Polymer Processing

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강의 개요

1. 고분자가공은 통상 고분자물질을 열이나 용매를 이용하여 용융체(melt), 용액(solution), 또는 젤(gel) 상태로 만들어 분자사슬에 충분한 유동성을 준 후 큰 변형 하에서 이루어지는데 이때 고분자의 사슬구조 특성상 **비선형적 점탄성을** 나타내어 공정 중 여러 가지 문제점을 야기시키는 경우가 많으며 이때 공정제어가 적절히 이루어지지 않으면 사용 중 치수불안정성이 발생기도 한다.

2. 고분자가공은 **고분자사슬의 공간적 배열을 제어하여** 요구되는 내부구조를 갖는 성형품을 만드는 것이다. 이를 위해서는 고분자물질계(polymer system)의 점탄성 현상에 대한 이론적 및 선험적 해석, 즉 유변학(rheology)에 대한 이해가 매우 중요하며 실제 유변학은 고분자공정 기술의 근간을 이룬다.

3. 본 강의에서는 유변학적 특성과 이를 이용한 공정설계에의 응용방법과 혼합공정(compounding), 압출공정(extrusion), 사출공정(injection molding), 및, 섬유방사공정(fiber spinning)의 원리와 기술, 반응동반 가공공정(reactive processing)의 개요를 설명한다.

Part I

Introduction :

The most characteristic features of polymeric materials are **polydispersity** and **orientation.**

Further, linear long chain nature gives rise to **viscoelasticity.**

What is Polymer Processing ?

- Materials Compounding Fabrication(Structuring) End-products

Chip	Melting	Melt	Absolutely	Desired
Bead	Dissolving	Solution	amorphous	structure:
Powder	Gelation	Gel-state		Orientation
Mixture	Dispersing	Solid-state		Grainy structure

- Polymer processing deals with **structuring by controlling the spatial arrangement of molecule chains during fabrication**
  → A precise regulation of **superstructure** such as **crystal size, crystallinity** and **orientation** is the very key.

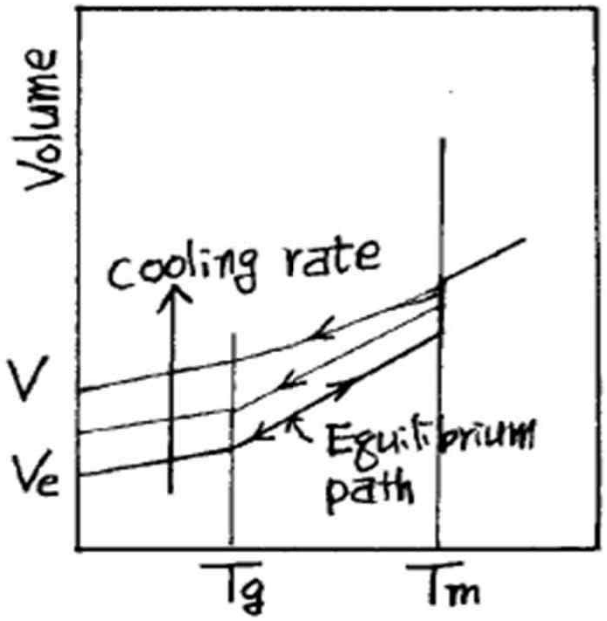
Ex. Film and fiber : desired degree of orientation and crystallization

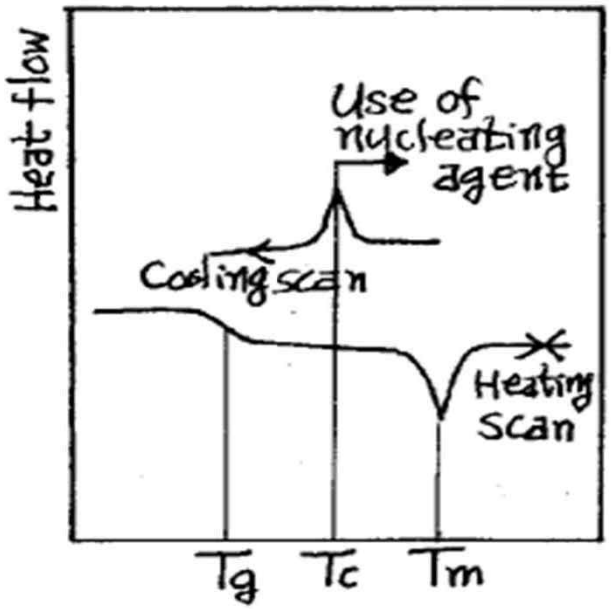
Molded article : **grainy structure** (maximum degree of crystallization but uniform and minimum in crystal size) is desired for good mechanical performance

Volume Change of Crystalline Polymers

- Post shrinkage during service : $\triangle V = V - V_e$
  : due to postcrystalization

- Degree of supercooling :
  $\triangle = T_m - T_c$
  : due to long chain and polydispersity nature





Role of Rheology in Polymer Processing

- Random morphology → Polymeric Materials ← Random memory
  Chip, Granule, Bulk
  ↓
- Absolutely amorphous → Melting or Dissolution ← Erasing memory

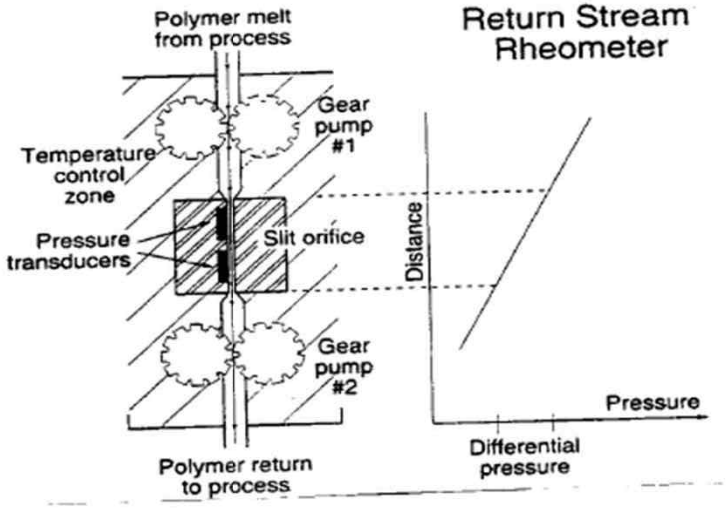
Viscoelasticity resulting from Entropy Spring

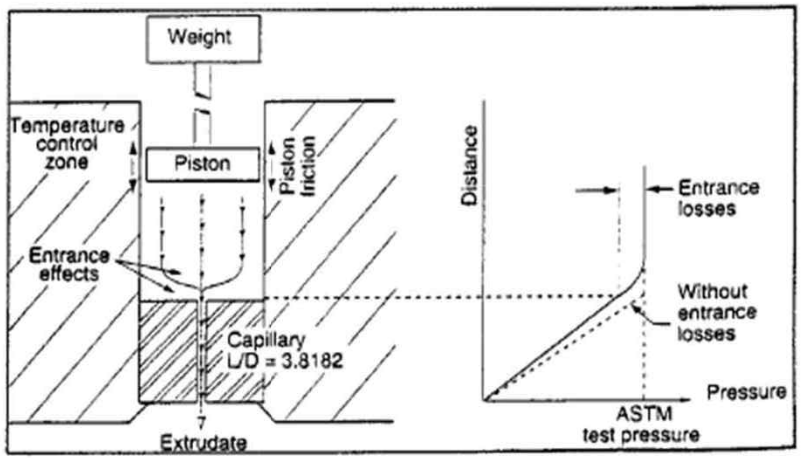
- Gel, solid, and mesophase ––– Residual memory should be considered
  ↓
- Equipment design : Process design and optimization → Fabrication : Well defined and stabilized macro– and microstucture to maximize properties and performance ← Rheology : Implantation of desired memory on rheological basis

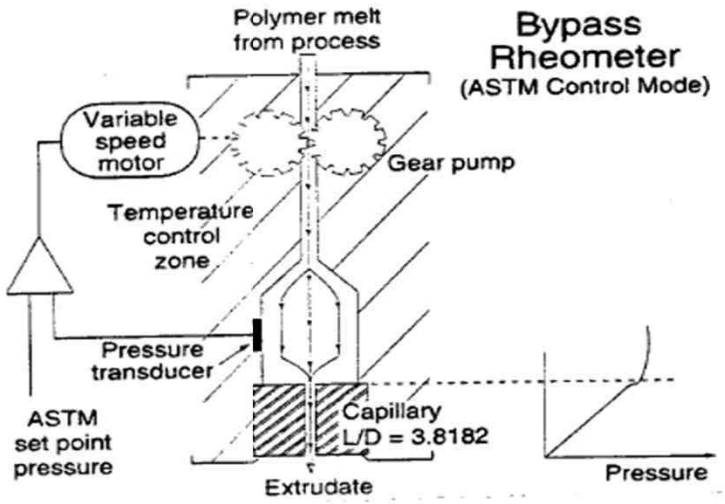
Shaping ↓ with Memory Regulation

- Regulated morphology → Plastics products Plague, Film, Fiber ← Desired memory

Ex. Realtime Rheometers & MFI







	Shear rate (sec^{-1})						
	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}
Melt indexer	----------						
Extrusion				-------			
Calendering				-------			
Injection molding					----------		
Coating					----------		
Spinning					----------		
Rotational rheometer	----------						
Capillary rheometer	----------						

Part II

Rheology

The Basic Principles of Polymer Processing

Viscoelasticity

1. Definition of viscoelasticity : Combined dual responses of reversible and irreversible deformation of polymers to mechanical stresses

- *Irreversible* or permanent **deformation** causes energy dissipation through **molecular slip (=flow)** : viscous property.
- *Reversible* or elastic **deformation** causes energy storage through molecular recoiling (relaxation)=elastic property
- Ex. Die swell (Barus effect), Weissenberg (rod climb-up) effect, stress relaxation and creep, etc.

