coated into kraft paper for industrial and heavy duty wrapping. One application is as one or more plies of the multiwall bag which is very widely used for shipping industrial chemicals, as well as cement, lime, gypsum, fertilizer, and similar products. Some retail packages use this as well.

A recent development in this field is to replace the closely adhered coating with a thin polyolefin film which is tacked to the paper only in spots or lines, leaving the major part free. This gives a better barrier with the same amount of polyolefin, because the paper fibers in the coating tend to penetrate the plastic and permit leakage. The loose film is also more durable because it can stretch when subject to load, while the coating tears the paper.

9.2.5 Sugar Pouches

A very thin low density polyethylene coating is used for the single portion sugar pouches widely found in restaurants. This coating is generally so thin that it is not really water proof; it is just enough to be heat sealable, and it prevents the sugar from sticking to the paper.

9.2.6 Adhesive Applications

Polyethylene is also used as an adhesive between two plies of a laminate. Paper and aluminum foils are joined together, and the resulting construction may also have a polyethylene coating on the outside of the foil layer for heat sealability and mechanical protection. Tobacco pouches, and some food products that require special protection against moisture and gas permeation, such as powdered milk, soup mixes, etc, use this construction.

9.2.7 Boilable Pouches

Medium density polyethylene is often applied on polyester film to make boilable pouches. In this use a prepared or fresh frozen food product is packaged so that it may be placed in the boiling water until hot enough to serve. These packages are distributed for retail sales, but the largest customers are the restaurants, where the quick preparation of large variety of dishes without making an accurate estimate of what will be used at any particular meal is

needed. The saving in time, storage space, and wastage of left over food far exceeds the cost of the package.

9.2.8 Other Coating Applications

Polyethylene coatings are widely used in military packaging, often as a component of complex constructions involving paper, aluminum foil, and fabric.

White pigmented and other colored polyethylene coatings are used to provide improved appearance as well as barrier properties. Polyethylene coatings on kraft corrugated board are commonly used to improve the moisture resistance of the board and sometimes also the appearance.

Ethylene Vinyl acetate copolymer are excellent coating material and replace polyethylene in many of the above applications where extra toughness, low temperature properties, or abrasion resistance are needed, or where superior adhesion to the substrate is required. This is a small but rapidly growing segment of the coating field. They also have an advantage where high pigment loadings are required for a very opaque coating, because they can take higher pigment loadings without loss of physical properties.

High density polyethylene gives a coating with improved grease resistance and reduced gas permeability; however,

consumption in coatings is still small because of processing difficulties. Most of the high density polyethylene used in coating is blended with low density.

9.2.9 Hot Melt Coatings:

Polyolefins in the form of EVA copolymers, are an important part of a rapidly growing hot melt coating business. Starting out simply as wax additives used to improve wax coatings, EVA containing hot melt coatings have developed into large family of high grade coatings far superior to wax. These coatings typically consist of a mixture of copolymer, a resin which may be wood rosin derivative, a hydrocarbon resin, polyterpene resin, or low molecular weight polystyrene and a wax. The wax primarily is the major component, but depending on application, the other components may also be quit large. Similar compositions are also used as hot melt adhesives.

While hot melt coatings are not generally as durable as pure olefin extrusion coatings, they can be formulated to serve a wide variety of [purposes. They have excellent sealability and show better performance in some high speed sealing operations than olefin coatings.

One of their main advantages is that they can be applied by coating equipment, which is less expensive than an extrusion coating line.

9.3 Containers and Lids

9.3.1 Reclosable Lids

The largest single item in this category is the low density polyethylene lid used for reclosing coffee cans, shortening cans, and many other kinds of cans. This is a recent and very rapidly growing application, and is in the process of being extended to any canned item, where the contents are not ordinarily used at one time. They can with separate polyethylene lid commonly replaces the key opening type cans, which are more expensive, hard to open, and often cut people. These lids are injection molded on very short cycles, making it possible to produce them in large numbers at a low cost.

