

Practical Rheology Section 1

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Plastics and Polymers

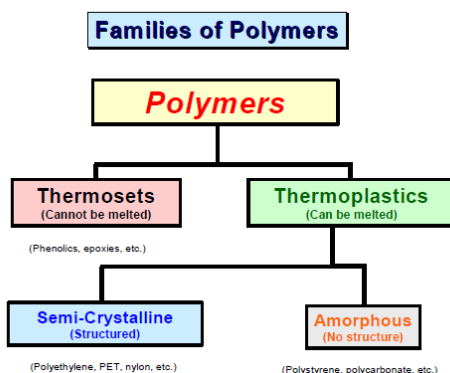
Over the past 50 years the use of plastics materials throughout the world has increased dramatically and now stands at approximately 100 billion pounds.

Polymers.

Most commercial plastics, also known as resins in North America, are composed of polymers, with which modifying or stabilizing additives have been compounded. Polymer molecules are generally based on the element carbon and are manufactured from simple, oil-based raw materials. Small molecules, which are the starting materials for polymers, are called monomers. These small molecules are combined, by a process known as polymerization, to form very large molecules or polymers. The term polymer arises from the fact that the final product consists of many, identical, repeating molecule units. Because the final size (or length) of these molecules and thus their molecular weight, or mass, is generally very large, the polymer may also be referred to as a 'high polymer' or, as a 'macromolecule'. All plastics are polymers, but not all polymers are plastics. Many natural products, such as cellulose, are polymers, but they cannot be processed like a commercial plastic material unless they are modified from their natural form.

Types Of Plastics Material

A plastic material is defined as a compound of polymer plus additives, which is capable of being shaped or molded, into a useful product, under conditions of moderate temperature and pressure. Generally, plastics are distinguished from rubbers or elastomers, by their higher stiffness/modulus and a lack of reversible elasticity. There are two main categories of plastic, thermoplastics and thermosetting plastics (thermosets). Thermoplastic products, for example injection molding or extrusion resins, may be repeatedly softened, melted, and reshaped (or recycled), whereas thermoset products cannot. In terms of tonnage, thermoplastics are by far the more important. When the polymer in the plastic is based on one monomer it is known as a 'homopolymer'. When the polymer used is based on two or more monomers it is known as a 'copolymer.'



Amorphous And Crystalline.

Thermoplastic materials may be further divided into two main categories, amorphous and semi-crystalline. An amorphous thermoplastic material has no uniform molecular structure and is usually a hard, clear, rigid material with low shrinkage, such as polystyrene. A crystalline polymer has an organized ("crystal-like") structure, but also contains amorphous material and is generally referred to as a semi-crystalline thermoplastic material. Such plastics are usually tougher and less brittle than amorphous thermoplastics and may have a higher heat distortion temperature. Such plastics are also translucent, or opaque, have a high shrinkage and a high specific heat. The best-known example of a semi-crystalline, thermoplastic material is polyethylene. (Note: Clear polystyrene is sometimes called as "crystal polystyrene". Polystyrene is an amorphous polymer, however, so this name refers to the fact that it is "crystal clear" and not a crystalline thermoplastic.) Both amorphous and semi-crystalline thermoplastics are commonly tested by rheometry and are widely used in rheological studies.

NAMES AND ABBREVIATIONS FOR THERMOPLASTICS

Of the two major types of plastics, thermoplastics and thermosets, thermoplastics are by far the ones most studied in rheology, therefore, this section will focus only on the major types of thermoplastic material.

Polymer Structure

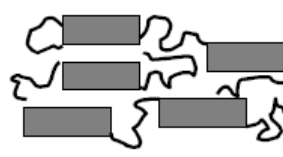
Solid State Structure of Thermoplastics



Amorphous

No polymer structure.

Examples: Polystyrene
Polycarbonate
PMMA



Semi-Crystalline

Contains both crystalline (ordered) and amorphous polymer.

Examples: Polyethylene
Polypropylene
PET
Polyamides (nylon)

Common Names.