2. Origin of viscoelasticity : Entropy spring by temporary networking

- Uncoiling and stretching on stressing decreases entropy → recoiled on releasing stress to recover entropy, that is, elasticity comes from reduced entropy on stressing

3. **Non-crosslinked polymers** have **fading memory** due to incomplete relaxation of deformed coils.

Definitions (1)

1. Stress(응력) : a quantitative measure of force

(1) Tensile stress(인장응력)
=stretching force/cross sectional area
$\sigma_E = F/A$

(2) Shear stress(전단응력)
=shear force/tangential area
$\tau = F/A$

2. Strain(변형): a quantitative measure of deformation
Deformation: the relative displacement of points or a body

(1) Tensile strain(인장변형)
$\varepsilon = (L-Lo)/Lo$

(2) Shear strain(전단변형)
=displacement/distance between plates
$\gamma = \Delta X/h$

Definitions (2)

Shear rate(전단속도)
=rate of change of shear strain with time

$\dot{\gamma} = d(\Delta X/h)/dt$
$= (1/h)(d\Delta X/dt)$
$= V/h\ [sec^{-1}]$

in which, V is the velocity of the moving plate in a **laminar flow**

Viscosity (점도)
=Resistance to flow

$\eta = \tau / \dot{\gamma}$ [Pa•s]

in which, η is viscosity and τ is shear stress

[cf.] **Modulus** (탄성률)
= Resistance to deformation

Rheometers

1. **Material functions** : Quantitative expression of viscosity and elasticity of polymeric materials vs. shear rate.

   1) **Viscosity function** :

   $$\tau_{12} = \eta(\dot{\gamma})\dot{\gamma}$$

   2) **Elasticity functions** :

   $$N_1 = \tau_{11} - \tau_{22} = \varphi_1(\dot{\gamma})\dot{\gamma}^2, \text{ and}$$

   $$N_2 = \tau_{22} - \tau_{33} = \varphi_2(\dot{\gamma})\dot{\gamma}^2,$$ in which N_1 and N_2 are first and second normal stress difference functions, respectively.

2. **Rheometers** : Equipments measuring the material functions by adopting rhelogical principles (**rheometry**)

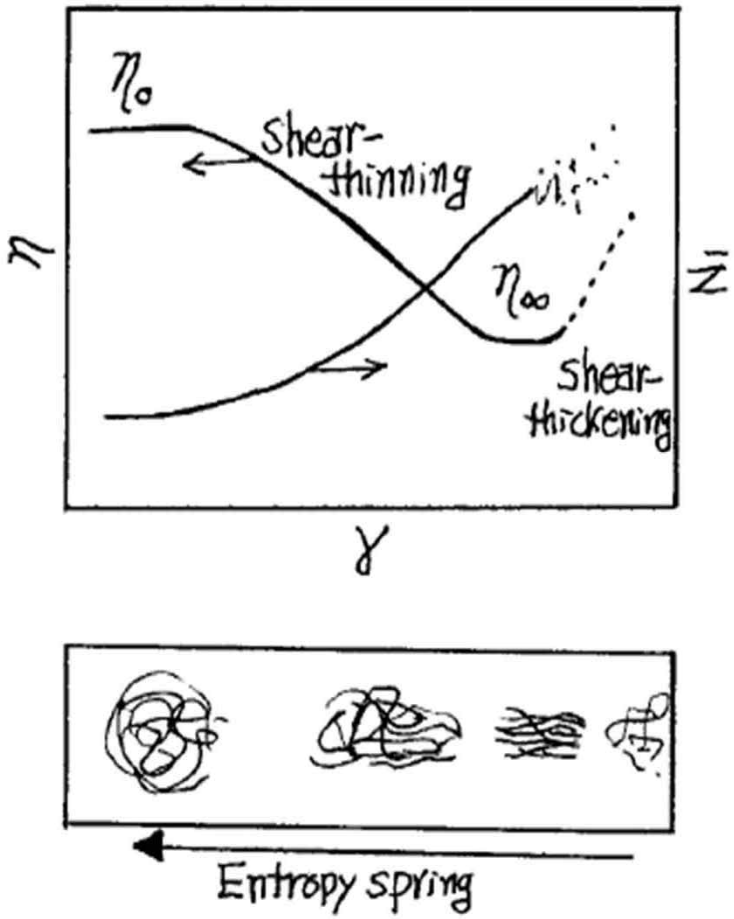
Newtonian vs. Non-Newtonian Fluids

1. **Newtonian fluids** give **$\dot{\gamma}$-independent viscosity** because they do not include any flow unit which deforms by shear or elongational stresses during flowing
- Newtonian viscosity depends on T and P.

2. **Non-Newtonian fluids** contain **flow units deformable** by stresses when flowing
- The extent of deformation greatly depends on $\dot{\gamma}$

  → **viscosity is dependent on $\dot{\gamma}$ as well as T and P**

Schematic Viscosity and First Normal Stress Difference Curves of Polymers



- Practical Importance

1. Viscosity : power supply, polymer blend conditions,

2. N1 : mold design, max production rate, elastic turbulence

Shear-dependent Viscosity Behavior (2)

(1) Pseudoplastic (or shear-thinning) fluids[의가소성유체]: Viscosity decreases with increasing $\dot{\gamma}$ because of **development of anisotropy.**

*At low $\dot{\gamma}$, polymer chains are disentangled but segments between entanglements become oriented before disentangled at high $\dot{\gamma}$.

Ex. Most polymer melts and solutions

(2) Dilatant (or shear-thickening) fluids[딜라턴시유체]: Viscosity increases with increasing $\dot{\gamma}$ due to (shear-induced) crystallization, phase separation, poor packing, or reduction of medium share of the total volume.

Ex. Concentrated suspensions, PVC pastes, etc.

Shear-dependent Viscosity Behavior (3)

- Lower Newtonian flow region gives zero-shear viscosity (η_o) which comes from the random location of molecules or particles due to Brownian motion
  → η_o is a relative measure of MW for homologue polymers
- Upper Newtonian flow region gives infinite-shear viscosity which comes from the high orientation of molecules or particles due to shearing
- Infinite-shear viscosity tends to converge to a value for a given polymer

- Very low value of N_1
- Very high value of N_1

Power-law Fluids

- Power-law fluids [지수법칙유체] : within a relatively narrow range of shear rates the viscosity curve gives almost a straight line with a constant slope.

- $\tau = k\dot{\gamma}^n$, or $\eta = k\dot{\gamma}^{n-1}$

  in which, n is power-law index (or power factor) to define the extent of shear dependence of viscosity.

- If n = 1, Newtonian
- If n > 1, Dilatant
- If n < 1, Pseudoplastic

- The fluids defined over the narrow $\dot{\gamma}$ range at one's convenience (or for simpler mathematical modeling) is called power-law fluids.

Bingham Body (1)

Disappearance of η_0 indicates heterogeniety of the system because it suggests the existence of **yield behavior**

Ex. Dispersions of particles in Newtonian fluids.
Suspensions, LCP's
Block copolymers

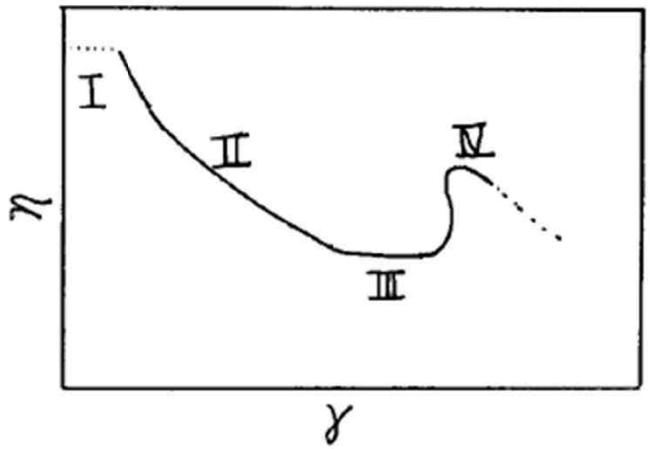
Cf. Some highly polar systems and nano dispersions, which are **optically transparent, may be rheologically heterogeneous**

Ex. Suspension viscosity

I : 3−D structure (too large viscosity to measure)

II & III : 2−D layering by shear− induced orientation

IV : Random structure gives rise to shear thickening



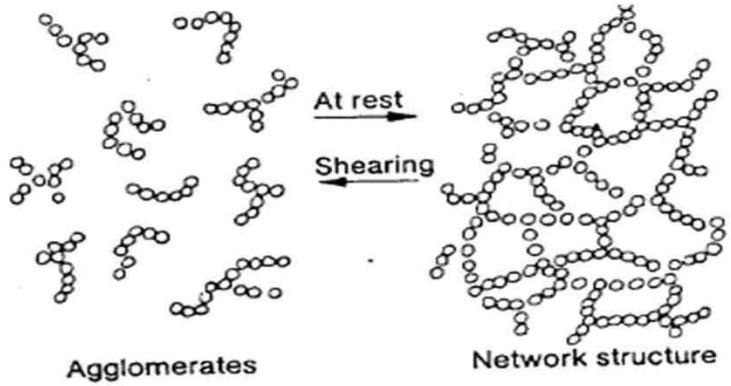
Bingham Body (2)

