Processing of polymeric products

~~Additi~~

Most polymers are products of industrial chemistry. Following its synthesis, the typical polymeric raw material is compounded with appropriate additives and then shaped into a product.

Additives

The materials added to polymers may be ~~micro~~ incorporated for purposes of strengthening or toughening ; or they may be included to produce flexibility.

PVC ~~is~~ + abrasion resistant filler = floor tile.
PVC + plasticizer (flexibility) = rain coat.

Polymer + ~~flame~~ stabilizers (reduce deterioration) = flame retardant.

Polymer + colorant = Aesthetic
Polymer + additive to reduce cost. & improve ~~some~~ other properties.

Rubber + carbon black (strengthening + absorbs UV light)
= rubber more resistant to deterioration in service

Fillers

Some additives are used in large proportions. ~~Thus, wood f~~ Most of the addittives ~~ao~~ are added to give strength or toughness to plastics. Thus wood flour (a very fine saw dust) is added to a PF (phenol-formaldehyde) plastic to increase strength. 35% wood flour more than doubles the toughness of a PF plastic. Wood flour is cheaper than PF and ~~can be~~ is a replaceable resource. The improvement in strength is a result of ~~a~~ the mutual interaction of the two components

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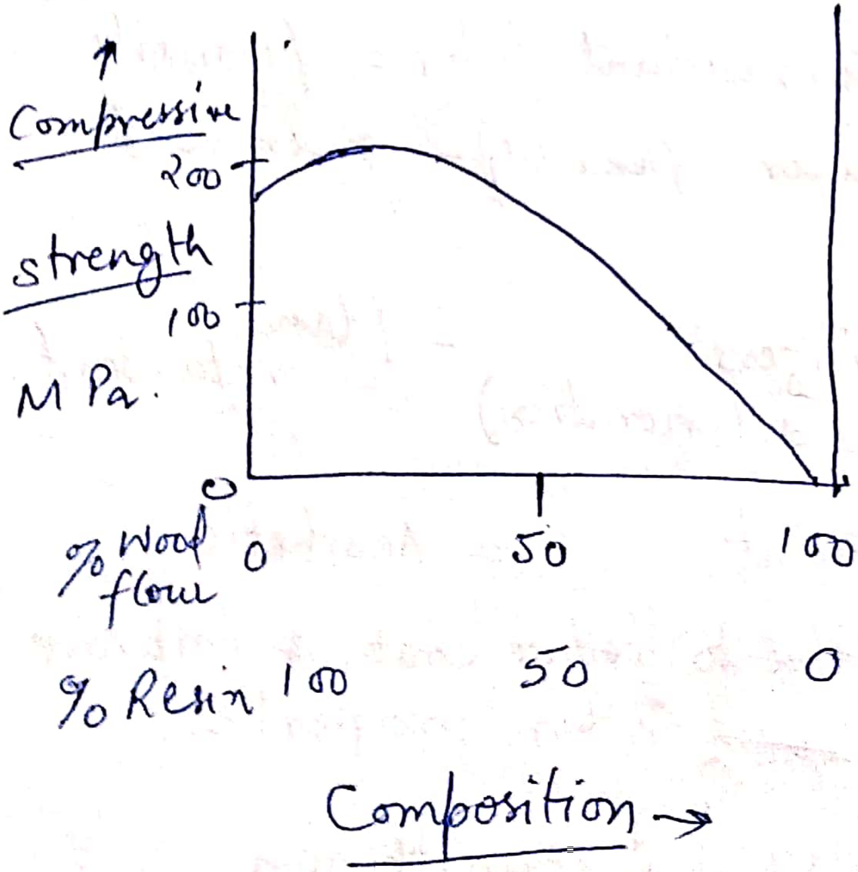


Addition of a filler to a plastic (wood flour added to PF)

The mixture of the two is stronger than is either alone

Fillers can be of various types. Wood flour is a polymer— one containing cellulose. Its density is ~ PF. Therefore the product retains low - specific gravity. Silica flour (finely ground SiO_2 made from quartz sand or quartzite rock) also is used. It is harder than wood. This imparts abrasion resistance to the plastic product. Furthermore, it neither burns nor softens at high temperatures; as a result it adds thermal stability to the product. Of course, it does increase the products' total density because the specific gravity of SiO_2 is about twice that of common resins. $\rho_{SiO_2} = 2.65$ g/cc . PF = 1.3 g/cc

Fibrous fillers are especially effective for adding strength to the product. eg. glass fibers, organic textile fibers, or fibers from mineral ~~ses~~ sources. They are often chopped into short lengths so that they can be mixed with the polymeric materials that are subsequently molded a fiber-reinforced plastics (FRP)

Plasticizers.

micro-molecules
At normal temperatures, the small molecules ~~or mers are~~ are generally liquids or gases
e.g. methanol, ammonia, benzene, ethylene, vinyl chloride, Formaldehyde, Acetone, urea, etc.

