Dynisco

From lab to production,
providing a window into the process

Materials and their Flow Properties

Polymers and Plastics

A polymer is a chemical compound made up of a large number of identical molecular repeating units. A plastic material is a polymer, generally modified with additives, which is capable of being shaped or molded under reasonable conditions of temperature and pressure. It generally is solid at room temperature and is distinguished from a rubber/elastomer by having a higher stiffness/modulus and a lack of reversible elasticity. A thermoplastic is a plastic material that will soften (melt) on heating and harden on cooling. This softening (or melting) by heat and hardening by cooling can be repeated. This allows thermoplastic materials to be recycled.

Synthetic Polymers

Most commercial polymers and rubbers/elastomers are composed of molecules based on the element carbon; that is to say, they are organic. They are synthesized, or made, from simple, oil-based raw materials called monomers. A process, known as polymerization, connects these simple low molecular weight materials together to form polymers, which consist of long chains containing many identical repeat units. Polymers and rubbers based on one monomer are known as “homopolymers”, while those based on two (or more) monomers and are known as ‘copolymers’. They may be linear, branched or “cross-linked” (i.e., two or more polymer chains are connected). Usually, polymer chains of a wide range of lengths (chains of varying molecular weight) are present in commercial materials. Since the final molecular weight (and size) is generally large, these materials are frequently referred to as “high polymers” or “macromolecules”. Although a high molecular weight is necessary to obtain useful properties (such as stiffness and strength) in a plastic material, it also means that the material is difficult to process. All plastics are polymers but not all polymers are plastics. Cellulose, for example, is a polymer, but it cannot be processed like a plastic material unless it is modified.

Long Chain Structure

The “high polymer molecules”, or “macromolecules”, that are used in plastics are incredibly long. There may be, for example, 50,000 atoms linked together in a long chain-like molecule or structure. Because of the structure of the carbon to carbon bond on which they are based, they generally are not straight, but are twisted or coiled. As a result of the nature of the polymerization reactions, the chains also have a distribution of different lengths. When there is no order in the system (an amorphous material), the chains prefer to exist in a random, coiled-up state (just like the shape obtained when a piece of string is dropped on the floor). The separate long chain molecules (or “chains”) are also normally intertwined one with the other. If crystallization of the polymer is possible, then the chains, or portions of the chains, may either fold back on themselves or lie side-by-side in a more ordered fashion. The great length of the chains and the entanglements between them prevent thermoplastic materials from crystallizing completely on cooling. This is why they are called “semi-crystalline thermoplastics”. Such materials contain both crystalline and amorphous regions.

Amorphous Thermoplastics

Thermoplastic materials may be divided into amorphous materials and semicrystalline materials. An amorphous thermoplastic is usually a glassy, hard material that, in the unfilled state, is transparent and rigid. This type of plastic material does not have a sharp melting point, but softens to a melt over a broad range of temperature. It, therefore, can be molded or processed over a comparatively wide temperature range. A major advantage of amorphous polymers is their low and consistent shrinkage, relative to that of semi-crystalline materials. As the natural color of an amorphous material is generally a clear, water-white, a very wide range of transparent or opaque colors may be produced. Typical amorphous polymers include polystyrene (PS), polymethylmethacrylate (PMMA), styrene acrylonitrile (SAN), polycarbonate (PC), polysulfone (PSU or PES) and polyvinyl chloride (PVC). Modified polyphenylene oxide (PPO-M) and acrylonitrile butadiene styrene (ABS), although not usually transparent, are based on amorphous thermoplastic materials. Some widely used abbreviations for thermoplastic materials are shown in Tables 1. and 2.

Semi-Crystalline Polymer

The amount of crystalline material (% crystallinity), in an extrudate made from a polymer that will form crystals, is typically not 100%. Amorphous areas are always present. Thus these materials are referred to as semi-crystalline. Typical semi-crystalline polymers are polyacetal (POM), polyamides (PA 6 and PA 66), polybutylene terephthalate (PBT), polyethylene terephthalate (PET), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyphenylene sulfide (PPS), and polypropylene (PP). Semi-crystalline polymers are usually malleable, tough, durable, and have a good chemical resistance. Usually they are not clear because the crystal structures that they contain scatter light. Semi-crystalline polymers may have a sharp melting point or, more usually, a fairly narrow melting point range. Considerable care is required in their processing. The properties of formed components may be greatly affected by the degree of crystallization and crystalline morphology (structure) that occurs during solidification. In addition, they exhibit greater shrinkage variations than amorphous polymers. Therefore a greater emphasis on the uniformity of cooling is required when processing a semi-crystalline material.

Orientation

The most commercially important polymer conversion processes involve meltprocessing methods in which the polymer is heated and made to flow. In the melted form all polymers are amorphous; that is they have no structure. When the polymer flows, the polymer chains slip, or slide, over each other while rotation around the carbon-to-carbon bonds also occurs. Layers slip one over the other in what is called laminar or shear flow. As the individual polymer molecules move relative to each other, they may change their direction or orientation as a result of chain entanglements and friction between layers. The chains thus become “drawn out” in the direction of flow. Because of the rapid cooling often employed in polymer processing, this orientation may be “frozen-in” and the product will contain, what are referred to as, frozen-in stresses or, frozen-in strains. These products thus contain molecules that are orientated in the flow direction, which means that there is a “grain effect” present – just like that which exists in wood. As the result of the grain, the wood is stronger in one direction that it is in another. Because of orientation, thermoplastic products may be much stronger in one direction than in another; that is, the product is anisotropic. Commercial use is made of this “uni-axial” effect in extrusion in the production of the tape used for strapping packages. Biaxial orientation (orientation in two perpendicular directions) allows the production of strong, stiff, film from brittle polymers, such as polystyrene (PS).