9.3.2 Thermoformed Containers

Low wide containers in quart, pint, and smaller sizes are used are used for sour cream, cottage cheese and many prepared foods that refrigeration but not sterilization. These are made of various plastics but high density polyethylene is being used in phi numbers. The margarine tub in particular is being made mainly of high density polyethylene. These containers are generally vacuum formed out of sheeting, although some are injection molded. Injection molding requires thicker walls, so is more expensive but makes a more durable container.

Large scale trial production of lubricating oils cans has been started, using high density polyethylene thermoformed sheet.

9.4 Bottles and Tubes

9.4.1 Bleach and Detergent Bottles

High density polyethylene is the large scale blown bottle resin. Bleach and detergent bottles are the largest applications at present. Scouring powder, distilled water, lubricating oil, and many non food uses are very common. The light weight and shock resistance give the polyethylene bottle a great advantage over the glass container, especially in large sizes where the glass bottle is quite fragile.

9.4.2 Drug Bottles

High density polyethylene bottles are also used widely in packaging of drugs. Recent research has shown that drug preparations that do not have components which permeate polyethylene are protected as well in polyethylene bottle as in glass. This includes almost any thing in the form of pills or capsules, as well as dry powders.

The office of the Surgeon General of Army initiated a study of the compatibility and stability of plastic containers for the 96 drugs most widely used by the Army

After a preliminary evaluation of the possible plastics, it was decided to make the study with high density polyethylene. The reason for this choice of plastic were economy and utility.

At the time the program was initiated, 99% of all plastic bottles were made of polyethylene. While there are other materials that have specific advantages for some special purposes, none of them have a broad enough applicability to warrant large scale investigations.

Inertness is probably the best single index of the suitability of a material for drug packaging. The fact that the material is inert means that there will be no reaction with the product. If there is a low order of solubility of the product in the polymer, then there will be little permeability or transfer of product through container walls.

The olefin collectively, low and high density polyethylene and polypropylene are outstanding in chemical resistance. They will dissolve only in hot solvents. If the polyolefins are compared to glass for instance, glass will dissolve in the hydrofluoric acid at room temperature, while polyethylene is the standard packaging material for it. Long storage of aqueous solutions in glass containers at room temperature will cause sodium and silicon, as well as other

glass components, to dissolve in solution; nothing of this sort happens with polyethylene.

With the exception of some fluorine containing polymers, polyethylene is the most inert available material, and from the practical; point of view the cost of fluorinated polymers is prohibitive.

Water vapor permeability is important in drug packaging material, and in the study the polyethylene was found adequate to the extent that the conditioning at 14 and 80 percent relative humidity at same temperature showed no effect on product stability.

High density polyethylene is a relatively poor barrier to oxygen, yet there was no evidence during the two year study that any of the 96 pharmaceuticals had undergone degradation because of oxygen entry into the packaging.

9.4.3 Milk Bottles

Linear polyethylene milk bottles have had small scale use for several years. They come in two forms, a returnable bottle for home delivery, which has also had some success in the gallon size in the supermarket business. While various dairies are using one or the other of these with considerable success, this must still be considered an experimental application. The possibilities inherent in this

application will be discussed in the chapter on the future of polyolefins.

The use of polyolefin milk containers is more widespread in Europe, where the single trip container, in the small sizes common there, has taken the form of thin walled flexible pouches. This pouch is generally vacuum formed from thin sheet and heat sealed around the edges. It has achieved a considerable degree of sophistication. One form is made from coextruded black and white sheeting, black on the inside to prevent the penetration of light which deteriorates milk flavor, and white on the outside for an attractive look. It is often heat sealed and opened by tearing and cutting, because, in Europe where home refrigeration is not common, milk is usually not stored after opening.

9.4.4 Squeeze Bottles

Low density squeeze bottles were the first large scale use of the polyolefin plastic bottles. In this application the bottle acted as dispenser as well as container, hence justifying the increased cost over glass. Although low density bottles continue to be used in considerable volume, it has been overshadowed by the high density bottle.