In contrast, the macromolecules are solids since they comprise long chains or networks. When small molecules are intimately mixed with macromolecules, they reduce the rigidity of the macromolecular — or polymeric — product. When small molecules Surround large ones, the large molecules move more readily, in responsse to either thermal agitation or external forces.

In brief, the micromolecules plasticize the macromolecules. ~~Plastics are~~

Plastics that are normally stiff, such as PVC can be made flexible, so that they can be used in sheet or film form.

A plasticizer, in effect, lowers the T_g, so molecular movements and rearrangements can occur at room temperature in polymers that would otherwise be rigid.

A plasticizer must have certain characteristics, It should have a high b.p. (low vapor pressure), so that it will not readily evaporate

eg. a plastisized raincoat would become useless if the coat would become useless if the coat were to become stiff and brittle with time, this, of course, could happen if the plasticizer gradually evaporated, leaving a plastic that was below its glass temperature.

The plasticizer must not be soluble in the liquids with which it comes in contact. Although some plasticizers are non volatile. solvents such as petroleum products can dissolve a large variety of micromolecules. Thus, the inner surface layer of a plastic container may be embrittled as the plasticizer is depleted by solvents that are stored in the container.

A plasticizer must be <u>compatible</u> with the polymer. ~~Att~~ For a plasticizer to be suitable the small molecules should be attracted to the surfaces of the large molecules; the small molecules should not segregate within the plastic.

[If small molecules ~~all~~ have greater attraction towards each other than to the surfaces of large molecules, they will segregate within the plastic. If large molecules attract each other with a stronger force, they will not allow the entry of ~~lar~~ smaller molecules between them for plasticizing purposes.]

The choice of the most suitable plasticizer depends on the details of the characteristics of the molecular structure and usually ~~depends~~ ~~upo~~ involves extensive testing by the manufacturer.

Mixing :

Uniformity is a necessity for quality materials. Materials that are composed of multiple phases must have a "homogeneity in their heterogeneity".

eg. steels should have uniformly distributed hard carbides in a tough ferrite matrix. Similiarly additives should be equally distributed in a plastic/~~pol~~polymer. Gradients in ~~coloring~~ colorants lead to obvious variations in products. Excess fillers or plasticizers at a point and deficient 1 mm away lead to sub optimal properties at both locations.

Mixing of additives into a plastic product is complex. eg. silica flour filler has twice the density of many of the polymers with which it is combined. Some additives are in the form of liquids, others are solids, whereas polymers are either viscous melts or semi solids during the mixing. This latter characteristic is critical. Simple stirring does not suffice.

Most polymer mixing, or "compounding" is performed as a batch process on an "open-roll mill" (also called "rubber mill").

Open roll mill (rubber mill)

The components of the plastic or rubber are blended by a shearing action in the nip region between the rolls. The two rolls rotate at slightly different speeds. They also are maintained at different temperatures.

The mill has two rolls that can be internally heated or cooled. The nip of the rolls can be adjusted to different size gaps as required. They operate at different temperatures and speeds (3 to 4 sec/revolution). The velocity & viscosity gradients that result introduce a kneading action that is quite effective. Also, the temperature difference causes the sheet compound to invest one of the rolls; i.e., the plastic mixture blankets one of the rolls and not the other. Typically, rubbers will coat the hot roll. Several ~~or~~ hundred passes through the nip achieve a uniform mixing if the ~~opt~~ operator cuts ~~back~~ the blanket and peels it from the coated roll several times each time feeding it back into the nip to form a new blanket.

Polymers that are subject to oxidation at the mixing temperature must be blended in an internal mixer that is enclosed and ~~ext~~ excludes air, Rotors and blades perform the kneading action.

Shaping processes

The steps between the polymer mixture & the final product are :—

ⓐ Softening
ⓑ molding
ⓒ hardening

Softening — It is commonly achieved by heating but may involve plasticization by solvents.

Molding — It commonly involves the application of pressure, although there are certain exceptions.

Hardening — It may occur by cooling, by a chemical reaction, or by the volatilization of a fugitive plasticizer.

A significant majority of polymers may have their thermal behaviour ~~&~~ categorized as :-

① Thermoplastic
② Thermosetting.

Thermoplast

~~The~~ Linear polymer with only limited, if any cross-linking or branching; therefore, they soften at elevated temperatures. As the temp. rises, the molecules can slide past each other.

~~&~~ Thermoplasticity is effective above Tg. Further, the normal temperatures of use must be in the range in which the plastic retains its shape.