Bigham body exhibits solid character below yield stress (τ_y) but a fluid above the τ_y

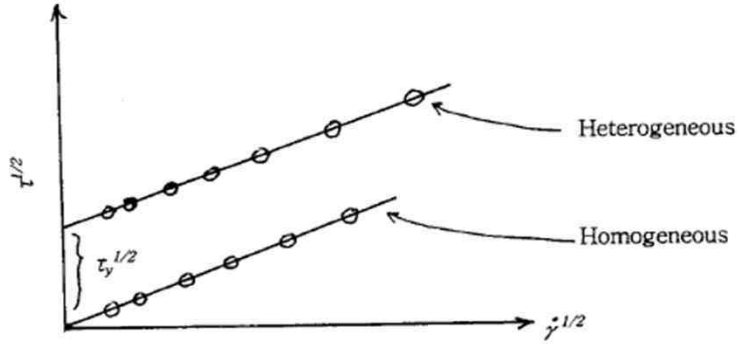
$\gamma = (\tau - \tau_y)/\mu$

if $\tau \geq \tau_y$

in which, τ_y is **yield stress**, a threshold shear stress to breakdown the 3-dimensional physical structures, that is, the minimum energy to breakdown intermolecular or interparticle networks formed by polar forces and/or van der Waals forces



Yield stress can be evaluated by **Casson plot** : a plot of (square root of) shear stress vs. (square root of) shear rate



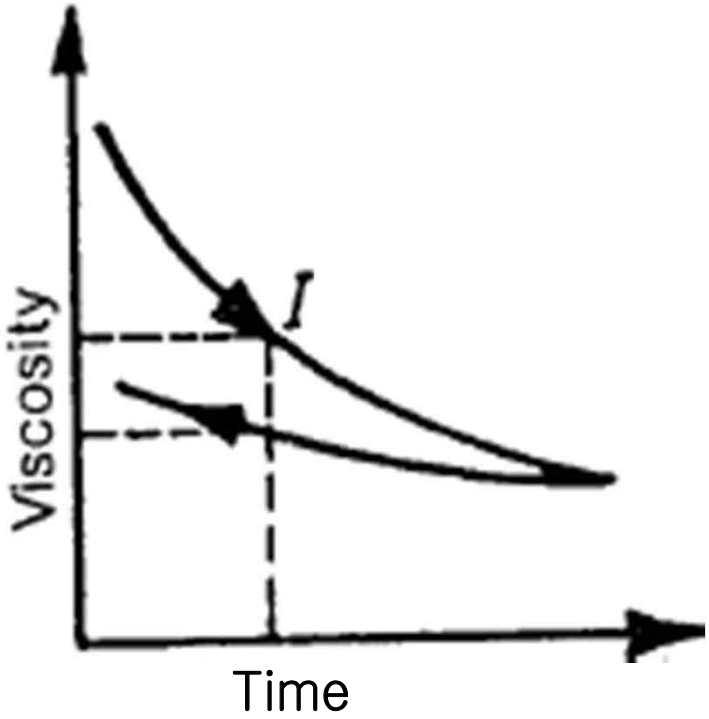
Time-dependent Viscosity Behavior (1)

- Time-dependent fluids give a **hysteresis loop** due to reversible structural processes, which comes from the **structural change during the process**
- **Thixotropy**[요변성]: viscosity decreases with **time at constant shear rate** because of **reversible breakdown of structure**

  Ex. Suspensions

- **cf. Rheopexy** [레오펙시]

Thixotropy



(at constant shear rate)

Time−dependent Viscosity Behavior (2)

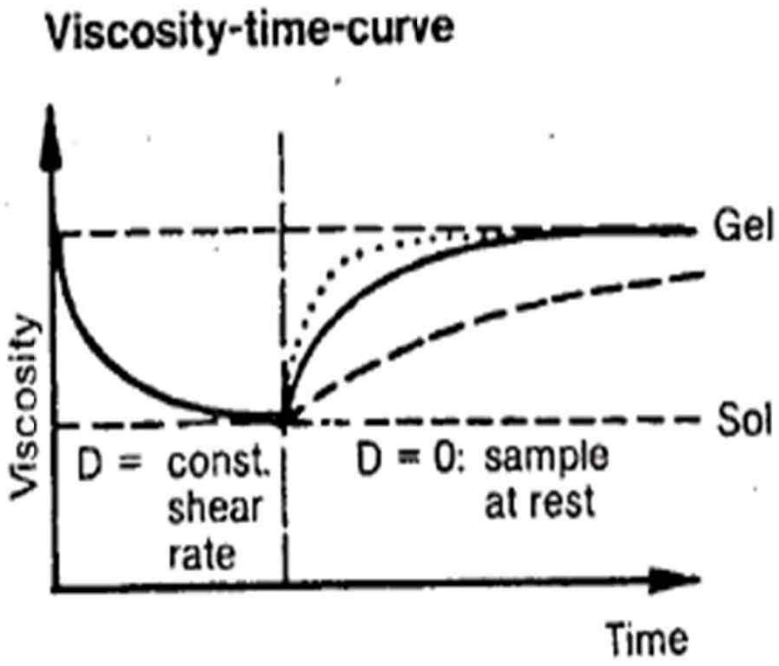
Ex. Thixotropy

Gel (3−D) structure

Shearing ↓ ↑ Relaxation

Sol structure

The rate of the structural processes is largely dependent on the **size and shape of dispersed particles** together with their **surface charge**



reversible breakdown of structure under shear

reversible formation of structure at rest

Factors for the Design of Polymer Processing Conditions

1. **Temperature** reduces viscosity and elasiticity.
2. **Pressure** increases viscosity.
3. **Molecular weight**(MW) increases viscosity and elasticity.
4. **MW Distribution** reduces the onset $\dot{\gamma}$ of **shear thinning**.
   E.g., Middleman's prediction in **resin blending**
5. **Branching** reduces shear viscosity and increase the temperature dependence of viscosity. Further, it causes **tension-thickening when elongated**.
6. **Any factor increasing T_g** increases viscosity
7. **Intermolecular attraction and linearity** increase viscosity.
8. **Dispersion state** of particles or dispersed phase has a profound influence on the suspension viscosity.
9. Increasing the **distribution of size of particles in a suspension** decreases the suspension viscosity.
   E.g., **Farris effect** in the suspension viscosity.

Part III

Compounding

Taylor's Theory for Mixing

1. Taylor's theory : Viscosity ratio of dispersed to medium and type of mixing

Long elongation < 0.005 – 4 < Limited deformation of disperdsed phase

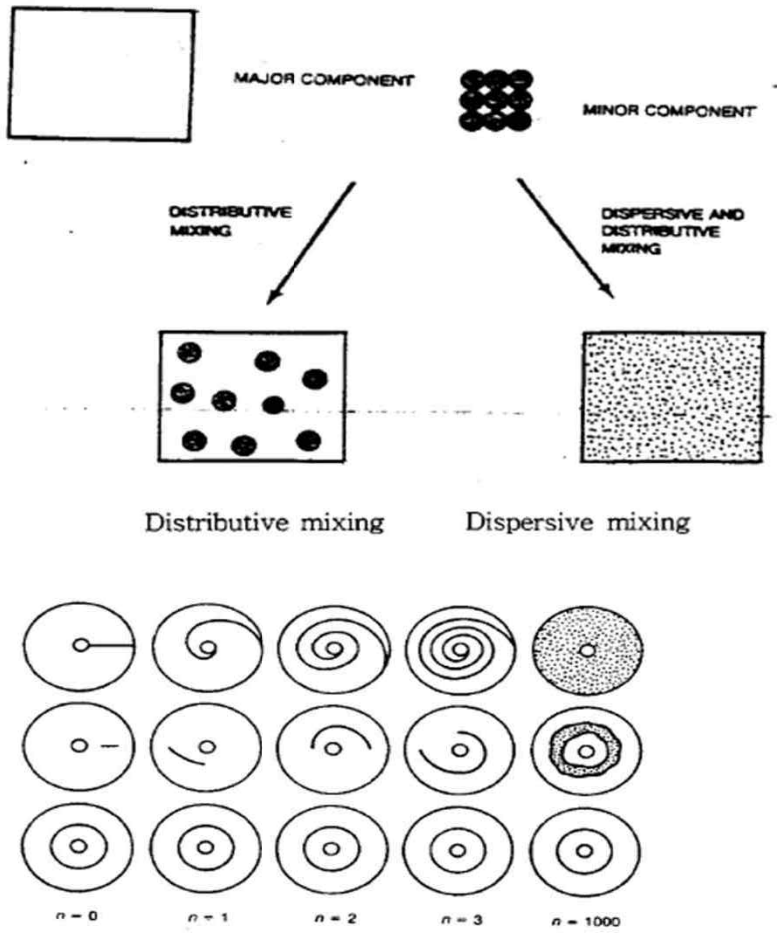
Droplet breakup (preferrably 0.3–0.6)

* The viscosity of polymers is dependent on shear rate

2. Total shear = Shear rate X Shearing time

Distributive vs. Dispersive Mixing

1. Distributive mixing increases only the degree of **randomness** of the dispersed phase
2. Dispersive mixing increases the degree of **randomness** and decreases **size** of the dispersed phase by **deagglomerization**
3. Deformation accompanying **change of flow direction** is necessary for efficient dispersive mixing