9.4.5 Closures

This application uses considerable volume of both high and low density polyethylene. The closure may also act as

dispenser. Bottle caps and tooth paste tube caps are examples. One advantage of low density polyethylene in these applications is that the material is resilient enough so that it does not require a gasket to form a tight seal. Polyethylene also has a surface that is slippery enough so that the cap does not stick tightly, as caps made of many other materials often do. The light weight and rapid molding cycles possible with low density polyethylene make it one of the most economical closure materials in cost per part.

9.5 Automotive Applications

The polyolefins have done much to convince the automaker that plastics were not cheap, breakable materials, unsuited to hard service in an automobile. Auto makers show a willingness to examine polyolefin plastics with the idea of using their unique properties to improve quality and cut costs.

An example of this is the polypropylene accelerator pedal with integral hinge. This replaced a molded rubber and metal part, in which the metal hinge very often failed prematurely due to rust and to grit. The hinge in the polypropylene pedal is a thin area in the plastic, which has excellent flex life and is completely immune to corrosion or dust. Another recent application based on the same property is an injection molded glove box with integral molded hinge.

Other propylene applications are an injection molded arm rest insert, and an injection molded heater deflector. A glass filled polypropylene formulation has been successful as a fan shroud. Expanded, rubber modified polypropylene has been used for a sun visor.

Linear polypropylene has been used for cowl side kick panels. The traditional painted hardboard rapidly deteriorated in service. The injection molded polyolefin plastic part was molded in color to match the interior and required no painting. Incorporating the wind lace at one edge eliminated the need of a separate windlace, so a great improvement in quality was accomplished at no net cost increase.

Thermoformed linear polyethylene truck door trim panels have also been successful. Die-cut polyethylene foam has seen considerable use in body gasket, like that used to seal tail lamps.

The largest single polyolefin piece used in an automobile is the linear polyethylene fender filler plate, which weighs upto six pounds. This is the plate that fits between the fender and the wheel, forming the wheel well. The polyolefin plate is completely corrosion resistant, which is very important in this location, for it is constantly exposed to moisture and corrosive material, such as the salts used for

deicing roads. The plastic requires no protective finish and does not show the tendency to rattle that metal plates have. It has so far only been used on a few cars, but it appears to be very satisfactory.

Polypropylene has been used in a variety of spots, such as an air conditioner blower wheel, air conditioner and defroster ducts, and for the backs of bucket seats.

9.6 Housewares

A wide variety of containers ranging from garbage cans through wash baskets, wastebaskets, hampers, on down to freeze containers, bowls, pitchers, and finally to salt or spices shakers are all made of polyethylene. Generally, a mixture of high and low density is used for injection molding these items. Some are made by blow molding, and material is then pure linear polyethylene.

Polypropylene has recently moved into this area on a large scale, both in the traditional lines and in some special items using its particular properties. For instance, a line of syrup servers uses the molded hinge to cover the spout. The exceptional ability of polypropylene to reproduce molded surface finish is used in wood grain and other special surface finishes which gives the part a high style appearance. The grain finish has appeared on a wide variety

of items not merely in the kitchen but appropriate to other rooms as well.

9.7 Appliances

Polyolefins are still a relatively small factor in the appliance field, but they are growing more rapidly than the major competitors in this field.

9.7.1 Major Appliances

Polypropylene is a favorite material for washing machine agitators, for baskets in dish washers, driers and clothes washers, and in general for any application requiring resistance to water, heat, and detergents. It is also used for pumps, fans, fan shrouds, and for many small parts.

In one dish washer there are 23 parts made of glass reinforced polypropylene.

9.7.2 Small Appliances

The small appliances, vacuum cleaners, blenders, and mixers, can openers, electric knives, vibrators, electric tooth brushes, razors etc. also consume a good deal of polyolefin plastics. The polyolefins are used as housings, cabinets, handles, knobs, and decorative features.

