

Chapter 1

HOW PLASTICS ARE MADE

Introduction

Plastic materials display properties that are unique when compared to other materials and have contributed greatly to the quality of our everyday life. Plastics, properly applied, will perform functions at a cost that other materials cannot match. Many natural plastics exist such as shellac, rubber, asphalt and cellulose. However, it is man's ability to synthetically create a broad range of materials demonstrating various useful properties that have further enhanced our lives. Plastics are used in our clothing, housing, automobiles, aircraft, packaging, electronics, signs, recreation items and medical implants, to name a few of their many applications.

Most plastics are different from other materials such as glass, steel and aluminum because they can CREEP or change shape when stressed. Ignoring this fact is the greatest cause of failures in designs using plastics. This subject is discussed in greater detail throughout the manual.

History of Plastics

The synthetic plastic industry started in 1909 with the development of a phenol formaldehyde plastic (Bakelite) by Dr. L. H. Baekeland. The phenolic materials are, even today, important engineering plastics. The development of additional materials continued, and the industry really began to blossom in the late 1930s. The chemistry for nylons, urethanes and fluorocarbon plastics were developed; the production of cellulose acetate, melamine and styrene molding compounds began; equipment to perform the molding and vacuum forming processes was made commercially available.

Acrylic sheet was widely used in aircraft windows and canopies during World War II. A transparent polyester resin (CR-39), vinylidene chloride film (Saran), polyethylene and silicone resins were also developed. The first polyethylene bottles and cellulose acetate toothpaste tubes were manufactured during this time period.

The post war era saw the production of vinyl resins, the use of vinyl films, the introduction of molded automotive acrylic taillights and back-lighted signs, and the development of the first etched circuit boards. The injection molding process entered commercial production.

Due to the newness of the materials, the properties and behaviors of the plastic materials were not completely understood. Many products were introduced that failed, creating a negative impression about plastics in the public's mind.

Chemists continued the development of materials such as ABS, acetals, polyvinyl fluoride, ionomers and polycarbonate. The injection molding, thermoforming, extrusion, transfer molding and casting processes were all improved. This allowed the industry to provide an even greater number of cost-effective products suitable for many, more demanding engineering applications.

Occasionally, plastics are still improperly used and draw negative comments. The thousands of successful applications that contribute to the quality of our life are seldom noticed and are taken for granted. Remember, materials don't fail, designs do.

The number of variations or formulations possible by combining the many chemical elements is virtually endless. This variety also makes the job of selecting the best material for a given application a challenge. The plastics industry provides a dynamic and exciting opportunity.

How Plastics are Made

Plastics encompass a large and varied group of materials consisting of different combinations or formulations of carbon, oxygen, hydrogen, nitrogen and other elements. Most plastics are a solid in finished form; however, at some stage of their existence, they are made to flow and may be formed into various shapes. The forming is usually done through the application, either singly or together, of heat and pressure. There are over 50 different, unique families of plastics in commercial use today and each family may have dozens of variations.

Polymerization

How are plastics made? The word "mer" is a Greek word that means "part." This part of a plastic is a unique combination of atoms combining to form molecules which are called "monomers." It is like a single link in a chain. "Mono" means "one"; therefore, "monomer" means "one part." The monomers are then

joined together to make long chains that result in a material with a useful blend of properties. Using another Greek word "poly" which means "many," the long chain of "mers" forms a "polymer." The monomers are held together in a polymer chain by very strong attractive forces between molecules. Much weaker forces hold the polymer chains together. The polymer chains can be constructed in many ways. Some simplified examples of the way polymers are built are shown in Figures 1.1-1.5:

MONOMERS: A, B, C

Examples of monomers are ethylene, styrene, vinyl chloride and propylene.



Figure 1.1

HOMOPOLYMERS: A-A-A-A-A-A-A-A

Homopolymers are polymers constructed from joining like monomers.

Some examples of polymers built this way are polyethylene, polystyrene and PVC.

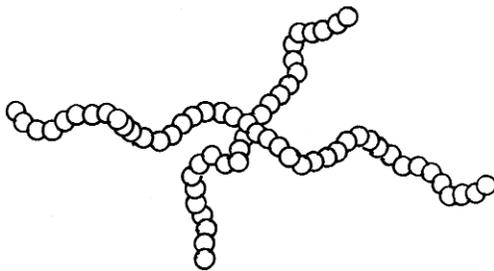


Figure 1.2

COPOLYMERS

Copolymers are polymers constructed from two different monomers.