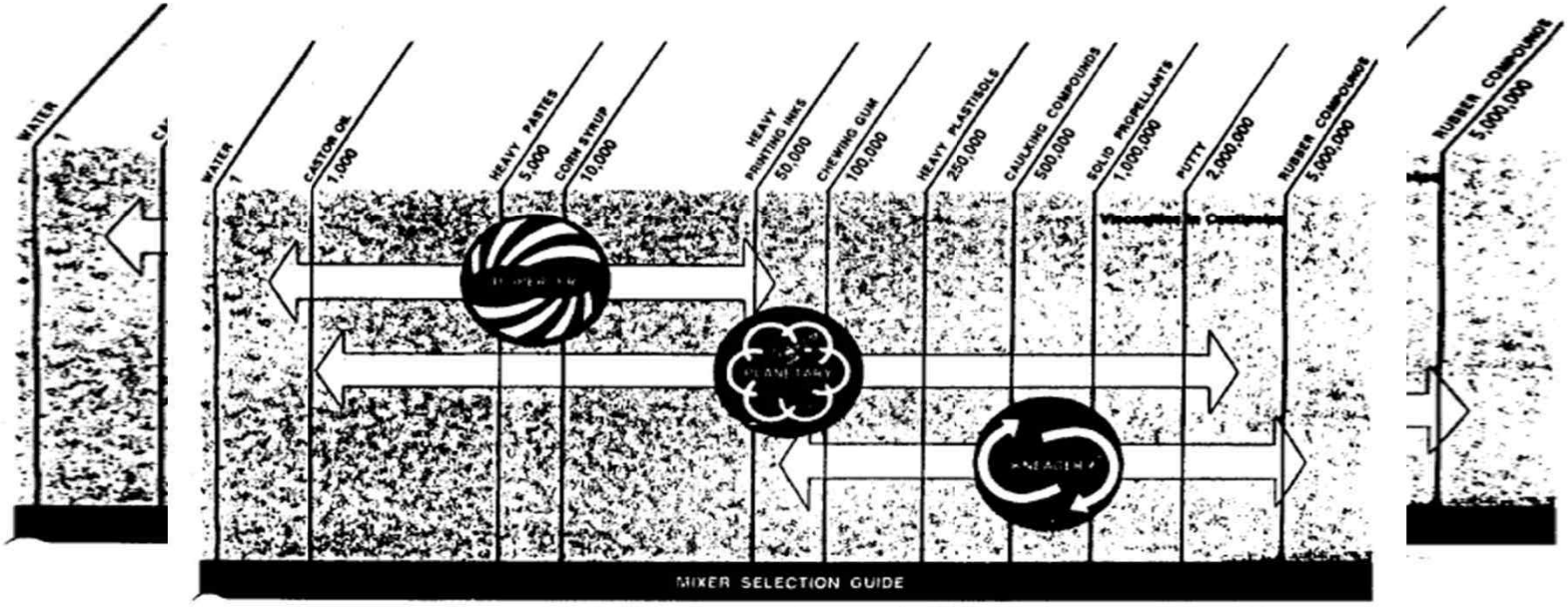


Laminar shear mixing between concentric cylinders for various initial orientations of minor component as a function of total strain.

Important Compounding Machines

(1) Batch compounders
- Ribbon blenders
- Planetary mixers
- Fluid mixers
- Banbury mixer
- Mixing rolls

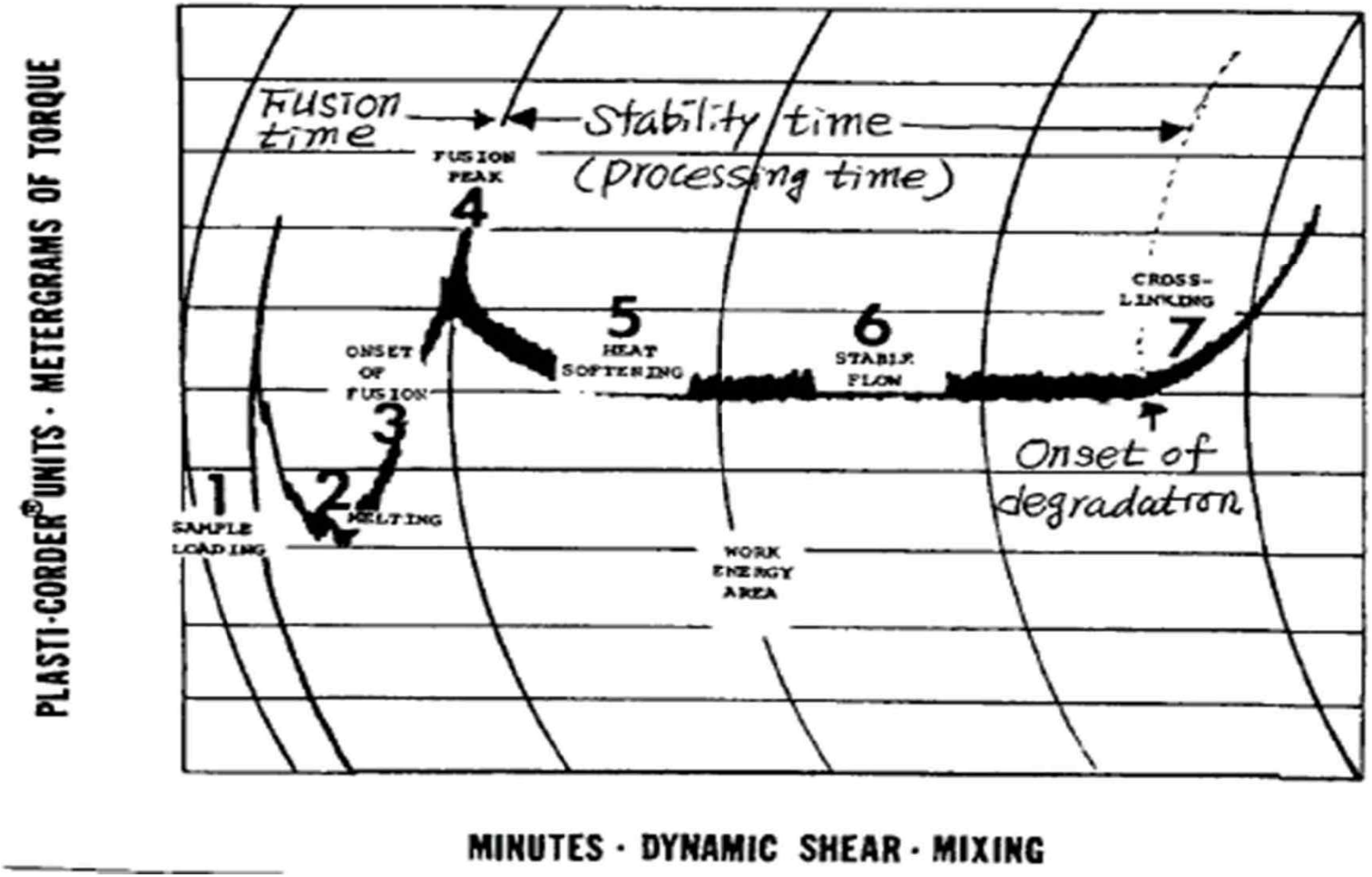
(2) Continuous compounders
- Single-screw extruders
- Two-stage single-screw extruders (or multistage)
- Twin-screw extruders (or multi-screw)
- Two-stage high-intensity mixers
- Two-stage compounding extruders



Application of Screw-type Compounders

Machine type and designation	*Manufacturer*	*Process*		
		Compounding + pelletising		*Calender-feeding*
		Plasticised PVC	*Rigid PVC*	
Single screw				
Plastifikator	Werner u. Pfleiderer, Stuttgart West Germany	X		
Buss-Kneader	Buss Ltd, Basle, Switzerland	X	X	X
Cascade extruder	Barmag, Remscheid-Lennep, West Germany	X	X	Extrusion
Twin screw				
Kombiplast	Werner u. Pfleiderer, Stuttgart, West Germany	X	X	
FCM continuous mixer	Farrel Corp., Ansonia, CT, USA David Bridge Co. Ltd, Rochdale, UK Pomini-Farrel, Castellanza, Italy	X	X	X
MPC/V	Baker Perkins Chem. Machinery Ltd, Hanley, Stoke-on-Trent, UK	X	X	
Bitruder BT	Reifenhäuser KG, Troisdorfsiglar, West Germany	X	X	
Planetary				
PWE and ZSE	EKK Kleinewefers Kunstoff Maschinen GmbH, Bochum, West Germany	X	X	X
WE	Hermann Berstorff Maschinenbau GmbH, Hannover, West Germany			X

Measurement of Processable Time of Compounds



Part IV

Extrusion

Functions of Extruders

1. *Plastication* in polymerization or compounding; generation of required pressure
2. *Mixing* generates heat generally in a non-uniform fashion : overheating, degradation or discoloration
3. *Devolatilization* in a multi-stage single-screw or multi-screw extruders
4. Mixing quality depends on the total shear of deformation (shear rate x shearing time), which is increased by :

   decreasing the height of screw channel,

   varying the angle of the pitch helix, and/or

   increasing the backflow (countercurrent or sinks) through an increase of head resistance