9.8 Building Construction

The polyolefins do not have a large share of the huge construction market. Their largest single use in this field is as film for vapor barrier.

The vapor barrier is of low density polyethylene film, the profile extrusions are of linear, and the pipe, fittings and conduits are of both. The use of copolymers of ethylene and polar monomers in some of the flexible profile extrusion used for gasketting and sealing is growing. It replaces flexible vinyl in these applications and achieves better low temperature flexibility and longer service life.

Chlorinated polyethylene is starting to be used in the roofing of commercial buildings, but this is not yet a large use. The growing use of cross-linked polyethylene in insulating electrical wire will be discussed under electrical applications.

9.9 Toys

The polyolefins are a considerable part of the plastics used in the toys. The polyolefins are the fastest growing material in this field, reflecting a continuing trend towards upgrading toys and making them safer.

The most popular method of fabrication is injection molding, and a tremendous number of injection molded polyolefin toys

is on the market. Blow molding is also used. Doll bodies are used in this way generally from linear polyethylene. Blocks, toy vehicle bodies, boats, and similar items also molded.

EVA copolymers are finding a small market in speciality items that require extra flexibility, like bellows, and for movable parts.

9.10 Artificial Flowers

Injection molded low density polyethylene artificial flowers and plants have nearly replaced all other kinds of artificial flowers and plants have nearly replaced all other kinds of artificial flowers. They are available in realistic copies of natural flowers, and also in the imaginative forms unlike anything that has ever grown. Plants of considerable size are used to decorate hotel and store lobbies almost to the exclusion of real plants.

Since these plants and flowers are usually made by the assembly of individual petals and leaves, a great deal of hand labor is involved. For this reason they are made in places where labor is cheap. Hong Kong has been the center for polyethylene flower market for years.

9.11 Electrical uses

Wire and cables is a large user of polyolefins. The main use of the low density polyethylene was in telephone cable insulation and jacketing. High density polyethylene was used for jacketing of buried cables, particularly those conforming to specifications Rural Electrification Administration (REA), because of its improved abrasion resistance. Foamed polyethylene was used mainly for dielectric in coaxial cable, and its big use was for cable TV installations.

Cross linkable polyethylene has become the main material used for the outer jacketing of power cable. This use is growing very rapidly because of the underground residential distribution (URD) program, the program for burying power distribution in residential areas, both for new construction and for area renovation. Cross-linkable polyethylene is also rapidly displacing rubber and vinyl in the medium voltage power distribution field.

Ethylene Vinyl Acetate (EVA) copolymers with a low level of comonomers are replacing low density polyethylene in some of its largest scale uses, like in telephone cable sheathing, because of their superior low temperature flexibility and resistance to stress checking.

Polyolefins are also finding their way into new electrical applications such as being substrates of flexible circuits, where polyethylene, polypropylene and ethylene ethyl acrylic (EEA) copolymers have been used. These flexible circuits are being considered for the replacement of the conventional automotive wiring, as well as for the electronics industry where they are now being used.

During the past year a new method soldering multilayer circuit board was developed. This consists of a sheets of radiation cross-linked Polyolefin which has precisely formed pockets containing balls of solder. When heated, the Polyolefin shrinks and forces the solder up into minute termination points. This is said to give superior solder into place when hot.

9.12 Agricultural Applications

Polyolefins, especially low density polyethylene, have a considerable use for agricultural purposes. The largest of these is for agricultural mulches in which a sheet of plastic is laid down the row in a field, and the crop is planted through holes in the plastic. Special machinery has been devised to lay the plastic down very rapidly, and at the same time to turn a strip of dirt over both edges to hold it down. This mulch increases soil temperature equally in the season, conserves water, prevents soil caking and packing, and reduces fertilizers washout. In many crops the

increased yields outweigh the considerable cost of mulch. Strawberries, for instance, are grown in considerable quantity under polyethylene.