The Thermosets ~~are~~

These are altered both chemically and structurally during thermal processing. They develop a 3D structure, either a network structure, or a cross-linked structure. These structures are only partially completed before forming. ~~and~~ They become one big 3-D molecule ~~before~~ when they are processed in the presence of heat & pressure. The curing within the heated mold completes the formation of the network. Therefore, a thermosetting polymer gains ~~rid~~ rigidity before the pressure and added temperature are removed. Thermoplastic polymers must be cooled in the mold (or on exit)

Polymer viscosity.

When a polymer is under pressure, the relationship between viscosity, η, and the rate of strain γ/t, is less ideal than that shown in $\eta = \tau/(dv/dy)$

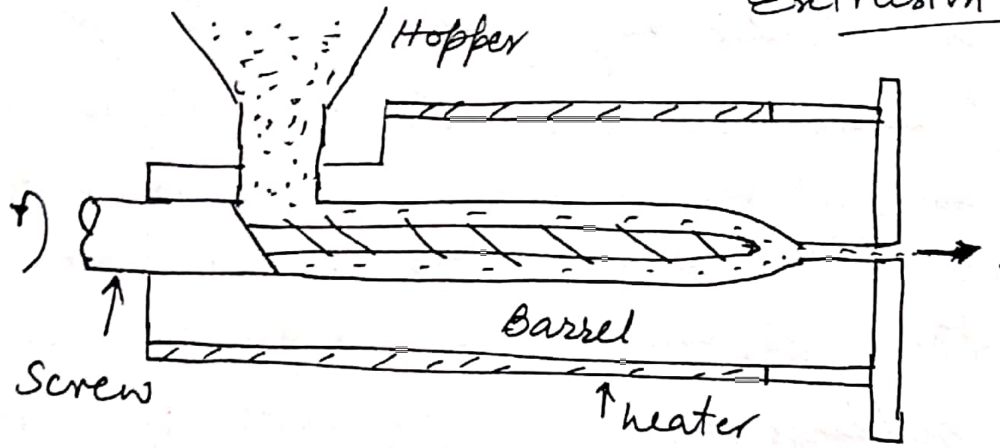
Several factors contribute to this variance; among them is the "free space" that is present in the supercooled liquid. This leads to a high compressibility that becomes evident as "die swell" (or volume expansion at the exit of the die) when the viscous polymer is extruded out of the die. Of course, this is undesirable when specific dimensions are required. It also leads to difficulties in predicting the rate of flow through feed channels (sprues) of closed dies. This can mean there will be incomplete filling of the dies during injection molding unless allowances are made.

Extrusion = Starting materials are commonly granules of a thermoplastic polymer that have been sized for easy flow. An "auger" (or screw) feeds the granules into a heated zone where

where the thermoplastic pellets soften. However the heating does not come entirely from external heaters. There is considerable energy that goes into the polymer melt from the work of the auger as it compresses the melt & forces it through the die. eg. the motor turning the auger uses as much as 50 kW (~70Hp) to drive a 10-cm screw. This power is absorbed by the plastic in the form of heat.

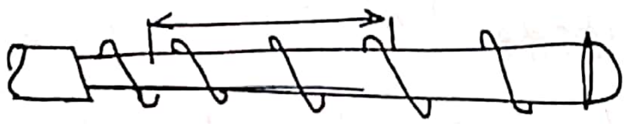
To control the temperature as closely as possible, we can segment the heater. The temperature of each zone is measured by thermocouples and is controlled separately, so that the desired ~~Ha~~ temperature profile is obtained along the barrel. (Why?) This is done, because various thermoplastics have different softening characteristics. For example, LDPE, which is amorphous, softens progressively as the temperature increases. In contrast, nylon softens rather abruptly at a higher temperature because it possesses high crystallinity. Thus, the screw design of the auger must be modified depending on the product. (See fig.)

Extrusion (Auger)

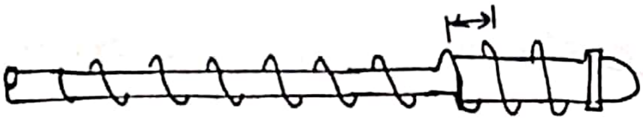


(a)

Solid pellets are fed into the heated zone by an auger. The melted thermoplastic is extruded through an open end die as bars, pipe, or sheet product.



(b) Auger for PE which softens gradually



(c) Auger for nylon, which softens abruptly. The compression & ~~The~~ metering sections (arrows) is much shorter in the latter.