Comparison of SSE and TSE

	Single-screw	Twin-screw
Conveying mechanism	Frictional force, or viscous forces	Positive displacement (I.e., gear pump)
Mixing mechanism	Within the channel	Screw intermeshes
Energy source for melting	Mostly by mechanical energy (shear forces)	Mechanical (54%) and thermal (46%) energies
Advantage	◦ Low machining cost ◦ Less external lubricant required	◦ Lower shear and lower T_m ◦ Little temperature gradient within a screw flight ◦ Even distribution of melt residence time in the barrel
Disadvantage	◦ Higher barrel wear rate ◦ More internal lubricant required	◦ Higher screw wear rate : counter-rotating > co-rotating ◦ Higher machining cost

Single-Screw Extruder (SSE)

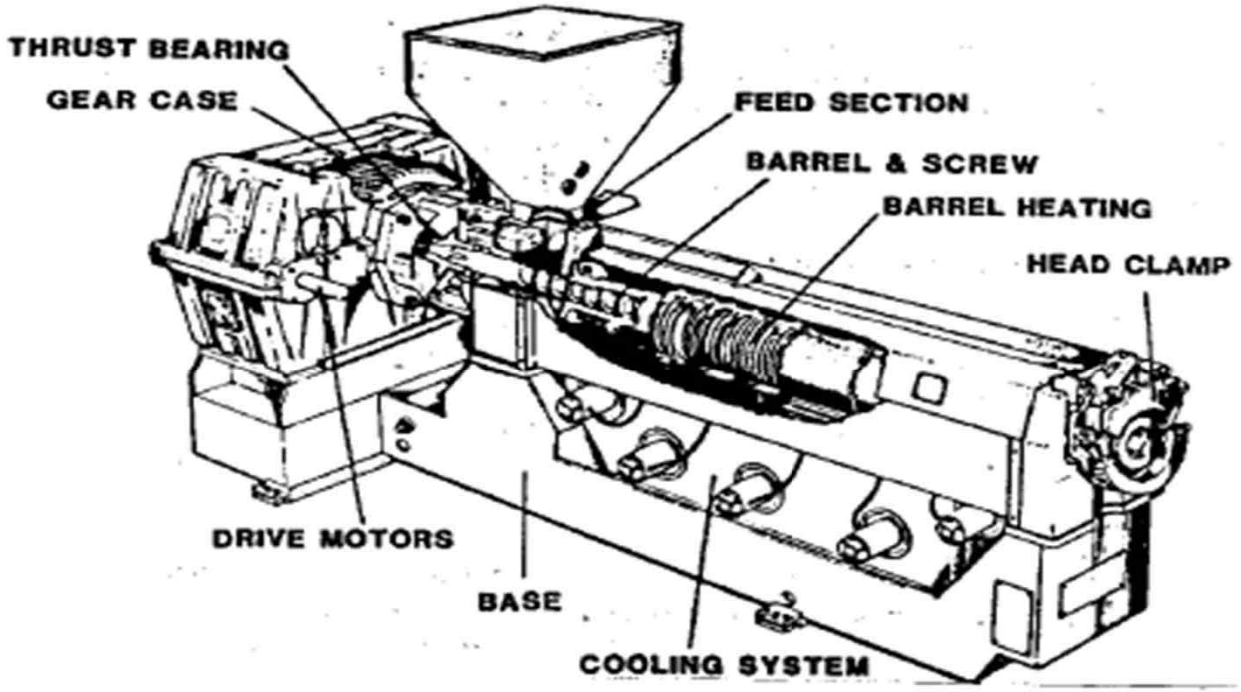


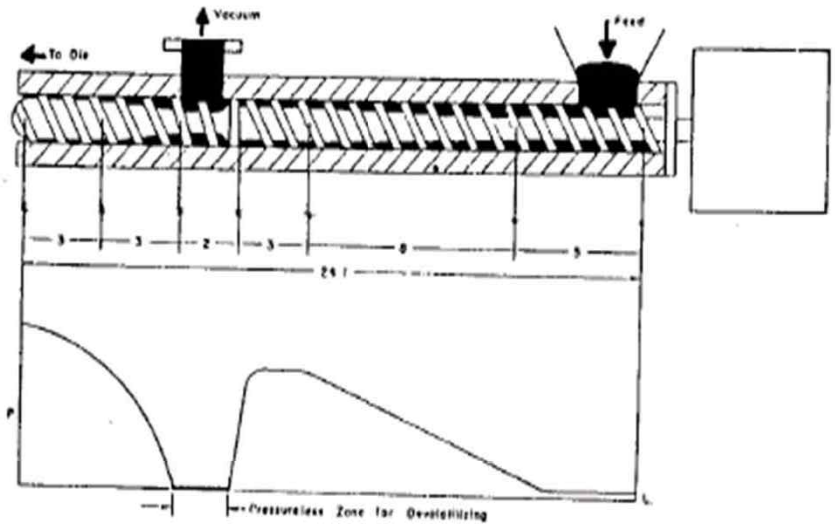
Fig. . Schematic of single-screw extruder.

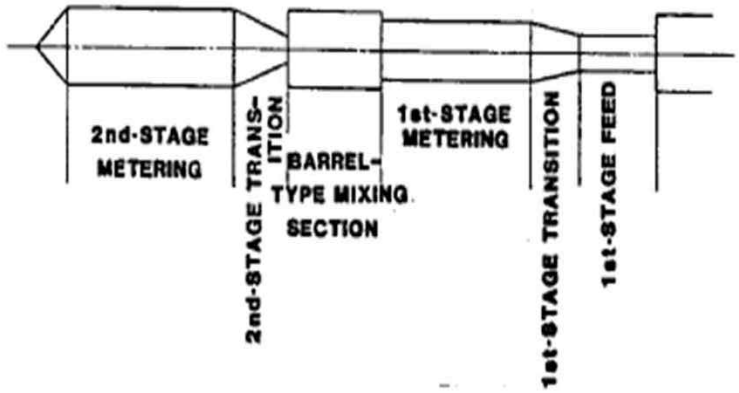
L/D ratio of barrel; Smaller < 20 to 30 < Larger			
Application;	Pumping	Plasticating	Devolatilization
Extruder type;	Single-stage SSE		Multi-stage SSE

Type of SSE

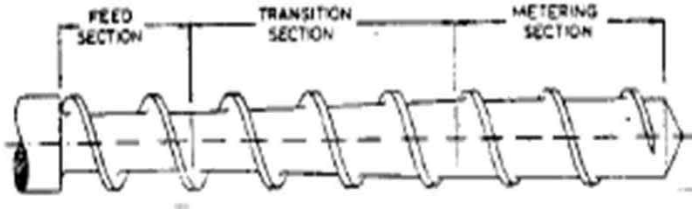
1. Feed zone : Conveying and compression [to compact a loose or granular feed into a dense solid form]
2. Melting zone : Melting or plasticating
3. Metering zone : Pumping and metering of melt

Two-stage SSE





Single-stage SSE = SSE



SSE for Compounding (1)

1. SSE can produce a **very limited mixing action** only to homogenize the melt. For an intensive mixing a special modification of screw (mostly in metering zone) is necessary.

2. **Requirements for mixing devices in SSE**

   Minimum pressure drop (continuous pumping)

   No dead spot (streamlined flow)

   Complete wiping the barrel surface

   Friendly operation (easy to assemble, clean, etc.)

   Low machining cost

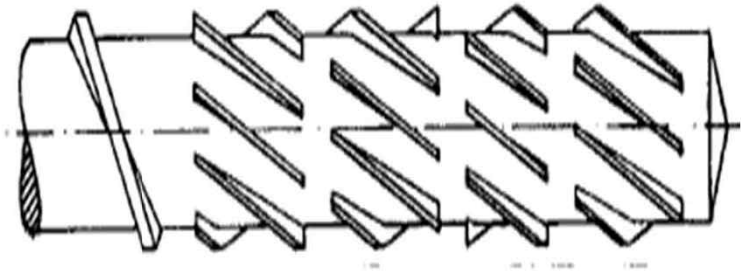
SSE for Compounding (2)

1. Distributive mixing enhancers
   (1) Substantial shear strain and frequent reorientation of the fluid elements promote the distributive mixing.
   (2) Cavity, pin, slotted-flight, and turbine mixers, and variable channel depth mixing sections

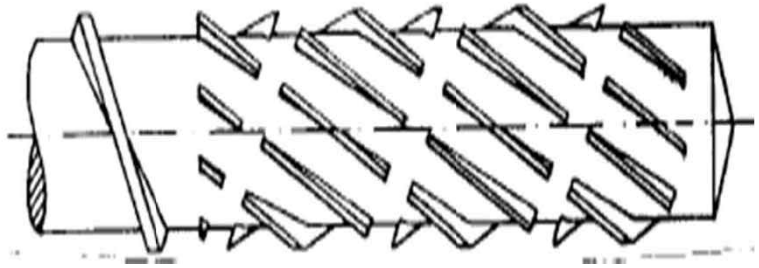
2. Dispersive mixing enhancers
   (1) Breakdown of agglomerates or gels (particularly important in thin-gauge extrusion)
   (2) Shear or blister ring, fluted and cross-barrier mixing sections, and planetary gear mixers

Examples of Typical Distributive Mixing Units in SSE

(5-5-2) Dulmage mixing section



(5-5-3) Saxton mixing section



1. Dulmage mixing section :

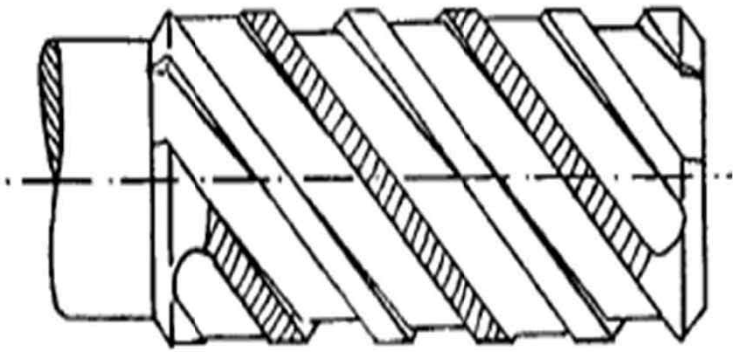
   Tangential grooves give only partial wiping of barrel