ALTERNATING TYPES: A-A-A-B-A-A-A-B-A-A-A-B

Some examples of alternating copolymers are ethylene-acrylic and ethylene-ethyl acrylate.

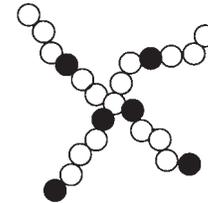
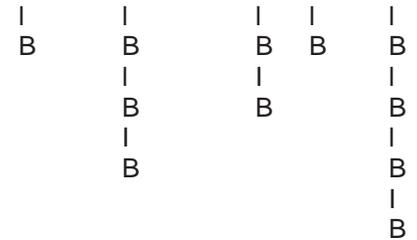


Figure 1.3

GRAFT TYPES: A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-



Some examples of grafted copolymers are styrene-butadiene, styrene-acrylonitrile and some acetals.

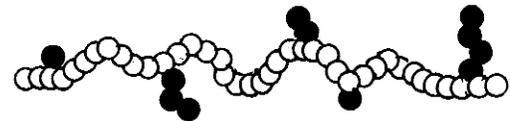


Figure 1.4

TERPOLYMERS: A-A-A-B-C-C-A-A-A-B-C-C

Terpolymers are polymers constructed from three different materials.

An example of a terpolymer is acrylonitrile-butadiene-styrene (ABS).



Figure 1.5

The two monomers in a copolymer are combined during the chemical reaction of polymerization. Materials called “alloys” are manufactured by the simple mixing of two or more polymers with a resulting blending of properties which are often better than either individual material. There is no chemical reaction in this process. Some examples of “alloys” are polyphenylene oxide-high-impact styrene, polycarbonate-ABS and ABS-PVC.

Molecular Weight

It is important for the chemist to know how long the polymer chains are in a material. Changing the length of the chains in a thermoplastic material will change its final properties and how easily it can be shaped when it is melted.

The “repeating unit” or molecular group in the homopolymer is A- (Figure 1.2), the group of molecules in the copolymer A-B- (Figure 1.3), and in the terpolymer A-B-C- (Figure 1.5). The number of repeating units in the polymer chain is called the “degree of polymerization.” If the repeating unit has a molecular weight (the combined weight of all of the molecules in the repeating unit) of 60 and the chain or polymer has 1,000 repeating units, then the polymer has an average “molecular weight” of $60 \times 1,000 = 60,000$. The molecular weight is a way of measuring the length of the polymer chains in a given material.

The molecular weight of plastics is usually between 10,000 and 1,000,000. It becomes increasingly difficult to form or mold the plastic with the application of heat and pressure as the molecular weight increases. A molecular weight of about 200,000 is about the maximum for a polymer to still permit reasonable processability. Some higher molecular weight materials, like ultra-high-molecular-weight-polyethylene (UHMW-PE), that has a molecular weight from 3,000,000 to 6,000,000, can be cast using processes specifically designed to shape it.

Crystalline and Amorphous Materials

Polymers are often described as being either crystalline or amorphous when it is actually more accurate to describe plastics by their “degree of crystallinity.” Polymers cannot be 100 percent crystalline, otherwise they would not be able to melt due to the highly organized structure. Therefore, most polymers are considered semi-crystalline materials with a maximum of 80 percent crystallinity.

Amorphous materials have no patterned order between the molecules and can be likened to a bowl of wet spaghetti. Amorphous materials include atactic polymers since the molecular structure does not gener-

ally result in crystallization. Examples of these types of amorphous plastics include polystyrene, PVC and atactic polypropylene. Presence of polar groups, such as a carbonyl group CO, in vinyl type polymers also restrict crystallization. Polyvinyl acetate, all polyacrylates and polymethacrylates are examples of carbonyl groups being present and the resulting polymers being amorphous. Polyacrylonitrile is an exception to this since carbonyl groups are present in their structure but they also crystallize. Even amorphous materials can have a degree of crystallinity with the formation of crystallites throughout their structure. The degree of crystallinity is an inherent characteristic of each polymer but may also be affected or controlled by processes such as polymerization and molding.