Most thermoplastics begin with 'poly', which means 'many' followed by the name for the monomer from which the plastic is derived. (i.e., the name is source-based.) As the result of this practice we get names such as polystyrene and polyethylene for homopolymers. When the plastic material has more than one word in the name, parentheses (or brackets) may be put around the words so that we get poly (vinyl chloride). This practice is, however, not universal and one may also see the same term without the brackets i.e. polyvinyl chloride. Since source-based nomenclature is not universally used, so names such as 'acetals' and 'cellulosics' also may be encountered. To add to the confusion, many plastics are known by more than one name. For example, acetals may be known as polyformaldehyde or polyoxy-methylene. When this is so, then the alternative name(s) should be listed. Some common names and alternative names of thermoplastics are given in Table 2.

Abbreviations

Because of the complex, chemical names used to describe polymers, they are frequently referred to by abbreviations. Such abbreviations take the form of a short string of capital letters, where each capital letter refers to a part of the common name. If the plastic material begins with 'poly' then the first letter is P and the other letter(s) are derived from the monomer unit. Names such as polystyrene and polyethylene are thus shortened to PS and PE respectively (See Table 2.). Copolymers are often referred to by means of initials, which represent the monomers used i.e. without a "P" for "poly". For example, the copolymer made from styrene and acrylonitrile is referred to as styrene acrylonitrile copolymer or as SAN. When mixtures are made from two or more polymers (blends or alloys), they are commonly represented by the abbreviations used for the individual materials, but each abbreviation is separated by an oblique stroke, for example, SAN/EVA. Some Relevant Standards Many standards organizations {for example, the American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO)} issue standards that specify what letters shall be used in naming plastics. See ASTM standard D1600-86 (that is standard number D1600 revised/published in 1986) and called 'Standard abbreviations of terms related to plastics'.

Standard And Non Standard Abbreviations

It must be appreciated that both standard and non-standard abbreviations are used. Often materials appear and a name becomes used before a standards committee has issued its suggestion. By this time a 'non standard' abbreviation may become established or more than one abbreviation may 'appear' for the same material. For example, the thermoplastic elastomer known as polyether ester elastomer may be referred to as PEEL or, as COPE (from copolyester) or, as TEEE (thermoplastic elastomer ether ester) or, as YBPO (an American suggestion). Some abbreviations are shown in Table 3.

THERMOPLASTIC MATERIALS

A thermoplastic material is one, which softens (or melts) on heating and hardens (or freezes) on cooling. This heating and cooling process can be repeated many times. Approximately 80% of all plastics used throughout the world are thermoplastics. This important group of materials can be divided into four groups (each of which may contain amorphous or crystalline materials):

1. Commodity thermoplastics
2. Engineering thermoplastics
3. Thermoplastic elastomers or rubbers
4. Blends or alloys

Commodity Materials.

This group of plastics covers materials such as polypropylene, polyvinyl chloride, polystyrene and polyethylene (PP, PVC, PS and PE). Each of these materials includes a number of sub-divisions, for example PP includes homopolymers and copolymers, PVC covers rigid and plasticized, PS refers to general purpose PS and toughened PS (TPS, or IPS, or HIPS) and PE includes LDPE, LLDPE and HDPE. The importance of commodity thermoplastics cannot be over-emphasized as approximately 80% of all plastics used fall into this category.

Engineering Thermoplastics.

Engineering plastics are a group of polymers that offer a combination of properties including superior strength, stiffness, toughness and resistance to wear, resistance to chemical attack and heat resistance. The major materials in this group include the polyamides (nylons), acetals, polycarbonates, thermoplastic polyesters and modified polyphenylene oxide (also known as modified polyphenylene ether or PPE).

Thermoplastic Elastomers.

Materials referred to as 'thermoplastic elastomers' (TPE) or, as 'thermoplastic rubbers' (TPR) are a comparatively new group of materials that have become significant in terms of both tonnage and value. This is because they are creating new markets as well as replacing both plastics and traditional rubbers in some of their applications. They exhibit some of the properties associated with traditional or "vulcanized" rubbers, but they also can be processed with the speed and ease of thermoplastics and can be reprocessed.

Blends.

Because of their ease of production, using twin-screw compounding extruders, there are many blends of plastics or blends of plastics with elastomers. Any of these materials may also be modified with fillers or glass fiber. Reasons for blending materials include the generation of "unusual" plastics materials, extending the performance of existing plastics quickly and cheaply and the recycling of plastic materials.

Property Guidelines.