Table 1.
Standard (Based on ISO and ASTM) Abbreviations For Selected Thermoplastics

Abbreviation	**Name**
ABAK	acrylonitrile-butadiene-acrylate (was A/B/A in ISO)
ABS	acrylonitrile-butadiene-styrene
A/B/A	See ABAK
A/CPE/S	See ACS
ACS	acrylonitrile-chlorinated polyethylene-styrene (was A/CPE/S in ISO)
AES	acrylonitrile-ethylene-propylene-diene-styrene (was A/EPDM/S in ISO)
A/EPDM/S	See AES
A/MMA	See AMMA
AMMA	acrylonitrile-methyl methacrylate (was A/MMA in ISO)
AS	acrylonitrile-styrene (SAN is more usual in Europe)
ASA	acrylonitrile-styrene-acrylate
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CN	cellulose nitrate
CP	cellulose propionate
E/EA	See EEAK
EEAK	ethylene-ethylene acrylate (was E/AK in ISO)
E/MA	See EMA
EMA	ethylene-methacrylic acid (was E/MA in ISO)
E/P	See EP
EP	ethylene-propylene (was E/P in ISO)
EPDM	ethylene-propylene-diene
E/TFE	See ETFE
ETFE	ethylene-tetrafluoroethylene (was E/TFE in ISO)
EVAC	ethylene-vinyl acetate
EVAL	See EVOH
EVOH	ethylene-vinyl alcohol (was EVAL in ISO)

FEP	fluorinated ethylene-propylene
LCP	liquid crystal polymer
MABS	methyl methacrylate-butadiene-styrene
MBS	methacrylate-butadiene-styrene
PA	polyamide
PAEK	polyaryletherketone
PAI	polyamideimide
PAK	polyacrylate
PAR	polyarylate
PAUR	poly(ester urethane)
PB	polybutene-1
PBAK	poly(butyl acrylate)
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCTFE	polychlorotrifluorethylene
PE	polyethylene
PEBA	poly(ether block amide)
PEEK	polyetheretherketone
PEEKK	polyetheretherketoneketone
PEEST	polyetherester
PEI	poly(ether imide)
PEK	polyetherketone
PEKEKK	polyetherketoneetherketoneketone
PEKK	polyetherketoneketone
PEOX	poly(ethylene oxide)
PES	poly(ether sulfone)
PESTUR	poly(ester urethane)
PET	poly(ethylene terephthalate)
PEUR	poly(ether urethane)
PFA	perfluoro alkoxyl alkane
PFEP	perfluoro(ethylene/propylene)
PI	polyimide
PIB	polyisobutylene or polyisobutene
PMMA	poly(methyl methacrylate)
PMP	poly-4-methylpentene-1
PMS	poly-α-methylstyrene
POM	polyoxymethylene or, polyacetal or, polyformaldehyde
PP	polypropylene
PPE	poly(phenylene ether)
PPOX	poly(propylene oxide)

PPS	poly(phenylene sulfide)
PPSU	poly(phenylene sulfone)
PS	polystyrene
PSU	polysulfone
PTFE	polytetrafluoroethylene
PUR	polyurethane
PVAC	poly(vinyl acetate)
PVAL	poly(vinyl alcohol)
PVB	poly(vinyl butyral)
PVC	poly(vinyl chloride)
PVDC	poly(vinylidene chloride)
PVDF	poly(vinylidene fluoride)
PVF	poly(vinyl fluoride)
PVFM	poly(vinyl formal)
SAN	styreneacrylonitrile
S/B	styrenebutadiene
S/MS	styrene-α-methylstyrene
SMA	styrenemaleic anhydride
VC/E	See VCE
VC/MMA	See VCMMA
VC/VDC	See VCVDC
VC/VAC	See VCVAC
VC/MA	See VCMAK
VC/OA	See VCOAK
VC/E/MA	See VCEMAK
VC/E/VAC	See VCEVAC
VCE	vinyl chloride-ethylene (was VC/E in ISO)
VCEMAK	vinyl chloride-ethylene-methyl acrylate (was VC/E/MA in ISO)
VCEVAC	vinyl chloride-ethylene-vinyl acetate (was VC/E/VAC in ISO)
VCMAK	vinyl chloride-methyl acrylate (was VC/MA in ISO)
VCMMA	vinyl chloride-methyl methacrylate (was VC/MMA in ISO)
VCOAK	vinyl chloride-octyl acrylate (was VC/OA in ISO)
VCVAC	vinyl chloride-vinyl acetate (was VC/VAC in ISO)
VCVDC	vinyl chloride-vinylidene chloride (was VC/VDC in ISO)

The above abbreviations may be modified by the addition of up to four specified letters after the abbreviation for the polymer under discussion. For example, PS could become PS-HI when high impact polystyrene is being described. In the case of PE, this would become PE-LD when low-density polyethylene (LDPE) is being described.

When mixtures are made from two or more polymers (blends or alloys), ISO 1043 suggests that the symbols for the basic polymers be separated by a plus (+) sign and that the symbols be placed in parentheses. For example, a mixture of * polymethyl methacrylate and * acrylonitrile-butadienestyrene should be represented as (PMMA+ABS) When a copolymer is being discussed, it is recommended (ISO) that an oblique stroke / be placed between the two monomer abbreviations. (For example, E/P for an ethylene propylene copolymer.) The oblique strokes may be omitted when common usage so dictates according to ISO 1043-1:1987 (E).

THERMOPLASTIC MATERIALS

Over the past 50 years the usage of plastic materials throughout the world has increased dramatically and now stands at well over 100 million tons. In terms of tonnage, thermoplastics are by far the most important, as they are approximately 80% of all plastics used throughout the world.

Advantages of Plastics

Plastic materials are widely used because they can be formed into complex components, or shapes, relatively easily. They also have a useful combination of properties that can be modified for use in a wide range of applications. Some of these desirable properties (which are not possessed by any one plastic) include physical strength, resilience, corrosion resistance, elasticity, electrical insulation, wide color range, thermal insulation, lightness in weight, chemical resistance and moldability. These materials are therefore versatile in their applications. Their use frequently simplifies production, due to the fact that they often allow several discrete parts to be incorporated into one component. The ease with which complex parts may be produced from plastic compositions at high speed, in many cases outweighs the disadvantages of plastic materials. Attractive decoration of such products adds to their sales appeal. However, thermoplastic materials sometimes lack strength, stiffness, temperature resistance, and fire resistance. Not only do some plastics burn relatively easily, but also they often evolve large quantities of smoke and fumes when they do burn. Many plastic components will creep or change their dimensions if subjected to relatively small loads for prolonged periods of time. Environmental stress cracking (ESC), changes of dimensions with temperature and humidity, and a sudden change from tough to brittle behavior are other factors that should be investigated before thermoplastics are used.

Major Thermoplastic Materials

There are two main categories of plastic materials, thermoplastics and thermosetting plastics (thermosets). Because of the commercial importance of thermoplastic materials this book will concentrate on their extrusion processing. This important group of materials has been divided into four groups:

1. Commodity or Bulk Thermoplastics
2. Engineering Thermoplastics
3. Thermoplastic Elastomers or Rubbers

4. Blends and/or Alloys
Commodity thermoplastics, such as the polyolefins (polypropylene and polyethylene), polyvinyl chloride plastics and styrene-based plastics comprise, the major tonnage of material produced.