2. Saxton mixing section :

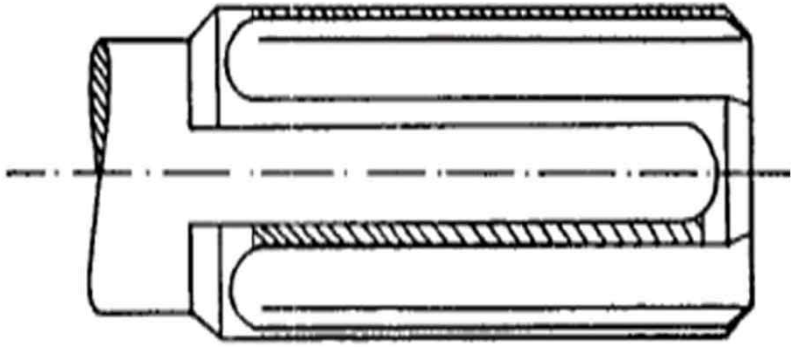
   Low pressure drop owing to forward conveying capability of mixing section

Examples of Typical Dispersive Mixing Units in SSE

(6-2-1) Egan mixing section



(6-2-2) UC (Union Carbide or Maddock)



1. Eagan mixing section :
   The barrier flights have a slightly smaller diameter :
   A uniform mixing action
   Little dead spot
   Little pressure drop

2. UC :
   No forward pumping action :
   Large pressure drop
   Stagnation in the dead spot

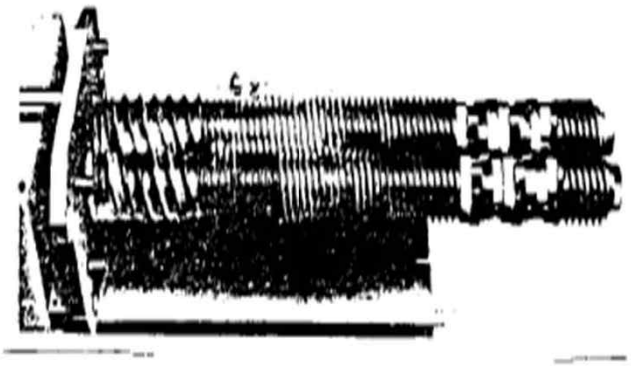
Characteristics of Mixing Units of SSE

Distributive mixing sections	1 Pressure drop	2 Streamlined flow	3 Barrel wiped	4 Operator friendly	5 Machining cost	*A* Shear strain	*B* Splitting reorientation
Pins (22)[b]	−	−	o	+	+ +	−	+
Dulmage (27)	+	+	−	+	+	+	+ +
Saxton (30)	+	+	+ +	+	+	+	+ +
CTM (17)	− −	o	−	− −	− −	+	+ +
Blockhead (17)	− −	− −	− −	+	+	−	+
Double blockhead[c] (18)	− −	− −	o	−	−	+	+ +
Slotted ring (18)	− −	−	− −	+	+	−	+
Pineapple (25)	−	+	o	+	+	+	+ +
Axon (28)	+	+	+	+	+ +	+	o
Stat-Dyn (26)	−	+	+	+	o	+	+ +
Turbine (17)	− −	− −	+	o	+	−	−
Double wave (24)	+	+	+	+	−	+	−
Cohen (24)	+	+	+	+	−	+	−
Pulsar (24)	+	+	+	+	o	o	−
Strata-blend (23)	+	o	+	+	o	o	−
Dray (21)	−	o	+	+	o	o	−

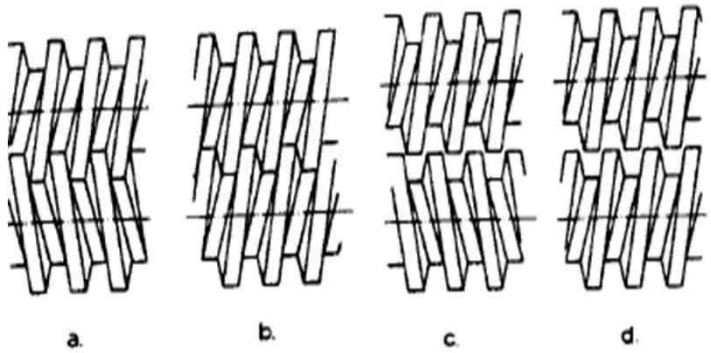
Dispersive mixing section	Pressure drop	Dead spots	Barrel wiped	User friendly	Manufacturing cost	Uniform mixing
Blister (16)[b]	− −	o	−	+	+	−
Egan (25)	−	+ +	+ +	+	+	+ +
Gregory (16)	−	−	−	+	+	−
LeRoy (22)	−	−	+ +	+	+	+ +
Troester (23)	o	−	+ +	+	+	+ +
Dray (20)	−	+	+	+	+	−
Zorro (26)	+ +	+ +	+ +	+	−	+ +
Helical LeRoy (28)	+ +	+ +	+ +	+	+	+ +
EVK (18)	− −	− −	+	+	+	+
SCCB (18)	− −	− −	+	+	+	+
PGE (24)	o	+ +	+ +	+	−	+ +

[a] + +, good; +, fair; o, neutral; −, poor; − −, very poor.
[b] Numbers in parentheses refer to total number of points (− −, 1; −, 2; o, 3; +, 4; and + +, 5); equal weighting was used for all criteria.
[c] Has dispersive mixing ability.

Type of Twin-Screw Extruder (TSE) (1)

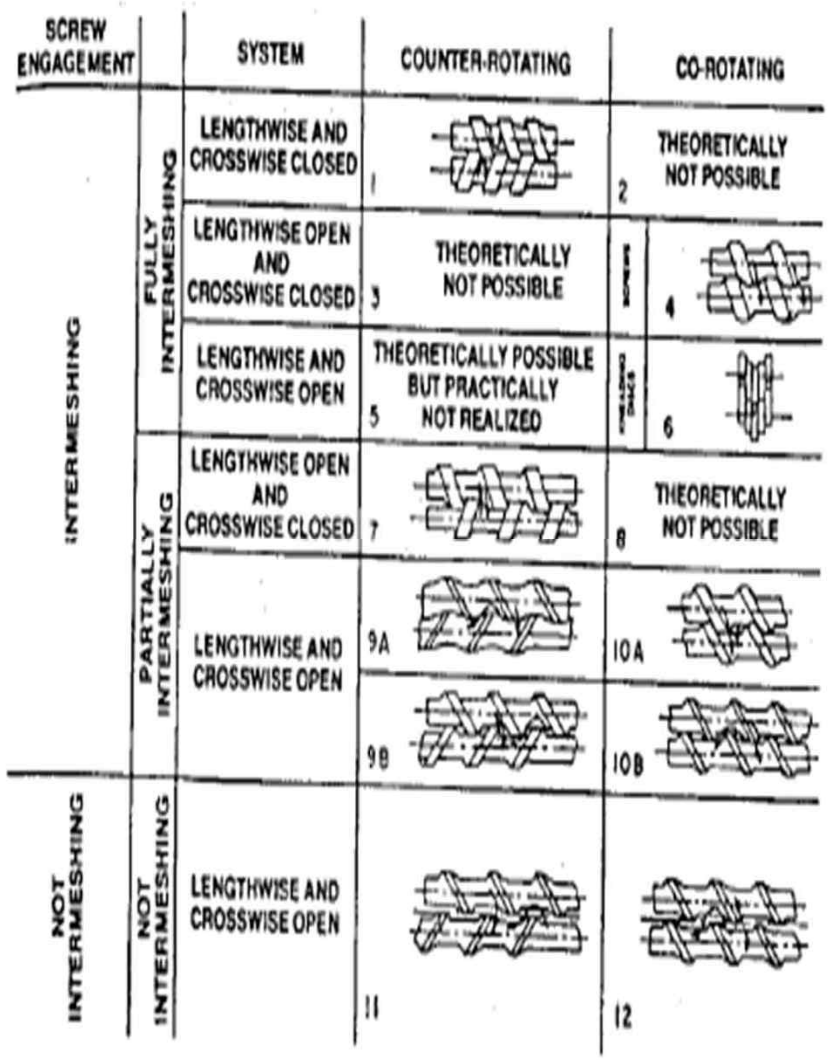


. Combination screws of a twin-screw compounding extruder.



. Different kinds of twin-screw extruders: (a) counterrotating intermeshing, (b) corotating intermeshing, (c) counterrotating nonintermeshing, and (d) corotating nonintermeshing.