~~The~~

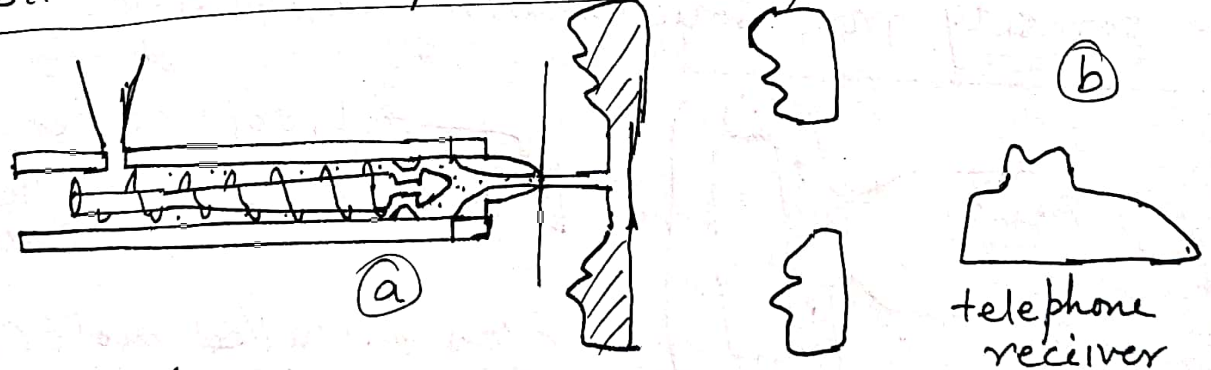
The feed into the heated zone and the compressio to eliminate the pores is simultaneous and continuous for PE. The compression is abrupt for nylon after the granules have passed well into the heated zones.

The die of an extruder may have a variety of geometries. Of course, the cross section along the length of the product must remain constant. A circular orifice produces a solid rod, and a slit produces sheet or film products. It is also possible to manufacture longitudinal moldings of irregular cross-sections. Tubing and pipe must be extruded by mounting a "mandrel" (or "torpedo") in the center of the hole, so that extrusion is through the annulus. ~~At~~ Alternatively, wire can be fed continuously into the center of the orifice to be coated with rubber insulation. Rates may approach 1km/min. The extrusion process is adaptable to large scale production.

The plastic must flow as it emerges through the die but must harden immediately on exit so as to retain its desired shape. The surface to volume ratio and the amount of mass to be cooled per sec dictate the choice of air or water for cooling.

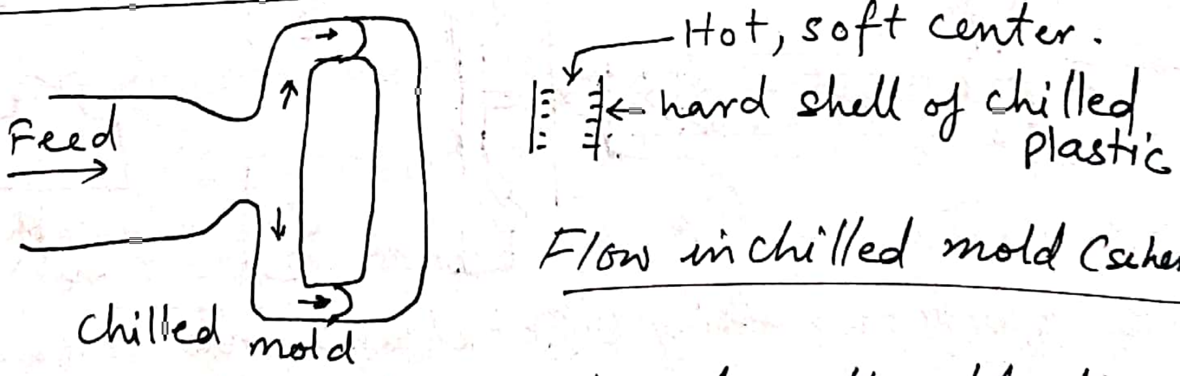
Injection molding.

The open die of the extrusion process may be replaced with a closed die, ~~as st~~ The die is a split mold that contains the negative contours of the product to be made. The hot plastic is forced ~~to~~ (injected) into the mold by either an augur or a hydraulic plunger. The injection process provides more flexibility in product geometry than does extrusion, because the cross-section is not fixed longitudinally. Examples of injection-molded products are plastic ice cream spoons to telephone receivers.



Injection molding ~~&~~ ⓐ Extrusion into closed die. The ~~sch~~ softened thermoplastic is forced through sprues to the cooled die cavity, where it hardens. ⓑ formed product in the opened die (rotated 90° since the large auger in part ⓐ is operated horizontally.