Commodity or Bulk Thermoplastics

Because of their relative ease of manufacture from readily available monomers, their low cost and versatility, usage of polyolefins has grown dramatically in recent years. Both homopolymers and copolymers in this family are available, as are rubbers and thermoplastics materials. The members of the polyethylene family include; linear low-density polyethylene (LLDPE), low density polyethylene (LDPE), high-density polyethylene (HDPE) and very low density polyethylene (VLDPE). The term polyethylene (PE) therefore covers a range of materials. A new class of these resins has recently been produced “using “metallocene” or “single site constrained geometry” catalysts. These catalysts allow the production of homopolymers and copolymers with molecules of more uniform size and structure. The term polyvinyl chloride (PVC) plastic refers to homopolymers and copolymers, both of which may be used with or without plasticizers. This gives rise to unplasticized grades (UPVC) and plasticized grades (PPVC). The term styrene-based plastic also refers to a range of materials. These include the homopolymer polystyrene (PS), the copolymer styrene-acrylonitrile (SAN), the rubber-toughened material called high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS). The importance of commodity thermoplastics cannot be overemphasized because of their high volume of production and usage. The advent of new catalyst systems (for example, metallocenes) will further increase the usage of bulk thermoplastics, as new types of polymer may be produced. It is also now being realized that the properties of this class of materials can be up-graded, so they can compete with many more expensive engineering thermoplastics.

Engineering Thermoplastics

The term engineering thermoplastics generally refers to materials that can be used to replace metal, glass or wood in manufactured products. They include both amorphous and semi-crystalline polymers. These plastics, characterized by properties such as high strength, stiffness, impact resistance, temperature resistance and fire resistance are widely used in automotive, transportation, appliance, electronics, communications and aerospace applications. These materials are produced in smaller volumes than commodity plastics, but they command a much higher price. Materials that are considered to be engineering thermoplastics include: polycarbonate (PC), polyethelene terephthalate (PET), polybutylene terephthalate (PBT), polyoxymethylene (acetal), polysmide (nylon), polymethylmethacrylate (PMMA) and acrylonitrile-butadiene-styrene (ABS).

New Material Supply

Raw material manufacturers or their distributors can supply a material as, for example, either prime grade material or as transitional material. Some may also supply reclaimed material. Prime grade material, also known as virgin material (or as first pass material or as first grade material) is a thermoplastic material (in the form of pellets or granules) that has not been subjected to use, or processing, other than that required for its original manufacture. Transitional material is material that does not meet the manufacturer's specification for prime grade material: it is off-spec or substandard material. Such material may be obtained from a continuous compounding line when a change is made from one grade to another. This means that the melt flow rate and the base color may be somewhat variable. The cost of virgin material is greater than that of these off-spec materials.

Thermoplastic Grades

A large number of grades may be available for any one material. These grades may differ in molecular weight, molecular weight distribution, chain branching, purity and the presence of additives or modifiers. Therefore, any properties quoted in the literature should be used only as a general guideline, as each of the many plastics available consists of a family of materials. Thus it is possible to get a wide range of properties for each material group. The properties of these thermoplastics may also be dramatically changed by the processing conditions employed. Processing may alter the material's color, its physical properties, amount of molecular orientation and even the type, and amount, of crystallinity.

Additives

It is generally understood in the thermoplastics industry that most plastic materials used contain small amounts of additives, as most of these materials cannot be commercially used without them. The properties of a particular material are altered by the use of these additives. Since additives are essential in commercial plastics, the size and scope of the additives industry is now enormous. It is estimated that approximately 7 million tons of additives of various kinds are used in plastics annually. In the thermoplastics industry, the largest amount of additives is used in polyvinyl chloride (PVC). With most thermoplastic materials, variations of the basic formulas are available to provide improved properties, such as, improved heat resistance or weatherability, by the use of additives. Processing and performance additives such as antistatic, nucleating and mold release agents may also be added to an existing material. These additives may form part of the color masterbatch (a masterbatch is a concentrate). Concentrates containing foaming agents, for structural foam molding, are also available for many materials. Examples of other additives are reclaimed material, fillers, reinforcements, impact modifiers, colorants, antioxidants, heat stabilizers, light stabilizers, lubricants, coupling agent, flame retardants, cross-linking agents, plasticizers, extenders, nucleating agents, antistatic agents and blowing agents.

Material Modification

The use of the term "materials modification" usually means the addition of larger amounts (greater than a few percent) of an additive. An additive is used in relatively large concentrations may be referred to as a modifier. Modifiers may include elastomers, flame-retardants and fillers. Material modification with rubber impact modifiers, fibers or fillers has been extensively used with engineering plastics to obtain a desirable combination of properties. These formulations may offer improved impact strength, tensile strength and heat distortion temperature together with ease of flow.

Trade Name/Trademark Usage

It is common within the thermoplastics industry to refer to a plastic material by a trade name because they are often simpler, and more widely known, than the chemical name of the polymer. The same trade name/trademark, however, is often used for a range of materials, the properties of which may vary widely. Such materials are usually based on the same type of thermoplastic material, for example, acrylonitrile-butadiene-styrene (ABS). However, one material may be largely unmodified whereas another, with the same brand name, may contain large amounts of glass fiber or other additives (Table 2.).

Table 2.
Common Abbreviations and Trade Names/Trademarks for Thermoplastics and Thermoplastic Elastomers

Abbreviations	Common Name	Common Trade Names or Trade Marks
ABS	Acrylonitrile butadiene styrene	Cycolac; Lustran
AMS	Alpha methyl styrene	Elite HH
ASA	Acrylonitrile styrene acrylate (AAS)	Luran S
BDS	Butadiene styrene block copolymer	K Resin; Styrolux
CA	Cellulose acetate	Cellidor; Tenite
CAB	Cellulose acetate butyrate	Cellidor; Tenite
CAP	Cellulose acetate propionate	Cellidor; Tenite
CN	Cellulose nitrate	Celluloid; Xylonite
CP	Cellulose propionate (CAP)	Cellidor; Tenite
CPE	Chlorinated polyethylene (PE-C)	Bayer CM; Tyrin CM
CPVC	Chlorinated polyvinyl chloride (PVC-C)	Lucalor
EA-MPR	Elastomer alloy melt processable rubber or melt processable rubber	Alcryn
EA-TPV	Elastomer alloy thermoplastic vulcanizate	Lomod; Santoprene
ECM	Ethylene-carbon monoxide	Carilon; Ketonex
ETFE	Tetrafluorethylene-ethylene copolymer	Tefzel
EVA	Ethylene vinyl acetate copolymer (EVAC)	Evatane
EVAL	Ethylene vinyl alcohol copolymer	Clarene; Eval
EVOH	Ethylene vinyl alcohol copolymer	Clarene; Eval
FEP	Fluorinated ethylene propylene (TFE-HFP)	HDPE High density polyethylene (PE-HD)