Because of the large number of grades of plastics available, properties quoted in the literature should only be used as a general guideline. The final properties of any plastic material may be dramatically changed by the processing conditions employed and/or by the use of additives. With many materials, variations of basic formulas are available using additives to provide, improved heat resistance, or weatherability. Some formulations offer improved impact strength while others, which contain fillers, are used where, for example, moldings are required to possess tensile strength and/or a high heat distortion temperature. Processing and performance modifiers may also be added. These include lubricants, antistatic additives, and nucleating agents. Such additives may be included as part of a color masterbatch.

Choice Of Grade

Once a type of plastic material has been selected for a particular application, then the melt viscosity or melt flow rate (MFR or MFI) may be used to further define the grade to be used. If, for example, the components are to be subjected to severe mechanical stresses, a high viscosity grade may be the best choice. This is because the high viscosity grades usually have the highest molecular weight and frequently exhibit superior mechanical properties. (See the section on High Shear Rate Rheometers.) In some cases, however, this advice should not be followed. For example, the case where unacceptable levels of frozen-in strains in the molded part may result. An easy flow grade would then be preferred. An example of this would be when filling thin injection molded wall sections or where very smooth surfaces are specified.

Feed Forms.

Most processing equipment, for example, injection molding machines or extruders, can be fed with plastic resins or compounds in various forms. The feed may be fine powder, regranulated material or pellets. In general, higher output rates are obtained if uniformly sized pellets are used. It should be emphasized that to obtain a consistent output a consistent feed must be used.

POLYOLEFINS

Probably the best-known example of a semi-crystalline, thermoplastic material is polyethylene. We will provide a short discussion of this material here. This type of material is commonly tested by rheometry and is also widely used in rheology studies. Polyolefin Materials. Polyethylene (PE) is a member of the family of plastics called polyolefins (PO). Both homopolymer and copolymer polyolefins are available. Members of the polyolefin family include:

- Very low density polyethylene or VLDPE
- Low density polyethylene or LDPE
- Linear low density polyethylene or LLDPE
- High density polyethylene or HDPE
- Metallocene catalyzed polyethylenes MCPE

- Polypropylene or PP.

Polyethylene.

Polyethylene is made from a hydrocarbon gas called ethylene by the process of polymerization. Ethylene is a simple, low molecular weight (mass) material, which has a molecular weight of 28. When the gaseous ethylene (sometimes called ethene) molecules join together (polymerize) to produce a long chain structure, the molecular size and weight increase dramatically. If ten thousand ethylene molecules are joined together, to make (for example) a film grade of PE, the average molecular weight will be 280,000 atomic units (au). As a result of the random nature of the polymerization reaction, some of the chains will be a different size. Some will be larger than the average value and some will be smaller. Some, for example, may only contain 20 ethylene units, while others may contain a hundred thousand ethylene units. This results in a statistical distribution of weights (sizes) of the molecules, which is called the molecular weight distribution. (MWD) Just how the ethylene units are joined together is also important. For example, when two ethylene units add onto another growing chain at the same point a branching in the chain will be the result. This means that polyethylene is not necessarily a simple long chain material, but one that may also contain a large number of short and long side branches. These branches affect how the material flows and how the molecules will pack together (crystallize) on cooling.

Material Properties.

Each of the many polyethylene plastic materials available is really a family of materials that may differ in molecular weight, molecular weight distribution and chain branching. Changing anyone of these factors can dramatically change the properties of the material. What this means is that it is possible to get a wide range of properties for any material group. The following table shows how changes in melt flow rate (MFR – a measure of molecular weight), density (a measure of molecular packing), and molecular weight distribution (MWD) affect the properties of HDPE.

Effect Of Structural Changes For HDPE

The effects of changes in molecular weight, density and molecular weight distribution (MWD) are shown in the table below.

Types Of Polyethylene

When the density of PE is low (0.910 to 0.925g/cm³) it is sometimes referred to as Type I. When the density is medium (0.926 to 0.94g/cm³) the material is sometimes called Type II. HDPE with a density of 0.940 to 0.959g/cm³ is sometimes known as Type III. If the density is very high (>0.959g/cm³) then the material is known as Type IV. The grades of HDPE that have a density below 0.96, are produced by using a second monomer at low levels (<1%). Strictly speaking they are, therefore, copolymers of PE with another olefin. (For example, with butene –1 or, with hexene –1.) The use of the second monomer reduces the density by introducing short side chain branches that interrupt the crystalline structure.