The injection molding of thermoplastic polymers generally uses water-cooled molds for hardening the product. This facilitates production, because the product becomes rigid almost immediately and can be removed, so there can be a sequel injection. However, this quick rigidity presents complications, since the viscous melt ~~mo~~ must enter through chilled sprues (feed channels) and mold cavities. In fig. we can see a rigid shell of chilled polymer that constricts the channel. Higher injection pressures are required to feed the far cavities and to avoid porosity from solidification shrinkage.



Flow in chilled mold (Schematic)

The mold is chilled to harden the plastic for stripping. However, this produces a rigid shell that constricts ~~t~~ the flow channels. High injection pressures are required.

Sheet moulding

In principle, sheet molding is the simplest forming process. An extruded sheet of thermoplastic material is clamped over the edges of a mold. The sheet is heated by infrared heaters. Gravity or a vaccum sags the sheet into the contour of the mold. Variants of the process use air pressure. Sometimes a mating mold is incorporated on the opposite side..

Sheet molding is an inexpensive process for products with suitable geometries,

Applications — raised letter signs, housing for instrument panels in automobiles, etc

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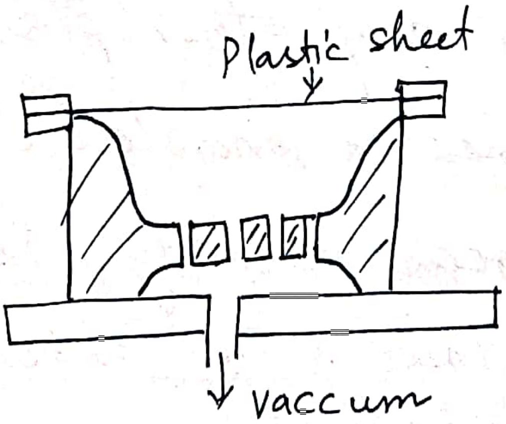
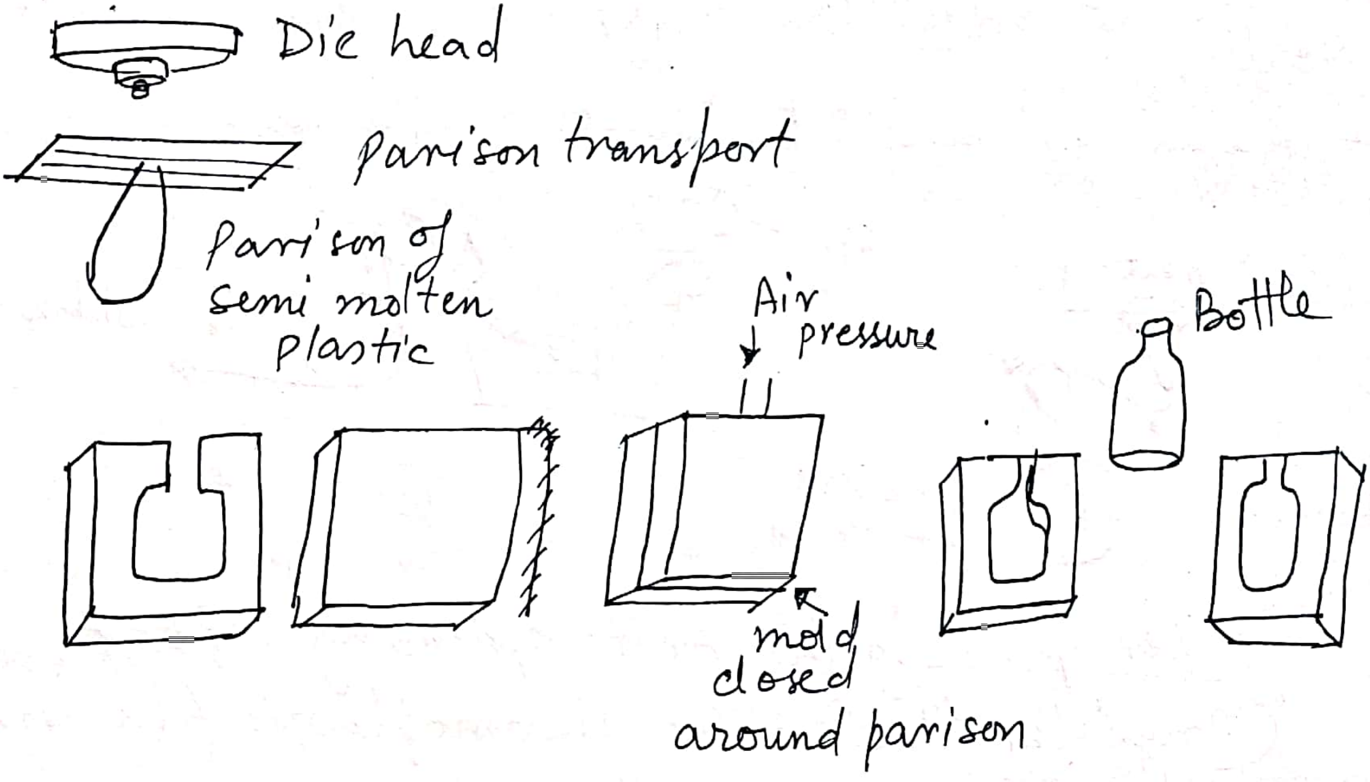


Sheet molding (vaccum molding.) The molding pressure may also be created by air pressure or by a mating mold in the upper side.