HDPE	High density polyethylene (PE-HD)	Lupolen HD; Rigidex
HIPS	High impact polystyrene (TPS or IPS)	Lustrex; Polystyrol
LCP	Liquid crystal polymer	Vectra; Xydar
LDPE	Low density polyethylene (PE-LD)	Alathon; Hostalen
MBS	Methacrylate butadiene styrene	Paraloid
MDPE	Medium density polyethylene (PE-MD)	Fortiflex
MPR	Melt processable rubber or, elastomer alloy melt processable rubber	Alcryn
PA	Polyamide or nylon	
PA 6	Polyamide 6 or nylon 6	Akulon K; Ultramid
PA 11	Polyamide 11 or nylon 11	Rilsan B
PA 12	Polyamide 12 or nylon 12	Rilsan A; Grilamid
PA 46	Polyamide 46 or nylon 46	Stanyl
PA 66	Polyamide 66 or nylon 66	Maranyl; Zytel
PA 610	Polyamide 610 or nylon 610	Brulon; Perlon N
PAA 6	Polyaryl amide or, poly-m-xyleneadipamide (PA MXD6)	Ixef
PAN	Polyacrylonitrile	Acrilan; Barex; Orlon
PBT	Polybutylene terephthalate	Pocan; Valox
PC	Polycarbonate	Lexan; Makrolon
PCT	Polycyclohexanedimethylol terephthalate	Thermx; Valox
PCTFE	Polychlorotrifluorethylene	Hostaflon C2; Kel-F
PE	Polyethylene	Alathon; Lupolen
PEBA	Polyether block amide (TPE-A)	Pebax
PEEK	Polyether ether ketone	Victrex PEEK
PEEL	Polyether ester (TPE-A or YPBO)	Arnitel; Hytrel
PE-HD	Polyethylene-high density	Lupolen HD; Rigidex HDPE
PEI	Polyether imide	Ultem
PEK	Polyether ketone	Hostatec
PEKK	Polyether ketone ketone(from DuPont)	
PE-LD	Polyethylene- low density	Alathon; Lupolen LD
PE-MD	Polyethylene- medium density	Fortiflex
PE-VLD	Polyethylene- very low density	Norsoflex
PET	Polyethylene terephthalate	Arnite A; Techster E
PES	Polyether sulphone (sulfone)	Victrex
PI	Polyimide	Vespel
PK	Polyketone	Carilon

PMMA	Polymethyl methacrylate (acrylic)	Diakon; Plexiglas
PMP	Polymethyl pentene	TPX; Crystalor
POM	Polyoxymethylene or, acetal or, polyformaldehyde	Delrin; Hostaform
POM-H	Acetal homopolymer	Delrin and Delrin II
POM-CO	Acetal copolymer	Hostaform; Ultraform
PP	Polypropylene	Profax; Propathene
PPE	Polyphenylene ether (see PPO)	
PPO	Polyphenylene oxide-usually modified polyphenylene oxide (PPO-M)	Luranyl; Noryl
PPS	Polyphenylene sulfide (sulphide)	Fortron; Ryton
PPPS	Polyphenylene sulfide sulfone (polyphenylene sulphide sulphone)	Ryton S
PPVC	Plasticized polyvinyl chloride (PVC-P) Plasticised polyvinyl chloride (PPVC)	Solvic; Vinnol
PS	Polystyrene (GPPS or PS-GP)	Lustrex; Polystyrol
PSU	Polysulfone (polysulphone)	Udel
PTFE	Polytetrafluoroethylene	Fluon; Teflon
PVC	Polyvinyl chloride	Corvic; Geon
PVDC	Polyvinylidene chloride copolymers	Saran
PVDF	Polyvinylidene fluoride	Dyflor; Kynar
PVF	Polyvinyl fluoride	Tedlar
SAN	Styrene acrylonitrile copolymer	Lustran SAN; Tyril
UPVC	Unplasticized polyvinyl chloride (PVC-U) Unplasticized polyvinyl chloride (UPVC)	Corvic; Geon
RMPP	Rubber modified polypropylene a TPO (also known as RRPP or PP/EPDM)	Uniroyal TPR; Keltan
SBS	Styrene butadiene styrene block copolymer or thermoplastic elastomer styrene based (TPE-S)	Cariflex TR; Solprene
SEBS	Styrene butadiene styrene block Copolymer (saturated) or thermoplastic Elastomer styrene based (TPE-S)	Cariflex
TPE	Thermoplastic elastomer (rubber)	
TPE-A	Polyether block amide (PEBA)	Pebax
TPE-E	Thermoplastic elastomer - ether ester or polyether ester elastomer	Arnitel; Hytrel
TPE-OXL	Thermoplastic elastomer - polyolefin	

	based with crosslinked rubber	Levaflex; Santoprene
TPE-S	Thermoplastic elastomer styrene based (usually styrene butadiene styrene block copolymer)	Cariflex TR; Solprene
TPE-U	Thermoplastic polyurethane (TPU)	Elastollan; Estane
TPO	Thermoplastic polyolefin - may be a blend, (see RMPP), a thermoplastic vulcanizate (see TPV) or a reactor made product	
TPR	Thermoplastic rubber (elastomer)	
TPU	Thermoplastic polyurethane	Elastollan; Estane
TPV	Thermoplastic vulcanizate (a TPE with crosslinked rubber)	Lomod; Santoprene
ULDPE	Ultra low density polyethylene (ULDPE)	
VLDPE	Very low density polyethylene (ULDPE)	Norsoflex

VISCOSITY AND VISCOSITY TERMS

To shape a polymer or plastic into a part requires that the material first be softened or melted and then forced to flow through a die or into a mold. Thus it becomes very important to understand how polymer and plastic materials flow. Shear flow is one of the most important types of flow occurring in polymer melts during conversion processes. In this type of flow, one layer of melt flows over another on application of a shearing force. This process is described by the relationship between two variables, the shear rate and the shear stress.

Shear Rate

Shear rate is usually designated by the Greek letter gamma with a dot above the letter (˙ γ). No matter what system of units is used, it is represented by 1/time (in seconds). That is 1/sec or s-1. The larger the number the faster is the material being sheared. The shear rate (the true shear rate) at the wall of a die (˙γw) is given by:

$$\gamma w = \frac{(3n1+1)}{4n1} \frac{(4Q)}{\pi R3} \qquad \textbf{(Eqn. 1)}$$

where, n1 = [dlog(PR/2L)]/[dlog(4Q/(πR3)]
τw = shear stress at the wall of the die = PR/2L
P = measured pressure
R = die radius
L = die length

γ_w = shear rate at the wall of the die
Q = volumetric output rate

By plotting shear stress (Pa or Nm^{-2}) against shear rate (s^{-1}) a flow curve may be obtained.