Crystalline materials exhibit areas of highly organized and tightly packed molecules. These areas of crystallinity are called spherulites and can be varied in shape and size with amorphous areas between the crystallites. The length of polymers contributes to their ability to crystallize as the chains pack closely together, as well as overlapping and aligning the atoms of the molecules in a repeating lattice structure. Polymers with a backbone of carbon and oxygen, such as acetals, readily crystallize. Plastic materials such as nylon, and other polyamides, crystallize due to the parallel chains and strong hydrogen bonds of the carbonyl and amine groups. Polyethylene is crystalline because the chains are highly regular and easily aligned. Polytetrafluoroethylene (PTFE) is also highly symmetric, like polyethylene, with fluorine atoms replacing all the hydrogens along the carbon backbone. It, too, is highly crystalline. Isomer structures also affect the degree of crystallinity. As the atactic stereochemistry resulted in amorphous polymers, those that are isotactic and syndiotactic result in crystalline structures forming as chains align to form crystallites. These stereospecific forms of polypropylene are those which are preferable for structural applications due to their degree of crystallinity.

The degree of crystallinity affects many polymeric properties. In turn, other characteristics and processes affect the degree of crystallinity. Molecular weight will affect the crystallinity of polymers. The higher the molecular weight the lower the degree of crystallinity, and the areas of crystallites are more imperfect. The degree of crystallinity is also dependent on the time available for crystallization to occur. Processors can use this to their advantage by quenching or annealing to control the time for crystallization to occur. Highly branched polymers tend to have lower degrees of crystallinity, as is easily seen in the difference between branched low-density polyethylene (LDPE) and the more crystalline high-density polyethylene (HDPE). LDPE is very flexible, less dense, and more transparent than HDPE. This is an excellent example that the same polymer can have

varied degrees of crystallinity. Stress can also result in increased crystallinity as polymer chains align orienting the crystallites. Drawing fibers, the direction of extrusion, and gate placement will also affect the orientation of polymers and therefore the crystallites of the material. This allows the processor to maximize the effects and benefits of the inherent crystallinity of the polymer being used in an application. The chart below describes other general effects due to the degree of crystallinity in a polymer.

COMMON CHARACTERISTICS OF CRYSTALLINE AND AMORPHOUS PLASTICS	
Higher Percent Crystalline <ul style="list-style-type: none"> • Higher heat resistance • Sharper melting point • More opaque • Greater shrinkage upon cooling • Reduced low temperature toughness • Higher dimensional stability • Lower creep 	Higher Percent Amorphous <ul style="list-style-type: none"> • Lower heat resistance • Gradual softening/melting point • More translucent/transparent • Lower shrinkage upon cooling • Greater low temperature toughness • Lower dimensional stability • Higher creep

Thermoplastic and Thermoset Materials

The terms thermoset and thermoplastic have been traditionally used to describe the different types of plastic materials. A **thermoset** allows only one chance to liquefy and shape it. These materials can be cured or polymerized using heat and pressure, or as with epoxies, a chemical reaction started by a chemical initiator.

A **thermoplastic** can be melted and shaped several times. The thermoplastic materials are either crystalline or amorphous. Advances in chemistry have made the distinction between crystalline and amorphous less clear, since some materials like nylon are formulated both as a crystalline material and as an amorphous material.

Again, the advances in chemistry make it possible for a chemist to construct a material to be either thermoset or thermoplastic. The main difference between the two classes of materials is whether the polymer chains remain linear and separate after molding (like

spaghetti) or whether they undergo a chemical change and form a network (like a net) by cross-linking. Generally, a cross-linked material is a thermoset and cannot be reshaped. Due to recent advances in polymer chemistry, the exceptions to this rule are continually growing. These materials are actually cross-linked thermoplastics with the cross-linking occurring either during the processing or during the annealing cycle. The linear materials are thermoplastic and are chemically unchanged during molding (except for possible degradation) and can be reshaped again and again.

As previously discussed, cross-linking can be initiated by heat, chemical agents, irradiation or a combination of these. Theoretically, any linear plastic can be made into a cross-linked plastic with some modification to the molecule so that the cross-links form in orderly positions to maximize properties. It is conceivable that, in time, all materials could be available in both linear and cross-linked formulations.

The formulation of a material, cross-linked or linear, will determine the processes that can be used to successfully shape the material. Generally, cross-linked materials (thermosets) demonstrate better properties, such as improved resistance to heat, less creep and better chemical resistance than their linear counterpart; however, they will generally require a more complex process to produce a part, rod, sheet or tube.

SOME EXAMPLES OF THE VARIOUS TYPES OF MATERIALS
Linear Thermoplastics <ul style="list-style-type: none"> • PVC • Nylon • Acrylic • Polycarbonate • ABS
Thermoplastics That Can Be Cross-linked After Processing <ul style="list-style-type: none"> • PEEK • Polyamide-imide • UHMW-PE
Thermosets <ul style="list-style-type: none"> • Phenolics • Epoxies • Melamines