Blow molding :-

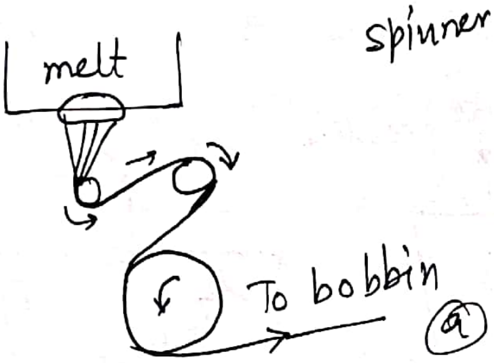
Bottles & related products that have a constricted neck cannot be molded by any of the previous processes. There would be no way to remove the interior mold. In the blow-molding process, which is an adaptation from the container glass industry, a soft plastic tube is extruded and is cut free from the die head. The resulting "hollow drop" or "parison" of soft plastic is surrounded by a mold. Air pressure is used to expand the parison until it takes on the shape of the mold. Blow molding - more than any other plastic forming process, requires a knowledge of the relationships between viscosity, temperature and viscoelastic behaviour. The experience of the operator is also important.

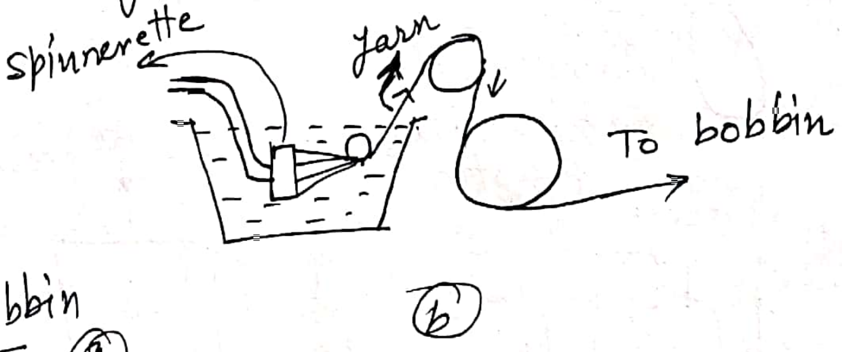


Blow molding = Air expands the viscous parison of plastic into the shape of the mold. Precise time and temp. controls are reqd in this process, which originated in the glass industry..

Spinning = Manufacturers make fibers by forcing the plastic through a multiple orifice "spinnerette". This device contains as many as 50 or 100 holes, each less than 0.2 mm in diameter. In melt spinning, the ~~thom~~ thermoplastic polymers, such as nylon and polyesters, are heated to low viscosity. The slender, emerging fibers cool quickly in a current of air before they travel over a take-up roll.

~~Rayon is made by a~~





Fiber spinning ⓐ Melt spinning ~~(PEf~~ (Polyester fibre) = The thermoplastic filaments solidify as they quickly cool.

ⓑ Wet spinning (cellulose fibers) The extruded filaments complete their polymerization in the bath. The rolls move at different surface speeds (arrow lengths), so the filaments are stretched between the two take-up rolls, extending and orienting the molecules.

Rayon is made by a "dry-spinning" operation. It is dissolved in acetone to produce a thick solution that is extruded through the Spinnerette. The acetone evaporates (collect–recycle) to permit the fibers to dry before they go over the take-up roll. In each of the above spinning operations, the filament travels at about $\boxed{15\ m/s}$ ✓.

it third slower process is "wet spinning". It is used when the fibers must react with the bath to complete the polymerization reaction after they leave the spinnerette.