Apparent Shear Rate

The expression for the shear rate at the wall of a tube or die is rather complex and in practice it is often simplified to give $\dot{\gamma}_{w,a} = 4Q/\pi R^3$, where $\dot{\gamma}_{w,a}$ is the apparent (or uncorrected) shear rate at the wall of a die. For Newtonian fluids, the apparent (or uncorrected) shear rate at the wall of a die ($\dot{\gamma}_{w,a}$) is equal to the true shear rate ($\dot{\gamma}_w$) However, with non-Newtonian fluids, such as polymer melts, the two are not equal but are related by the equation:

$$\gamma_w = [(3n_1 + 1)/4n_1]\,\dot{\gamma}_{w,a} \qquad \textbf{(Eqn. 2)}$$

where, $n_1 = [d\log(R\Delta P/2L)]/[d\log(4Q/(\pi R^3)]$

Shear Stress

Shear stress is the stress or force applied to a body in the direction of one of its faces. In rheology, shear stress is that force that is applied to a material to cause shear flow. Thus, it may be defined as the stress (the force per unit area – F/A) required to make one layer of melt to flow over another at a specific rate. It has the dimensions of force per unit area and is usually designated by the Greek letter tau (τ). The shear stress at the wall of the die (given the symbol τ_w) and is

$$\tau_w = PR/2L \qquad \textbf{(Eqn. 3)}$$

where, P = measured pressure
R = die radius, and
L = die length

Shear stress has the units of force per unit area. $1\ Nm^2 = 10\ dyn\ cm^{-2} = 0.000\,145\ lbf\ in^{-2}$ (psi). By plotting shear stress (Pa or Nm^{-2}) against shear rate (sec^{-1}) flow curves may be obtained. Dividing the shear stress by the shear rate gives the viscosity (η) with units of (Pa-sec) or (Nsm^{-2}).

Apparent Viscosity

Viscosity is defined as the resistance to flow. By dividing τ_w (the shear stress at the wall) by the apparent wall shear rate ($\gamma_{w,a}$) one may obtain the viscosity (η_a) at a particular shear rate. This is the apparent viscosity. (In practice the word "apparent" is often omitted and the symbol η is used in place of (η_a). Another form of viscosity, the kinematic viscosity is obtained by dividing the viscosity (the "coefficient of viscosity") of a fluid by its density. The units are m^2s^{-1}. Dynamic viscosity is an alternative name for the viscosity or coefficient of viscosity of a fluid. The usual symbol is η but μ is sometimes used. In the cgs system, the units are dyne sec cm^{-2} and such units may be referred to as "poise" (P). One poise = 1P = 10^{-1} Pa-s = $10^{-1}\ Nsm^{-2}$ = $0.000\,014\,5\ s\ ft^{-2}$. That is, one poise = 1P = 0.1 Pa-s = 0.1 Nsm^{-2} and 1 Pa-s = 1 Nsm^{-2} = 1 $kgm^{1}s^{-1}$ = 10P = $0.020\,88\ lbf\ s\ ft^{-2}$ = $0.000\,145\ lbf\ s\ in^{-2}$.

Units Used Property	Symbol	System of Measurement			
		cgs	**fps**	**ips**	**S.I.**
Shear stress	τ	dyn cm-2	lbf ft-2	lbf in-2	Nm-2
Shear rate	γ˙	s-1	s-1	s-1	s-1
Apparent viscosity	ηa	dyn s cm-2	lbf s ft-2	lbf s in-2	Pa-s

cgs. - abbreviation used for centimeter-gram-second.
fps. - abbreviation used for foot-pound-second.
ips. - abbreviation used for inch-pound-second.
SI. - abbreviation used for Système International d'Unitè.

Flow Curve

Polymer melts are not Newtonian, but pseudoplastic fluids (i.e., the viscosity decreases with increasing shear rate or stress.). Since there is not a linear relationship between pressure and flow, the flow properties cannot be represented meaningfully by a single number. Therefore, flow testing over a range of conditions is required. The information so obtained is usually presented in the form of a series of flow curves where each one represents data obtained at a particular temperature. Figure 8a. shows individual flow curves for a number of commodity resins while Figure 8b. shows similar curves for some engineering polymers. A flow curve is sometimes referred to as a rheogram. It is generally a plot of apparent shear stress (τw,a) against apparent shear rate at the wall of a die (˙γw,a). This is done because the expressions for the true shear stress and shear rate at the wall of a die are rather cumbersome. In practice it is often just as useful to use the much simpler expressions τw,a = RΔP/2L and ˙γw,a = 4Q/πR3. It may be shown that, as with the true shear rate, there is a true shear stress at the wall of the capillary. To obtain this from capillary rheometer measurements one must correct for the pressure drop caused by the polymer entering the die. (This is called the Bagley correction.) Flow curves generated in most industrial laboratories are, however, generally obtained by plotting τw,a against ˙γw,a.

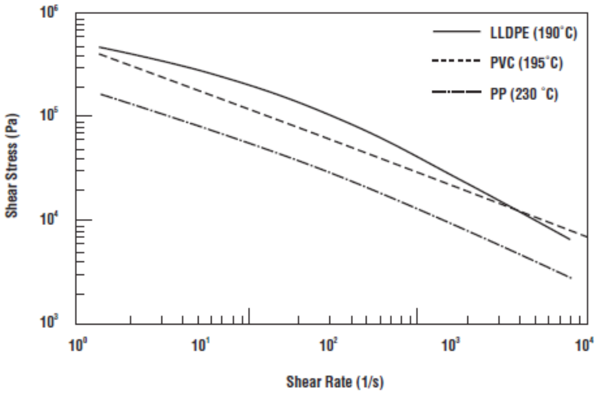


Figure 8a. Viscosity Curves for Some Commodity Thermoplastics

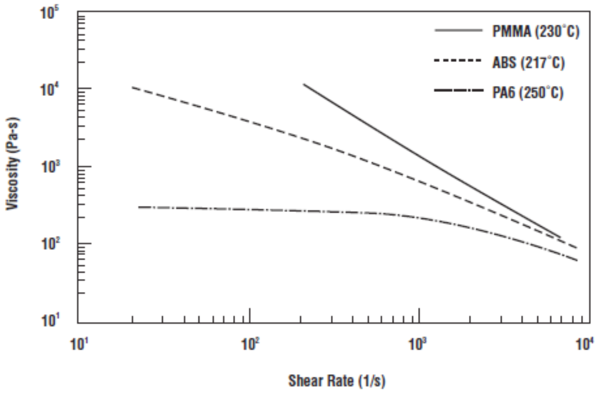


Figure 8b. Viscosity Curves for Some Engineering Thermoplastics

By plotting shear stress in Pa (Nm-2) against shear rate in s-1, a viscosity in Pa-s (Nsm-2) may be obtained by from the slope of the flow curve. The shear stress is generally plotted on the vertical axis and the shear rate plotted on the horizontal axis. Conversion from shear rate to shear stress is also obtained for plastic melts by reading from such a flow curve. Flow curves are used because the equations, used to describe the flow behavior of pseudoplastic fluids, can be imprecise. Log-log plots are generally use to easily read the curves over several decades of shear rate. Although the wall of the die is specified in the measurement, this is simply a place at which the shear stress and shear rate may be calculated from knowledge of flow rates and pressures. The relationship between τw and ˙γw will, however, be independent of the position in the flow system and indeed will be equally applicable to flow in other geometries such as slits.