Such materials may be called MDPE. HDPE/MDPE copolymers account for approximately 55% of all plastics used in blow molding.

<u>Property</u>	<u>Effect of Increasing:</u>		
	<u>MFR</u>	<u>Density</u>	<u>Breadth of MWD</u>
Pseudoplasticity			Increases
Tensile strength at yield		Increases	
Tensile strength at break	Decreases	Increases	
Elongation at break	Decreases	Decreases	
Impact strength	Decreases	Slight decrease	Decreases
Modulus		Increases	
Transparency		Decreases	
Long term load bearing		Increases	
ESC resistance	Decreases	Decreases	
Softening temperature		Increases	
Melt strength	Decreases		Increases
Melt elasticity	Decreases		Increases
Melt fracture tendency	Decreases		Decreases
Gloss			Decreases

PROPERTY DIFFERENCES FOR POLYETHYLENES

(Compared to the one left blank.)

<u>Property</u>	<u>Polymer Density in g/cm³</u>		
	<u>Low</u> (Type I)	<u>Medium</u> (Type II)	<u>High</u> (Type III)
Tensile strength at rupture	Highest	Higher	
Elongation at break	Highest	Higher	
Impact strength	Highest	Higher	
Modulus	Highest	Higher	
Transparency	Highest	Higher	
Long term load bearing		Higher	Highest
ESC resistance	Highest	Higher	
Softening temperature		Higher	Highest
Melt strength		Higher	Highest
Gloss	Highest	Higher	
Resistance to shrinkage	Highest	Higher	
Resistance to warpage	Highest	Higher	
Resistance to brittleness at low temperature	Highest	Higher	
Resistance to grease and oil absorption		Higher	Highest
Impermeability to gases and liquids		Higher	Highest
Freedom from film haze		Highest	Highest
Molding cycle times		Higher	Highest

ADDITIVES USED WITH PLASTICS

All plastics consist of one or more polymers plus additives. Essentially no polymers are sold without some form of additive compounded into them. It is generally understood in the thermoplastics industry that the materials used contain small amounts of additives. Most thermoplastic materials cannot be commercially used without the addition of additives such as heat stabilizers and lubricants. The properties of the polymers used in plastic products may be dramatically changed by the processing conditions employed and by the use of additives. Variations of basic material formulas are available with additives to provide, for example, improved heat resistance or weatherability. Some formulations offer improved impact strength. Others, which contain fillers, are used where the products require greater modulus, flexural strength and heat distortion temperature. Processing and performance modifiers, such as antistatic and nucleating agents, may also be added. Frequently the additives form part of a color masterbatch.

Masterbatches

Processing equipment, such as injection molding machines, are often fed with a mixture of a plastic material and a masterbatch. A masterbatch is a mixture of one or more additives in a base polymer material. The use of such a mixture often produces significant cost savings, as a compounding step may be eliminated. Most commonly, masterbatches are only used to color a finished product, however, they may also contain other additives as well. The use of a masterbatch can sometimes cause problems. The most frequent problem is one of color shade differences between different machines. Another is separation of the masterbatch components from the plastic in the hopper, which may lead to variable properties in the molded parts.

Materials Modifications.

The use of the term 'materials modification' usually means the addition of larger amounts of additives. Such additives may include elastomers, flame-retardants and fillers.

Fillers And Reinforcements

Materials modification, such as with fibers or with fillers, is extensively used with engineering thermoplastics to obtain a desirable combination of properties. For example, the use of fibrous fillers, such as glass fiber, usually improves the modulus. These modifications are seldom produced in order to save money, since a molding made from a filled compound, is often the same price as one made from the unfilled plastic material. This arises from the high density of most fillers and high compounding costs. By the use of such fillers it is possible to lift a plastics material from one category to another. In the case of the commodity resin polypropylene, it can be changed into an engineering plastic by materials enhancement.