Type of Twin-Screw Extruder (TSE) (2)



1. Counterrotating fully intermeshing [ex. 1] : Positive displacement
2. Corotating fully intermeshing
   [ex. 4] : Greater drag : A twist restraint on the material
3. Counterrotating partially intermeshing : Better homogenization
4. Counterrotating not intermeshing : Used along with a SSE discharger

Conveying Characteristics of Screw Elements of TSE (1)

(3-1) Conveying characteristics of screw elements

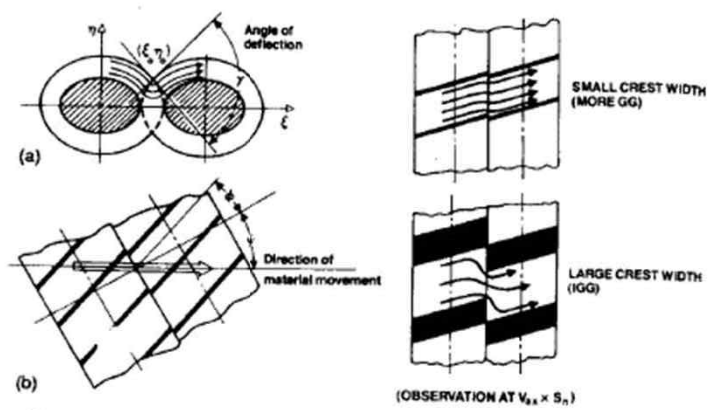


Fig Change of flow direction of the wedge volume (absolute movement)
(b) Change ... direction of mater... low as a function of screw crests.

Mixing characteristics of fully intermeshing corotating TSE

Compression is caused by left-hand screws

Frictional force (little shear-free dead zone)

Partial positive conveying due to the wedge resistance

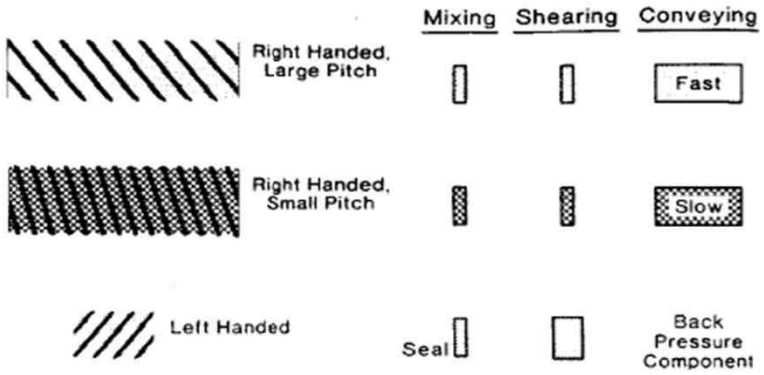
- Screw pitch determines residence time in the conveying section

1. Small crest width : little twist restraints

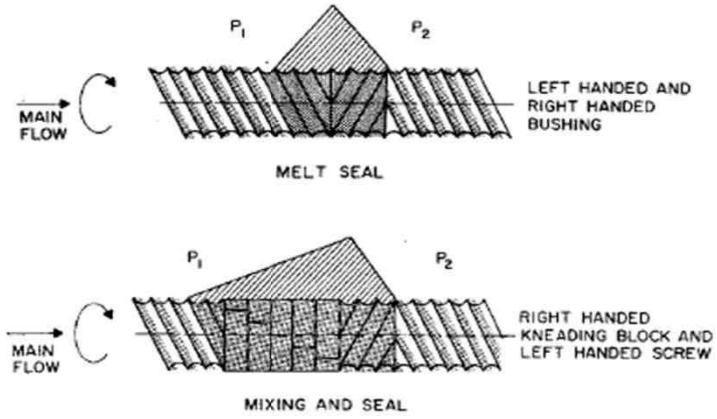
2. Large crest width : drastic change in material direction (large twist restraints)

Conveying Characteristics of Screw Elements of TSE (2)

(3-1-1) Action of various screw elements



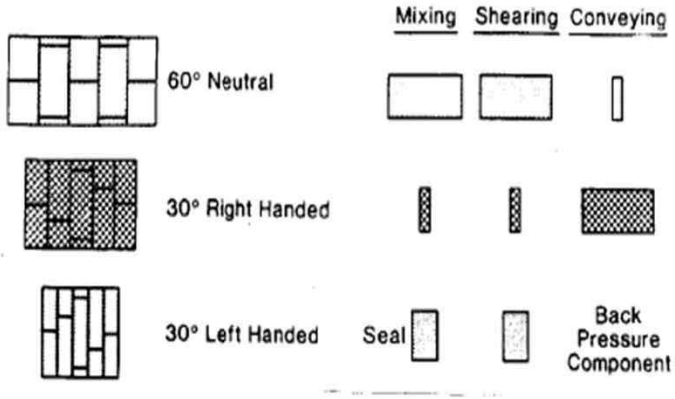
(3-1-2) Local pressure generation by different elements



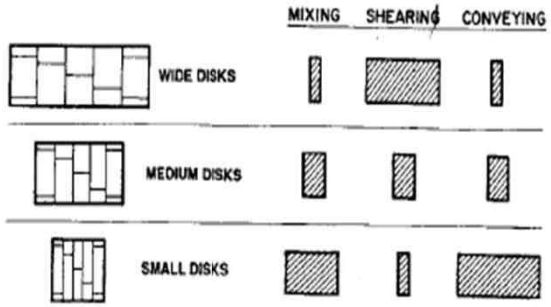
- Right handed large pitch : low degree of fill in the vent area and reduced residence time
- Right handed small pitch : high degree of fill for effective heat transfer process (contact between material and barrel)
- Left handed reverse pitch : backpressure to enhance mixing in combination with kneading elements

Conveying Characteristics of Mixing Elements of TSE (1)

(3-2-1) Action of various kneading elements



(3-2-2) Kneading elements: (a) wide disks, (b) medium disks, and (c) small disks



- 30° right handed for forward
- 30o left handed for reverse
- Wide disk for intense shearing across the disk face
- Small (or narrow) disk for good longitudinal mixing and conveying

Conveying Characteristics of Mixing Elements of TSE (2)

(4) Counterrotating nonintermeshing twin screw extruder:

Easy to control the residence time because of large free volume.
More efficient mixing but high maintenance cost.

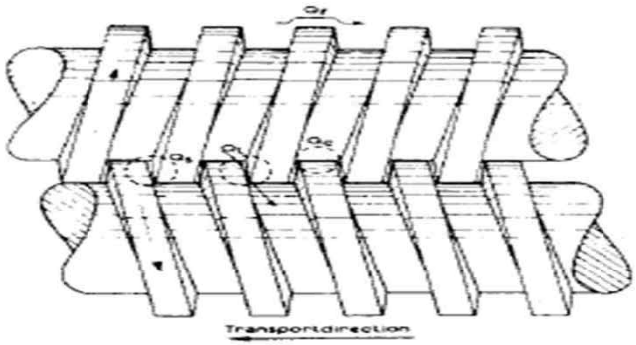


Fig. . Leakage flows in the counterrotating closely intermeshing TSE: flight leakage (Qf), calender leakage (Qc), tetrahedron gap leakage (Qt), and side-gap leakage flow (Qs).

Mixing characteristics of counterrotating TSE

Plug flow resulting from low clearance leads to poor longitudinal mixing
Positive conveying may cause fluctuations in pressure and volumetric flow rate

Part V

Injection Molding

Pressure Profile in Injection Molding

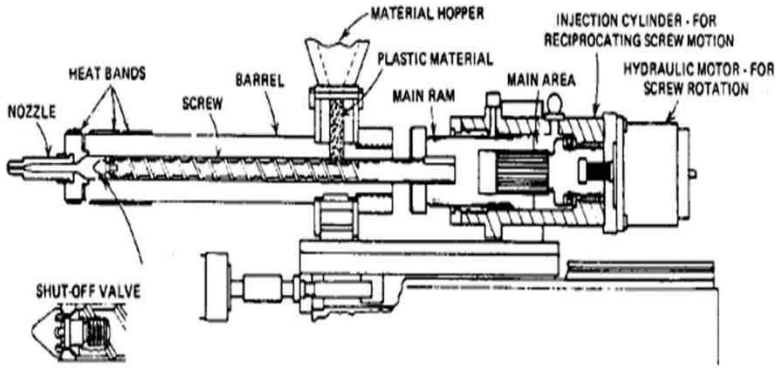


Fig. Injection section of a reciprocating screw machine.

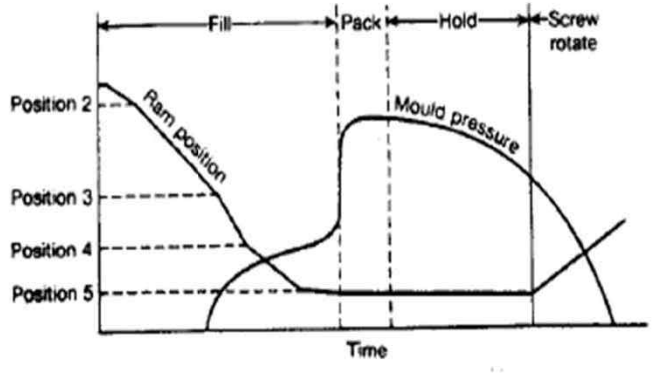
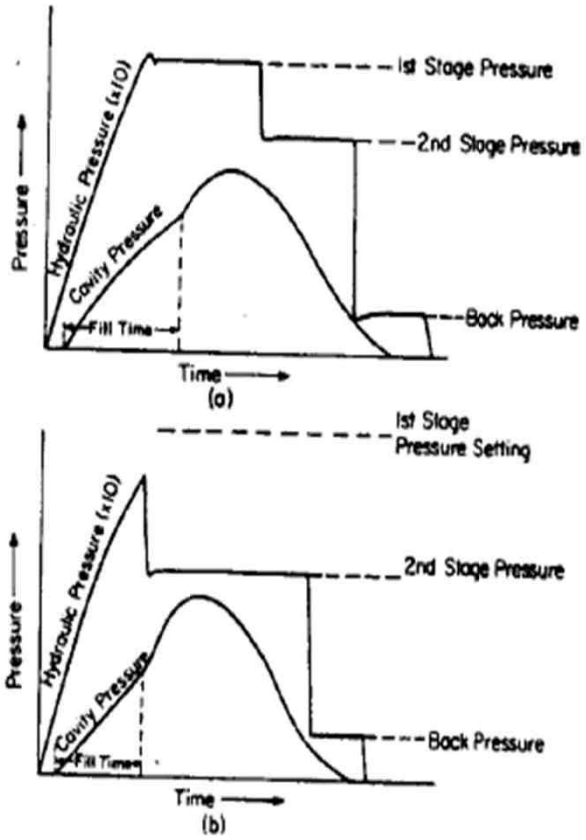


Fig. Dependence of ram position and mould pressure on time during mould filling and packing.