Molecular orientation:-

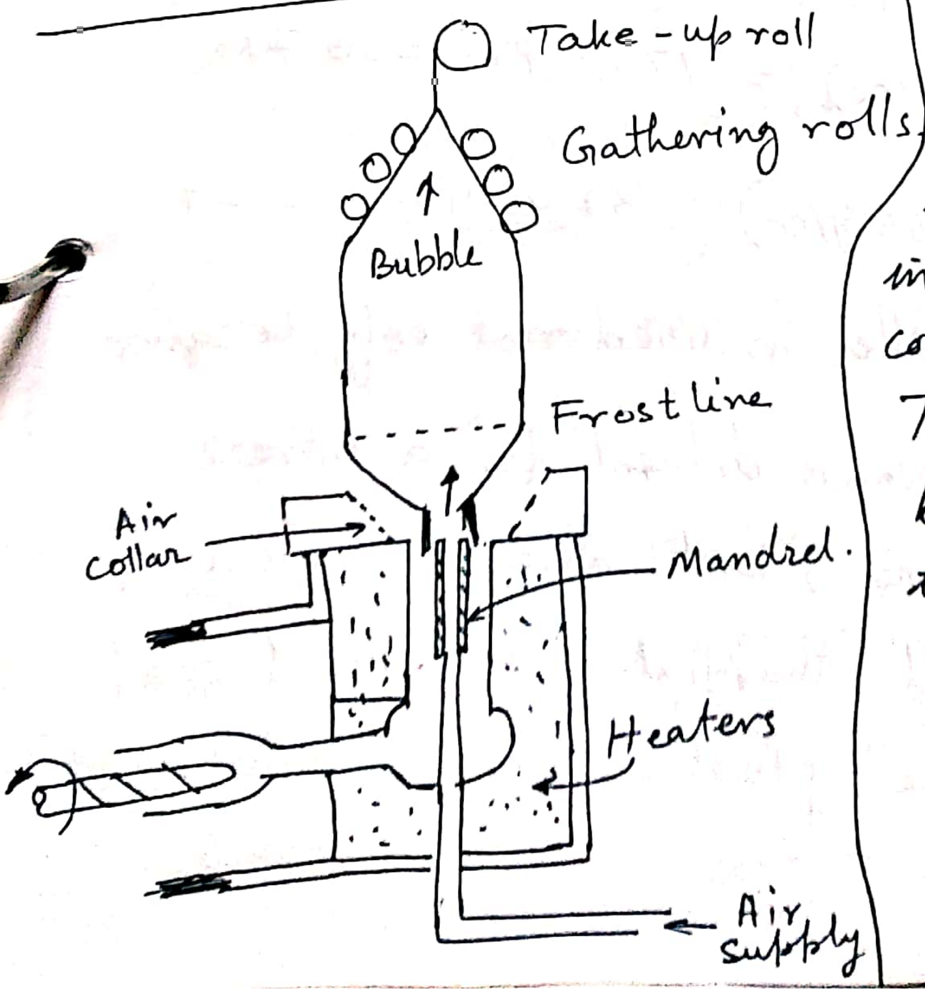
As linear molecules become uncoiled and straightened, they align ~~to~~ themselves with one another, and the crystallinity increases. Concurrently, the stress requirements increase for each additional increment of strain. Thus the elastic modulus increases. Also the strength, the heat resistance, & the moisture resistance increase.

The warm fibers emerge from the spinnerette as a viscous, but deformable, supercooled liquid. They have been wrapped 360° around each roll; the second roll travels appreciably faster than does the first roll. Therefore, the fibers are uniformly stretched several 100%, inducing crystallization. The slender fibers cool rapidly to ambient temperatures while still under tension, thus preserving the crystallization. Not only is the more fully crystalline product stronger and more stable in service, but also the property changes that accompany the Tg are less abrupt since only a minor fraction of the product is amorphous. Essentially all fibrous products that are made artificially are stretched in processing for molecular orientation & crystallization.

The molecules of film products also can be oriented; however, the process is more complex, since the alignment must be bidirectional within the plane of the film, rather than uniaxially along the length of ~~t~~ a fiber.

The same principle could be used for a film product. Here, however, an undesirable anisotropy would be introduced. Specifically, the film would be strong in one direction and weak at right angles to it. [eg. newsprint — the wood fibers are preferentially aligned during the paper making process. As a result, it is easy to tear newsprint straight in one direction, but more difficult to do so in the $\perp$ direction.]

A better process includes the simultaneous stretching in the two coordinate directions, so that the molecular orientation is biaxial. The "bubble method" is one such process. A cylindrical film is extruded through an annular die. Air is blown through the mandrel and expands the sleeve into a larger cylinder. ~~Both~~ (Expansion ceases when the film temperature drops below Tg) Both Circumferential and longitudinal stretching provide the biaxial orientation. The film may be slit if desired, or it may be heat sealed into plastic bags.



Bubble forming (plastic film). = The cylindrical sheet is expanded simultaneously in two directions as it cools below the Tg. Therefore, it develops biaxial strength in the two dimensions of the film.