Impact Modification (Elastomer Addition)

Strictly speaking an elastomer or rubber that imparts added toughness when used with a thermoplastic material is called an impact modifier. These additives are extensively used in engineering thermoplastics for applications where high impact strength is required (for example, automotive bumpers). The impact strength of commodity resins may also be upgraded by the addition of impact modifiers. When rubber is added to styrene, and the mixture polymerized, a thermoplastic material called high impact polystyrene (HIPS or, TPS, or, IPS) is produced. Rubbers are added to other materials, such as polypropylene (PP), in order to improve the low temperature impact strength. What is required for these applications is a material, which can be processed like a thermoplastic and yet, has many of the properties of a cross-linked material. This is one reason for the current interest in polymer alloying and thermoplastic elastomers. One approach to making such thermoplastic materials is to disperse cross-linked rubber particles in a thermoplastic matrix. An example of this is Acrylonitrile Butadiene Styrene (ABS) copolymer, where butadiene rubber is used to improve the impact properties to SAN copolymer and produce a widely used plastic material. The impact strength of such UPVC bottles is improved by the use of methacrylate-butadiene-styrene polymers (MBS). These thermoplastic rubber materials, when used at approximately 10% addition, still give transparent bottles. However, because they are comparatively expensive, alternative cheaper solutions are now commonly used.

Flame Retardants.

Since they are based on carbon, most will polymers burn. It is natural for a carbonbased material to react (burn) with atmospheric oxygen to form carbon monoxide and carbon dioxide. Halogen atoms such as chlorine and bromine, however, form compounds that are naturally fire or flame retarding. In the case of PVC, the halogen atom is “built-in” the plastic material molecular structure. With other plastics, however, the halogen must be added in the form of compounds such as tribromotoluene. The efficiency of these compounds is often improved by the use of antimony trioxide. Unfortunately, the use of halogens can produce toxic smoke and fumes, so other flame-retardants may be preferred. One such material is aluminum trihydrate. The large amounts of this material required, however, can change the properties of the plastic material (for example, the flow properties). It may also introduce processing problems, because of aluminum trihydrate decomposition at processing temperatures. Phosphorous based compounds and some silicones are becoming more popular for use as flame-retardants.

Plasticizers.

Plasticizers, which are usually liquids, were first added to plastic materials, such as cellulose and PVC, in order to allow them to be processed at temperatures below that at which they thermally degrade. Most commercial plasticizers are phthalate compound that include dioctyl phthalate (DOP) and di-iso-octyl phthalate (DIOP). By adding such materials to PVC, plasticized PVC (PPVC) is produced. This material flows much more easily than the unplasticized material (UPVC) and is softer and more flexible. The term “primary plasticizer” indicates that a compound is more compatible with the basic plastic material than a “secondary plasticizer”.

Softeners And Extenders

The term “softener” is used by the rubber industry for products such as hydrocarbon oils, which are used as additives for hydrocarbon rubbers/elastomers. They produce soft compounds, which are relatively easy flowing. Extenders, sometimes referred to as “liquid fillers”, are commonly associated with PPVC, where their use reduces compound costs. The chlorinated waxes used in this application also act as flame-retardants.

Anti-Aging Additives. (Anti-Oxidants, UV- Stabilizers, Etc.)

These additives are widely used with polymeric materials since heat and light will often cause their properties to change in normal use or during processing. Heat and light cause chemical reactions, including oxidation, ozone attack, dehydrochlorination and ultraviolet (UV) attack, to occur within the material, or on its surface. Which type of chemical attack occurs depends, on the type of polymer and the particular circumstances. As polyolefins (PO) readily degrade by oxidation, antioxidants are widely used in polyethylene (PE) and polypropylene (PP). PVC degrades more readily by dehydrochlorination and additives, which restrict this type of attack, are more widely used in PVC compounds. Ultra-violet (UV) attack is common with most polymeric materials. Thus UV stabilizers are usually found in products that are to be exposed to sunlight or used outdoors. Aging by ozone is peculiar to the rubbery class of materials and is combated and controlled by the use of anti-ozonants.

Lubricants.

Lubricants are usually added to polymers in order to prevent the polymer from adhering to processing equipment or to ease the flow of the polymer compound. Stearic acid is an example of a lubricant that is added to PVC in order to prevent the compound sticking to the processing equipment. Such a lubricant is called an “external lubricant” as it comes to the surface of the molten polymer. An “internal lubricant” is one that is primarily used to increase flow. An example is glyceryl monostearate, which is used with UPVC. With some plastics materials, lubricants are added in order to reduce friction in use. For example, the addition of 2% graphite will reduce the friction between two molded gears. Silicone oils may be used for the same purpose.