These houses are generally of light frame construction and in cold areas will consist of layer of polyethylene film both outside the frame and inside, leaving an air space for insulation. The green house may be heated by warm air distributed through polyethylene tubing ducts. In regions of heavy sunlight exposure a polyethylene film covered usually lasts only a season, but in northern countries where the summers are cool and short they may last several years. It is also possible to put an ultra violet light inhibitor in the film to increase its life.

Polyolefin film has many uses on the farm for the temporary protection of materials and produce.

It is possible, for instance, to make a "silo" that satisfactorily stores ensilage simply by putting down a sheet of heavy gage polyethylene film, piling the ensilage on the sheet and covering this with another sheet, sealing the edges by folding them together and covering them with dirt. Black film is necessary at least for the top sheet because light will spoil the ensilage. A "silo" of this sort will keep fodder in good condition for an entire winter. It is inexpensive to make, and it may be placed near either

where the crop was grown, or where it will be used, to reduce the hauling.

Wire mesh coops for chickens and other small animals can be wrapped with polyethylene film in severe weather for protection. The nursery industry uses Polyolefin film and Polyolefin coated paper to a great extent. The roots of dug plants and in many cases the entire plant are protected from drying a polyethylene bag or a wrapping of polyethylene coated paper. Polyethylene film is also used as a water proofing liner for farm ponds and irrigation ditches to prevent water loss. Bags made of oriented Polyolefin tapes are finding increased use as heavy duty sacking, and for use as sand bags for flood protection, and even for permanent control purposes. Polyethylene pipe is widely used for irrigation and for farm water systems. Its flexibility makes it very convenient for use in wells because continuous lengths for the entire depth of the well can be used. for use with the popular jet well system a special form of pipe containing both a small high pressure tube and a larger low pressure tube all made in one piece, makes installation possible in smaller bores than possible with two separate pipes. Pipe made of very high molecular weight, linear polyethylene is finding increased application. Lacking the flexibility of low density pipe, it must be used in straight lengths like metal pipe and hence, require many couplings in a long run. It is much stronger; it can be used for higher

pressures; and it can withstand domestic hot water temperatures. While not yet a large factor in the plastics pipe business, it is growing rapidly. Very large high density polyethylene pipe with diameters up to 40 inch is made for irrigation purposes. While pipe of this size is not flexible in the usual sense, it is flexible enough so, that long sections extending over many freight costs can be moved by rail. The pipe can flex enough to permit the train to round any curve.

9.13 Telephone Jacketing

In the United States, polyethylene for use as telephone jacketing was pioneered by Bell Telephone Laboratories and Union Carbide Corporation in the late 1940's. Over the years the more stringent requirements for weather resistance, toughness, permanence, environmental stress crack resistance, and extrudability were met by a succession of improved jacketing compounds. A major breakthrough occurred in the 1960's with the development of EVA copolymers, which further improved these overall physical properties.

9.14 Insulation for Submarine Cable

The development of Polyethylene for primary telephone insulation has been as dramatic as that of jacketing.

In the 1950's under water cable insulated with polyethylene resin helped open up a new era in intercontinental ocean telephone communications; many thousands of miles of this cable have been performing continuously for more than 25 years.

At the time, electrical property requirements were much less stringent than those now in effect for today's broad band cables, in the first generation submarine cables, low density polyethylene served as the dielectric between the coaxial conductors.

As cable requirements became more demanding new polyethylene insulations had to be developed. These new resins provide a lower level of contamination and a very low dissipation factor.

9.15 Primary Telephone Insulation

For many years low density polyethylene was used as the primary insulation for multi-pair cable constructions. This material was considered the standard for both underground as well as overhead cable in the 1940's, 1950's and into the early 1960's. During the 1960's, when processing equipment improved, there was a need to modify LPDE so it would run at higher speeds. Today many cables are made with these LPDE's and run successfully at these high rates.