FLOW PROPERTIES MEASUREMENT

The information necessary to generate a flow curve may be obtained from a variety of types of machines. These include cone and plate and parallel plate rheometers, co-axial cylinder viscometers and capillary rheometers. Because of the similarity of its operation to that of many conversion processes and its ability to generate rheological information at processing conditions, the capillary rheometer is possibly the most useful of these instruments.

Capillary Rheometer

A capillary rheometer (Figure 9.) is a test instrument that is used to measure the rheological properties of polymer melts. It does so by using a piston to forcing polymer melt, from a reservoir, through a capillary die. This type of rheometer is of greatest interest to the plastic technologist as it, in many respects, is similar to injection molding and extrusion machinery and provides data in the shear rate range used in these processes (in fact, early extruders and injection molding machines used rams rather than screws to move the molten resin). The data so obtained may in turn be used, for example, to size dies or runner systems. A capillary rheometer, when used in the shear rate range seen in melt processing, may sometimes be called a high shear rate rheometer. The analysis of shear flows in a

capillary rheometer employs some important assumptions. Of these the most important are:
1. The flow is isothermal.
2. There is no slip on the die wall.
3. The melt is incompressible.
4. The flow pattern is the same throughout the die.
5. Dissipation of energy at the die entrance, or due to chain uncoiling, is negligible.

Measuring $\dot{\gamma}$ w,a and τw

When the above assumptions are considered to be valid, then the shear stress and shear rate may be calculated as follows. If the piston speed of the rheometer is s (measured in mm/s) and the barrel diameter is D (measured in mm), then the volumetric flow rate Q is

$Q = \pi SD3/4$ (Eqn. 4)

This is the same in both the barrel and the capillary. The apparent shear rate at wall is given by

$\dot{\gamma}w,a = 4Q/\pi R3$ (Eqn. 5)

Where R is the radius of the capillary in mm.
Combining the above equations and simplifying,

$\dot{\gamma}w,a = SD3/R3\ s{-1}$ (Eqn. 6)

If the barrel diameter is 9.550 mm (the standard size) then, the formula becomes

$\dot{\gamma}w,a = 91.203S/R3\ s{-1}$ (Eqn. 7)

(when the capillary radius is in mm and the ram speed is in mm/s). Since the shear stress at the wall is given by τw = PR/2L then, for a 20:1 die, τw = P/80 (where P is the recorded pressure at the entrance to the capillary). By plotting τw against $\dot{\gamma}$w,a a flow curve may be obtained.

Flow Data

Below are shear flow data obtained from a capillary rheometer. Such information is available in several material databases, such as those maintained by Moldflow Inc. These data are used, for example, to help predict how an injection mold will fill. For this application the effect, on the viscosity, of changing shear rate at a constant temperature is required. In addition, the effect of changing temperature a constant shear rate is required. A die with a high L/D ratio, for example 20/1, is generally used. The viscosities (in units of Pa-s) at 1,000 s-1 for the following grades of PA 6 (Akulon from Akzo) at a range of temperatures are:

Grade	**240˚C/464˚F**	**260˚C/500˚F**	**280˚C/536˚F**	**300˚C/572˚F**
Easy flow	98	78	63	50
Medium flow	149	115	89	69
Stiff flow	394	319	259	210

The viscosities (Pa-s) at a temperature of 240˚C/464˚F for a range of shear rates (s-1) are:

	100s-1	**1,000s-1**	**10,000s-1**	**100,000s-1**
Easy flow	197	63	20	6
Medium flow	323	89	25	7
Stiff flow	1220	259	55	12

Ease of Flow

The data in the above table were obtained when samples of nylon 6 (PA 6) were tested. They clearly show that the three injection molding grades tested have very different viscosities. The first grade, which has the lowest viscosity, (it is the easiest flowing grade) can be used where mold filling is difficult, or where long flow lengths are involved. The viscosity of all three materials falls as the shear rate is increased. Thus mold filling becomes easier. Raising the melt temperature, while keeping the shear rate constant, reduces the amount of injection pressure required to maintain a certain rate of flow. This is because most plastic melts become less viscous (flow more easily) with increasing temperature. Such information is frequently presented in tabular form in the “Flow Properties” section for a material. Although the viscosity of most plastics falls as the temperature is raised, with some materials the effect is more pronounced. Thus, for materials whose viscosity falls markedly with a rise in temperature (for example, PA 66, PC and POM) the ease of mold filling is helped significantly by a moderate increase in melt temperature. For materials where the effect of temperature increases is less pronounced, it is more useful to increase the mold temperatures and/or the molding pressures to ease the filling of a mold.

Flow Property Assessment

Because most methods of shaping plastics are melt processes, such as extrusion or injection molding, the measurement of melt flow properties is extremely important. A large number of tests have been devised, many of them empirical, to measure these properties. Such tests may be roughly grouped into low shear rate tests and high shear rate tests. A low shear rate test, such as the melt flow rate (MFR) (or melt flow index (MFI)) test, is one of the most widely used tests (See the Section 3 on Testing).

ELASTIC EFFECTS IN POLYMER MELTS

The long chain molecules that make up polymeric materials become distorted when they are subjected to shearing forces during processing operations. Such shearing tends to stretch the molecules. However, when the shearing process ceases the molecules tend to coil up again, providing they are still molten. If cooling occurs rapidly after shear, this re-coiling may not be complete. Such un-coiling/re-coiling processes can give rise to a number of effects, which are often referred to as elastic effects. The most important elastic effects are die swell, melt fracture, sharkskin, frozen-in orientation and draw down.

DIE SWELL

When polymer melt emerges from a die the extrudate may swell, so that its cross-section as it leaves the die is greater than that of the die orifice. For a capillary die, the ratio of the extrudate diameter to the die diameter is known variously as the die swell ratio, swelling ratio or as the puff-up ratio. For a slit die, the relevant ratio is thickness of extrudate/depth of slit.