Colorants.

Most plastic components are colored by techniques in which the coloring system is dispersed throughout the polymer. (It is possible, however, to color only the skin in order to save on colorant and compounding costs. This may be done, for example, by sandwich molding and extrusion.) Generally speaking, colorants are divided into two major types: dyes and pigments. Dyes are soluble, generally organic, coloring systems that produce transparent colors. Pigments are dispersed insoluble solids that produce opaque colors. Pigments are the most widely used. The most widely used colors are white (TiO₂) and black (carbon black).

Blowing Agents.

A great many polymeric products are cellular materials filled with gas cells. Either a gas (usually nitrogen) is added during processing or a chemical compound (a blowing agent) is used to generate the gas when required. A widely used class of blowing agents is the azo compounds. These organic materials can be structured so they decompose over a fairly narrow temperature range at the melt processing temperatures.

Cross-Linking Additives.

Many polymers can be cross-linked (cured, vulcanized or set) after shaping (usually during processing), so that either a vulcanized rubber (an elastomer) or a thermosetting plastic material results. Two well-known cross-linking systems are sulfur (used with diene rubbers) and peroxides (used with some rubbers and polyolefins). Accelerators and activators are often associated with cross-linking systems. Accelerators, as the name implies, speed up the cross-linking reaction and may, in turn, only function efficiently in the presence of an activator.

Degradants.

Once a plastic part has fulfilled the function required, it often becomes a nuisance and the once valuable component becomes classed as litter. This problem is most serious for plastic materials used in packaging. One way of overcoming this problem is make the plastic material subject to decomposition, or degradation. This may be done by incorporating a filler, such as starch, into the plastic material. Another route is to use a biodegradable plastic material such as polyhydroxybutyrate (PHB), either on its own, or in combination with other plastics. PHB is produced by bacterial action on glucose and is a semi-crystalline, thermoplastic material similar, in some ways, to polypropylene (PP).

Reclaimed Material.

The most common additive used with thermoplastic materials, is reclaimed (or recycled) material. This is usually added to reduce component costs. It is most important that this additive (as with any additive) is added at a consistent, pre-selected ratio so that the flow properties of the resultant blend, for example, remain constant. It is also important to ensure that the reclaimed material is clean, dry and of regular particle size.

Good Dispersion.

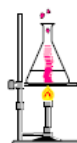
To get the best results from additives they must be very well dispersed within the basic polymeric material. This is why melt mixing is very important to the polymer industry. Such melt mixing is done at relatively low temperatures in order to keep the polymer viscosity at a high value and so increase the shear input, which improves dispersion.

MELT PROCESSES AND THERMOPLASTIC BEHAVIOR

Most processes used to shape thermoplastics are melt processes. That is, the plastic material is heated until it becomes molten; next it is shaped and then cooled to set the shape. There are several ways of obtaining a desired shape and these are summarized in the following section. It must always be remembered that plastic processing equipment can be very dangerous, unless used correctly, and must therefore only be used by people who know what they are doing.

Steps in Thermoplastic Conversion Processes

1.) Melting of the Polymer.



2.) Forming of the Polymer Melt.



3.) Cooling and Re-solidification of the Polymer.



SUMMARY OF SHAPING METHODS

1. Deformation of a polymer melt – either a thermoplastic or a thermosetting melt. Processes using this approach include blow molding, calendaring, extrusion and injection molding.
2. Deformation of a polymer in the rubbery state. This approach is used in sheet shaping techniques such as thermoforming and the shaping of acrylic sheet.
3. Deformation of a polymer solution either by spreading or by extrusion to make films and fibers.
4. Deformation of a polymer suspension. This approach is used in rubber latex technology and in PVC plastisol technology.
5. Deformation of a low molecular weight polymer. This approach is used in the manufacture of acrylic sheet and in the preparation of glass reinforced product.
6. Machining operations. In terms of tonnage, those processes involving the deformation of a thermoplastic polymer melt are by far the most important. These include extrusion and injection molding, which are the most common.