Example 10-2.1

Assume we mix 84g of silica flour (finely powdered silica, SiO_2) with 100kg of phenol-formaldehyde (PF), The densities are 2.65 and 1.3 g/cc, respectively. What fraction of the volume is filler?

Procedure :- Determine the true volume of each.

Calculation :- Basics :- 100g PF and 84g SiO_2

$$100g\ PF/(1.3 g/cc) = 77\ cc\ PF = 0.71$$

$$84g\ SiO_2/(2.65\ g/cc) = 32\ cc\ SiO_2 = 0.29$$

Comment = A filler is used not only because it is an inexpensive diluent for a more expensive polymer, but also because it gives additional thermal and dimensional stability to the plastic.

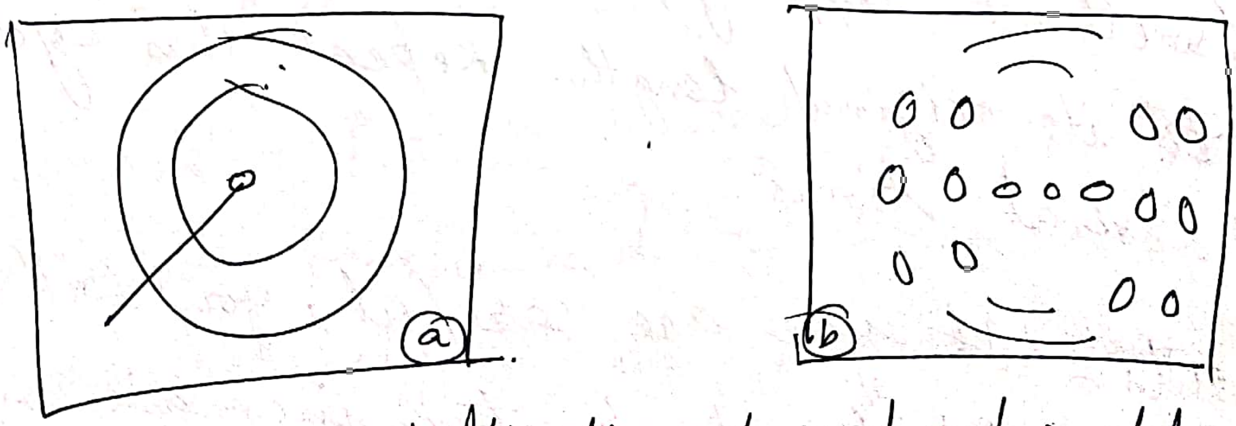
Example 10-2.2

Direct evidence of the ordering that accompanies the orientation of rubber molecules into ~~the~~ longitudinal bundles when the rubber is stretched. Explain the results.

Procedure :- For this simple experiment, use a heavy but easily deformable rubber band. Your lip can serve as a sensitive detector of temperature changes. Place the band in contact with your lower lip. Stretch it rapidly; after a few seconds, quickly (without snapping) return the rubber band to its original length. Repeat this cycle several times.

Results = If you are careful, you will be able to detect a temperature increase on stretching, and a temperature decrease on release.

Explanation (see discussion of conformational disorder) Stretching the rubber molecules produces longitudinal alignment, and introduces a greater amount of order to the structure (less entropy). In fact, crystallization can occur. This raises the heat of fusion, but, since rubber is a very poor conductor & dissipator of heat, this heat raises the temperature of the rubber. Relaxing the rubber allows the oriented molecules to rekink, increasing the amount of disorder (entropy). This change requires energy, which must be drawn from the sensible heat, lowering the temperature



Deformation crystallization of natural rubber (polyisoprene) revealed by ~~X~~ XRD.
ⓐ unstretched ⓑ stretched.

10-P21
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Forty five kg of silica flour (finely ground quartz sand) are mixed with each 100 kg of melamine formaldehyde (mf). What is the volume fraction of filler?

(0.2)

~~Silica~~

~~ρSilica~~

ρ_{silica} = 2.65 g/cc

ρ_{MF} = 1.5 g/cc (Google)

Procedure = Determine the true volume of each

Calculation = Basis = 100g MF & 45g silica fluor

$\frac{100g\ MF}{1.5 g/cc}$ = 66.67 c.c. MF = 79.7% v/o MF

$\frac{45g\ Si}{2.65 g/cc}$ = 16.98 cc Si = 20.3% v/o Si

Total = 83.65 c.c.

~~10-P 43 Calculate the density of a glass reinforced plastic fishing ~~rod~~, in which the glass fiber content is 15 w/o (A borosilicate glass is used for the longitudinal ~~glass~~ fibers. The density of the plastic is 1.3 g/cc.)~~

Find Vol. fraction
use Rule of mixture

$\rho_{comp} = \rho_f V_f + \rho_m V_m$