Causes of Die Swell

Die swell (Figure 10.) occurs because shearing of the melt as it passes through the die causes the molecules to become extended (with the greatest orientation near the die wall). On emergence from the die, the molecules tend to coil up (recoil) resulting in a contraction in the flow direction and an expansion in directions perpendicular to the flow. If an extrudate is cut at the die face, it will be seen that the leading edge of the extrudate is convex. This indicates that the greatest contraction in the flow direction is nearest to the wall where the shear has been greatest.

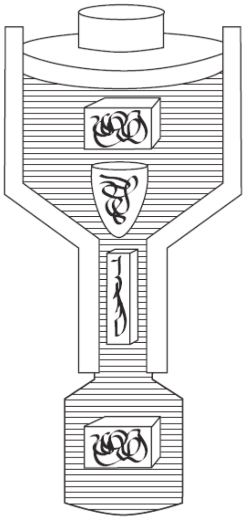


Figure 10. Die Swell

Reducing Die Swell

For a given material, die swell may be reduced by:

- Decreasing the extrusion rate
- Increasing melt temperature
- Increasing the length of the die parallel or lands
- Streamlining and/or reducing the die entry angle
- Increasing the draw down ratio

Often the addition of a lubricant will reduce the die swell. The lubricant will cause slip at the wall and ease the flow of polymer through the die. Low molecular weight polymer functions as a lubricant and so broadening the molecular weight distribution of a material will also reduce die swell.

Changing Shape

It is common industrial practice to compensate for die swell by stretching, or drawing down, the extrudate so that it can just pass through a sizing die. When this technique is used it is not necessary that the two be exactly balanced. It should, however, be noted that drawing down causes molecular orientation, which gives rise to an increase in strength in the flow direction and a decrease in directions transverse to the flow. This may or may not be desirable. The method is also somewhat limited where the solid extrudate has varying section thickness. Shear rates, and hence die swell, will be higher at the thinner sections. These thin sections may also have a shorter die parallel, to ensure that extrusion rates are constant across the cross-section, and this will increase the die swell even further. In the production of pipe and tubing, the situation is further complicated by the fact that the extrudate is usually inflated to the dimensions of a sizing die. In this case it may be assumed that on emergence from the die, the wall thickness will expand appropriate to the die swell for the shear rate used. Subsequently, the wall thickness will be reduced proportionally to the amount of inflation given by the ratio diameter of the sizing die/ the external diameter of the pipe die.

Die Entry Angle

The die entry angle is the angle of convergence provided for the melt entering the extrusion die. As the melt leaves the extruder barrel the shape of the flowing melt stream must be changed to that of the shaped extrudate. This transition takes place in the die adapter and is best done as gradually and as streamlined as possible. The higher the viscosity of the melt, the more streamlining is required. It is also necessary to keep the lengths of the flow paths, to each part of the die, the same in the streamlined region, as this will reduce subsequent extrudate shape changes. The die entry angle for a particular material can be found practically by using a plate die, which has a properly shaped die orifice, in a nonstreamlined die holder. Plastic is then run through the die, followed by a change in the color of the material. When the second color starts to extrude from the die, the machine is shut down. The hot die and the die holder are removed and cooled and the cross section of the cold material is examined. The color changes seen in the cross section will show the streamlined shape required. A thermoplastic material, which contains a heat fugitive dye, may talso be used to show the streamlining required.

Predicting Die Swell

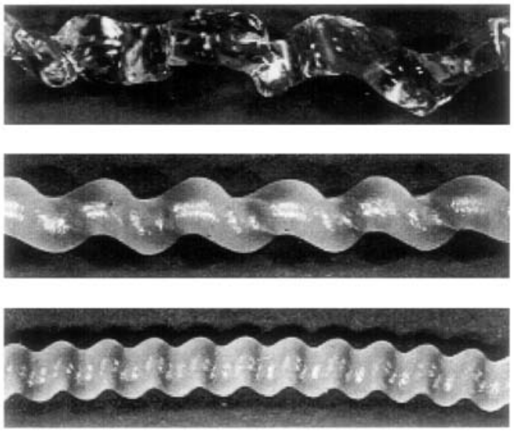
Computer programs are available that simulate the flow of polymeric materials through a die and will predict die swell. This type of program takes die swell into account in predicting the die shape and size required to produce a desired profile shape and size. To do this, the program incorporates a materials database that contains the data (thermal, rheological and viscoelastic properties) needed to do a flow analysis. Such software allows the design of a die that is balanced to produce uniform flow. Methods for the measurement of die swell are given in a later section.

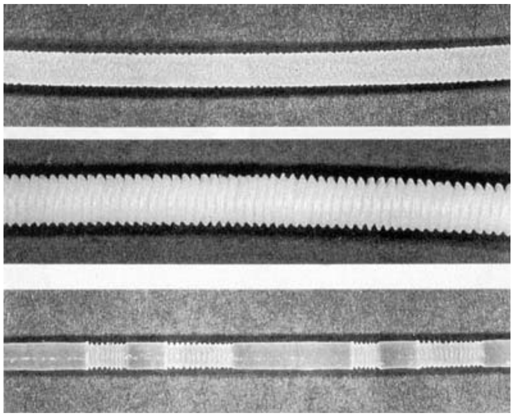
MELT FRACTURE

It is frequently observed that when extrusion is carried out at high rates, a distortion of the extrudate may occur. The distortion may be due either to the phenomenon known as melt fracture (also known as elastic turbulence or bambooing) (Figure 11.) or, it may be due to sharkskin. Although not fully understood, these do appear to have different origins.

Critical Shear Rate

Melt fracture occurs when the shear rate in a die exceeds a critical value for the polymer melt at a particular temperature (the critical shear rate). There is also a critical shear stress. The point on the shear rate-shear stress diagram (flow curve), corresponding to these two values is known as the critical point. Melt fracture is believed to occur in the die entry region where material is being funneled from the melt reservoir into the capillary or die. In a full-scale extruder, this would correspond to the point where melt moves into the die parallel portion of the die. Some further complicating effects may occur at the wall of the die.





Form of Distortion

The form of the melt fracture distortion varies from one polymer type to another, but it is generally helical in nature. With materials such as polyethylene and polypropylene a distortion like a screw thread may appear, while with polystyrene the extrudate may form a spiral. Other polymer melts may show ripples, or bamboo-like repetitive kinks. With all melts, the helical nature becomes obscured by severe distortion that looks random, at rates well above the critical point. Melt fracture is most likely to occur where small diameter extrudates are being extruded at high rates. The most notable example occurs with wire covering.