In the late 1960's and early 1970's HDPE begin to find use as a primary telephone insulation. HDPE is inherently tougher material and is used in both overhead air-core cable and direct buried jelly filled cables. HDPE insulation is less prone to damage and also resists the attack of the jelly filler in filled cable, yielding a cable with better capacitance stability.

9.16 Power cable

The overall use of the polyethylene for power cables has been growing rapidly in recent years.

In subsequent years, specifications evolved that required polyethylene used for power cable to be cleaner, more uniform and have even better physical and electrical properties. Thermoplastic PE has provided the continues to provide excellent service for medium voltage power cable insulation. {Refer to 1,4,5,6,10 and 11}.

CHAPTER 10

DISCUSSION AND CONCLUSION

Polyolefin is one of the top volume thermoplastics used in the world today. Sales in the U.S. alone exceed 10 billion pounds annually. Resin producers and processors continue to stretch the performance of polyolefins grades conversion processes and product assuring the continued growth of this material into 1990's.

Looking into future, it appears very likely that polyolefins plastics production costs will continue to decline. There has been a tremendous increase in ethylene production capacity in recent years. This capacity has been in the form of very large single train production tires, with much lower production costs than lines built earlier. Since markets for the new capacity are not yet visible, it appears likely that there will be a great over-capacity of ethylene. This situation will almost inevitably bring ethylene prices down nearly to the low production costs of the new plants.

At the same time new polymerization techniques are reducing the polymerization costs of polyolefins. The tremendous strides achieved in the understanding of catalysts, for instance, makes it possible to produce catalysts so efficient that the costly catalyst removal steps here therefore needed for linear polyethylene and polypropylene,

can be eliminated and this ability will undoubtedly soon be extended to all polyolefins.

Polyolefins are the lightest of all the plastics so their price per unit volume is in fact lower than the per pound price would imitate and their production in terms of volume is proportionally even greater than their production in pounds. It is almost impossible to separate resin developments from the processing methods now under developments. To a great extent it is new resin developments that make possible revolutionary processing changes. The ability of the polyolefin producer to tailor a resin to meet specific use requirement has progressed enormously.

High-density polyethylene is the oldest of the linear, having been introduced in 1957. It is characterized by density above 0.94; provides stiffness, toughness, good environmental stress-crack resistance and low temperature properties and has found wide use in many major markets. Some examples are blow molded containers, injection molded parts, extruded pipe and profiles and rotationally molded large hollow parts.

Linear low density polyethylene is one of the newer linear having first appeared widely in 1980, though grades were available commercially as far back as the 1960's. Its density is generally 0.940. The greatest market penetration by linear low density polyethylene has been in blown and cast films for stretch applications grocery and heavy-duty

shipping sacks, other film uses include diaper liners, household food wraps.

Ultralow-density polyethylene is a new class of linear polyethylenes with densities between 0.89 and 0.9515. It provides flexibility plus toughness and a broad operating temperature range and is finding use in film and sheet applications. Polyolefin plastics have penetrated almost every aspect of modern life. Traditional markets for polyolefins are in packaging films, extrusion coating of paper, wire and cable coating, injection molding pipe tubing and containers.

The steady penetration of polyolefins into the automotive market is being accelerated by the development of plating techniques which will permit the use of polyolefin plastics on all exterior trim as interior trim and finish items. A recent application of linear polyethylene as automotive fender filler plates is the largest single item in terms of pounds per car that has yet been developed. This could well be the start of use of polyolefins on a large scale in automotive structure.

Polyolefins are one of the fastest growing segments in the plastics recycling market. This is due to its ability to be reprocessed readily with minimal degradation of properties and its large use in packaging applications. A typical recycling application includes 25% of recycled material such as post consumer recycle, with virgin high density

polyethylene and is reprocessed and used for non-food contact bottles.

The significance of polyolefin has grown immensely since that first 8 gram of a white, powdery solid were scraped off the walls of a reaction vessel approximately 50 years ago. The next 50 years offer technological challenges that will be continued, directed process and product research.

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