Factors Affecting Melt Fracture

Since it is easily observed in the laboratory, melt fracture has been widely studied and experiments have shown that:

- The critical shear rate ($\dot{\gamma}c$) increases with increasing temperature
- The product τwMw is a constant. Melt fracture will start at lower shear stresses and shear rates as the molecular weight of the material is increased (τw is critical shear stress and Mw is weight average molecular weight)
- Two polymers differing in their levels of branching, but which have similar melt viscosities tend to have similar critical points
- The extrudate quality may be markedly improved by tapering the die entry. When this is done externally, undistorted extrudates may be obtained at rates well above the critical point. However, there is some evidence that there may still be some internal distortion
- There is some evidence that increasing the length to diameter (L/D) ratio of the die parallel increases the critical shear rate. Tapering the die parallel may also substantially increase the critical point

The above factors have now been well known for some years and as a result high speed wire covering, and other operations involving high shear rates are operated without undue trouble from melt fracture effects.

SHARKSKIN

The phenomenon of sharkskin has been less widely studied than melt fracture, but it is probably a greater problem in industrial extrusion.

Melt Tearing

In the case of sharkskin, the distortion consists of transverse ridges (as opposed to helical distortions). It is believed to occur as a result of the melt tearing as it extrudes from the die. This occurs because, within the die, melt close to the wall is moving very slowly (in the case of the layer next to the wall this movement is zero). As the melt emerges, the whole extrudate moves away from the die face at a constant speed so that the outer layers are suddenly stretched and may tear.

Incidence of Sharkskin

Experimental studies indicate that the critical shear rate for onset of sharkskin ($\dot{\gamma}$c.sh) is inversely proportional to the die radius (R); that is, $\dot{\gamma}$c.sh R = a constant. This means that the critical shear rate is much lower with larger diameter dies. One result of this is that the small dies (such as those used in typical laboratory rheometers) generally show melt fracture occurring at shear rates below those for the onset of sharkskin, while the reverse may be seen with typical full-scale industrial dies.

Critical Linear Extrusion Rate

It can be shown, as a consequence of the above relationship, that sharkskin is likely to occur above a critical linear extrusion rate irrespective of the die size. For example, for a particular hypothetical polymer melt, it may occur at an extrusion rate of approximately 30 in./min whatever the die size.

Conditions Favoring Sharkskin

Sharkskin is most pronounced when the melt is partially elastic and has the consistency of a friable cheese. Improved results may sometimes be obtained by reducing the melt temperatures, so that the melt is more strongly elastic as it emerges from the die. Alternatively, some improvement has been seen when the die is heated at the point of exit. This makes the surface layers of melt more fluid, thus making melt tearing less likely. The severity of sharkskin may vary enormously. At one extreme, the distance between a ridge and adjacent trough may be 1/3 of the extrudate cross-section. At the other extreme, the effect may be barely detectable to the naked eye, but shows up as a matt finish or, may be felt by running a fingernail over the surface. In blow molding, a rough surface on the inside of a bottle is indicative of sharkskin (The outside is usually flattened against the wall of the blow mold).

Molecular Factors

The only molecular factor within a polymer type that appears to greatly influence sharkskin is molecular weight distribution (MWD). A broad distribution is generally effective in reducing any tendency to show sharkskin effects.

FROZEN-IN ORIENTATION

In the molten state, and when not subject to external stresses, polymer molecules tend to coil up. That is, they prefer to exist in a random coil configuration. When external stresses are applied (as occur during extrusion, molding and other shaping operations) the molecules become distorted from their randomly coiled state and tend to become oriented. In most processing operations it is generally desirable to “set” the polymer as soon as possible after it has been shaped; usually by cooling in a water bath after the extrusion die. In such circumstances, the polymer molecules may not have time to coil up (recoil) completely before the melt freezes. This results in the effect known as frozen-in orientation.

Anisotropy

As a result of frozen-in orientation, plastic products may be anisotropic in their behavior. That is, their properties differ if measured in different directions. For example, tensile strength is greatest in the direction of orientation. Impact strength is also affected by frozen-in orientation. When the sample has been injection molded with the gate at one end of the sample, the molecules will be roughly aligned with the long axis of the sample. Thus to break the sample, in a standard Izod test, requires fracture across the elongated molecules, which gives a higher impact strength than is recorded with unoriented samples. On the other hand, if impact strength is measured by dropping a weight onto a flat plate, lower impact strength will be seen with more oriented moldings. In this case fracture can occur more easily parallel to the direction of orientation since this largely requires fracture between, rather than across, molecules.

Biaxial Orientation

Increased orientation may be introduced into a system by stretching the polymer melt just before it freezes. Uniaxial orientation, that is stretching in one direction, is important in the manufacture of tapes and fibers, while biaxial orientation, simultaneous stretching in two directions, is important in film production. It may also be desirable to build-in biaxial orientation into piping, bottles, and other hollow containers, in order to enhance the hoop strength and fracture resistance of these products.

Desirable or Undesirable?

Frozen-in orientation may thus be either desirable or undesirable according to circumstances. It is greater when the melt is subjected to higher stresses and when there is a short interval between shearing and freezing (or setting) of the melt. Such conditions are obtained with low melt temperatures and low cooling temperatures after shaping, as found with low injection mold temperatures or low extrusion cooling bath temperatures.

DRAW DOWN

In a number of extrusion processes, such as the manufacture of film, the extrudate may be subject to extensive stretching after leaving the die. In other cases, like chill-roll casting of film, it is important that the extruded web does not tear on stretching.

Viscous Behavior

In cases where stretching is important, viscous rather than elastic behavior is often more important. It is reasonable to expect that, although the melt should have some strength and elasticity, the main requirement is that the molecules of the melt can flow past each other.

Neck-In

One phenomenon associated with chill roll casting is that of neck-in. The edge of the extruded web tends to shrink inward towards the center of the web and, at the same time, tends to become thicker than the bulk of the film. It is found here that more elastic melts, which can maintain a tension in the extrusion direction, are less susceptible to neck-in.

Parison Sag

Elastic effects may also influence the parison sag that occurs during blow molding. Parison sag is the thinning of the parison caused by the stress of its own weight as it leaves the die. Part of the sag may be due to an elastic effect (chain uncoiling) and part due to viscous flow as the molecules slide past each other. It is reasonable to assume that the elastic component of the sag increases as a proportion of the total as the:

- Molecular weight, and hence viscosity, increases
- Melt temperature decreases (increasing viscosity)
- The length of parison per unit weight increases. This is because an elastic deformation under a standard load depends on the length of the part being stretched, whereas the viscous flow does not (as long as the weight of the parison is constant).