Typical hydraulic oil pressure/cavity pressure relationships: (*a*) thick-walled part; (*b*) thin-

Injection Molding Cycle Diagram

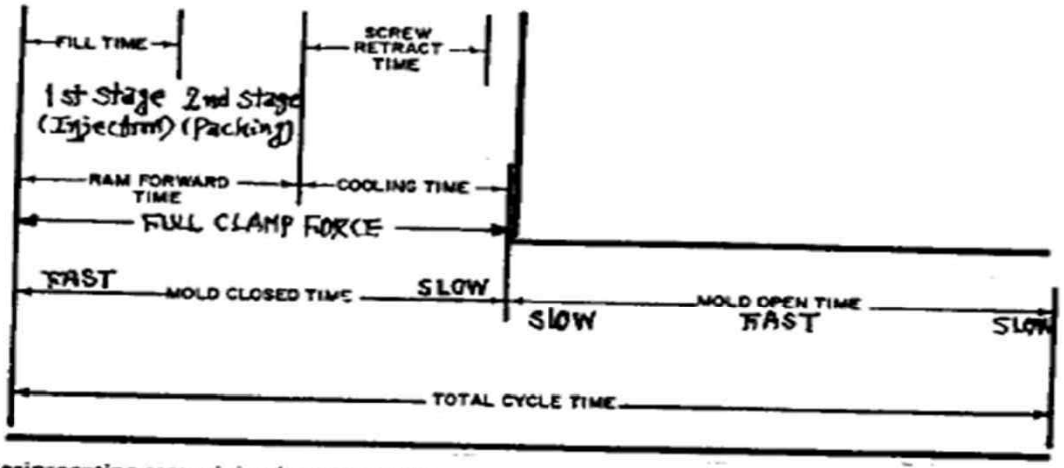


Fig. Reciprocating screw injection mold cycle.

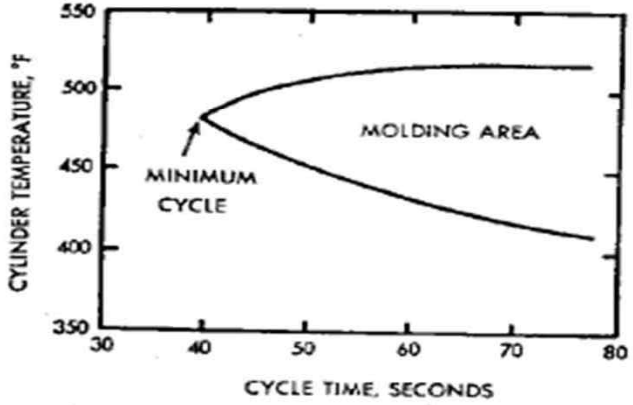


Fig. Minimum cycle diagram.

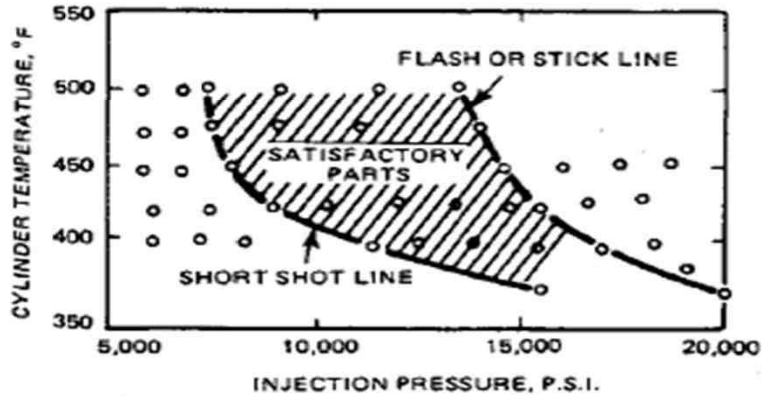


Fig. Molding diagram

Ex. Process Control in Injection Molding

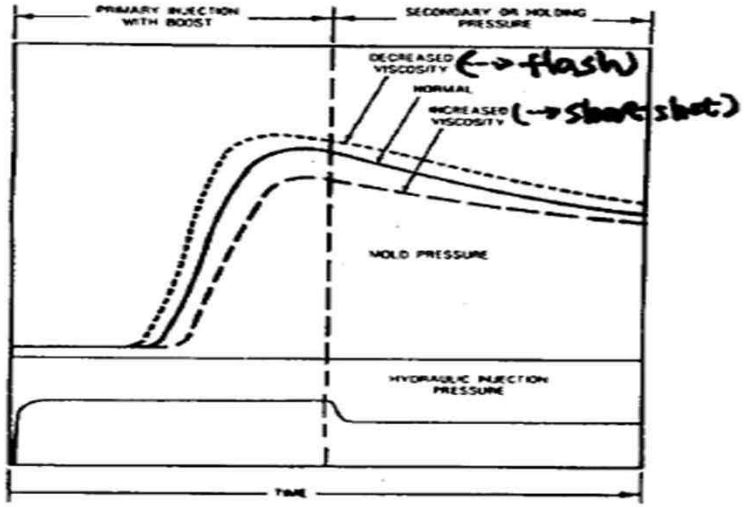


Fig. Effect of viscosity on mold pressure. Different curves are obtained because of changes in material viscosity. Note that hydraulic injection pressure is the same in all cases and the differences are the result of material changes only. The figure shows three different curves—one for normal viscosity, one for increased viscosity, and one for decreased viscosity. With a decrease in viscosity, mold pressure builds up sooner and also reaches a higher peak value. The result on the molded part, in this case, will be increased part weight and flashing if pressure builds up significantly. With an increase in viscosity, it takes longer to fill the mold and, consequently, longer for mold pressure to build up. In this case, because it does take longer to fill the mold, the part does not completely pack and results in a lighter part and possibly even a short shot.

From the above description, it follows that the control system must be capable of compensating for both increased and decreased viscosity conditions. With a decrease in viscosity, injection pressure should be cut off early in the cycle to prevent overpacking and flashing. With an increase in viscosity, injection pressure must be applied longer, and at the same time be high enough in value to insure that the mold fills and packs.

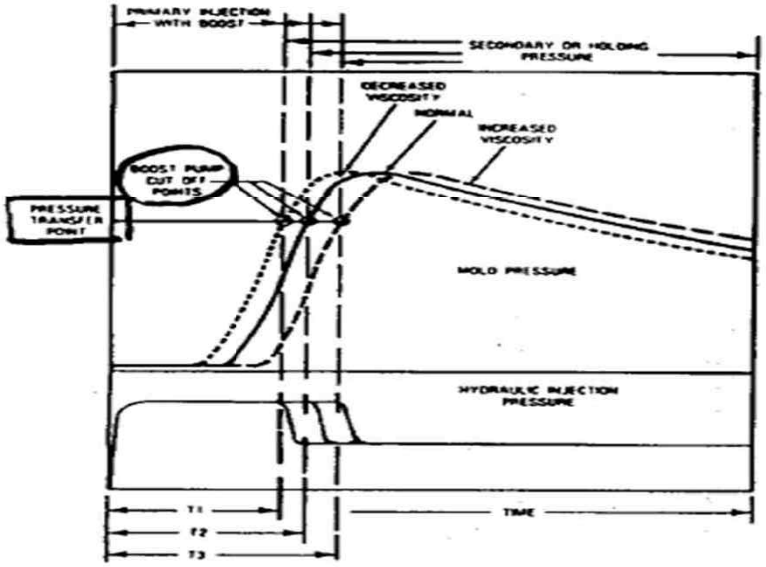


Fig. Effect of 916 PTC on mold pressure with different apparent viscosities. The curves show the results of applying the Pressure Transfer Controller (PTC) to the different conditions described above. Note that with the 916, primary injection pressure can be increased thereby causing a faster rate of fill. This is possible because the controller monitors mold pressure during fill and cuts off primary injection pressure when mold pressure reaches a predetermined value. By being able to fill the mold faster, boost time can be reduced thus reducing the overall cycle time.

As shown in the figure, due to increased injection pressure, the mold fills faster and consequently mold pressure builds faster. When mold pressure reaches the Pressure Transfer Point, primary injection pressure is cut off and secondary or holding pressure is applied. Note that even though primary injection pressure is cut off, mold pressure continues to increase due to the dynamics and response of the hydraulic system. For all three conditions, injection pressure is the same, but the length of time that it is applied, varies, dependent on the apparent viscosity of the material. In this manner, injection pressure time is adjusted as a function of mold pressure and results in more consistent molded parts despite changes in material viscosity.

Part VI

Reactive Processing

Utilization of Processing Equipments as Chemical Reactors

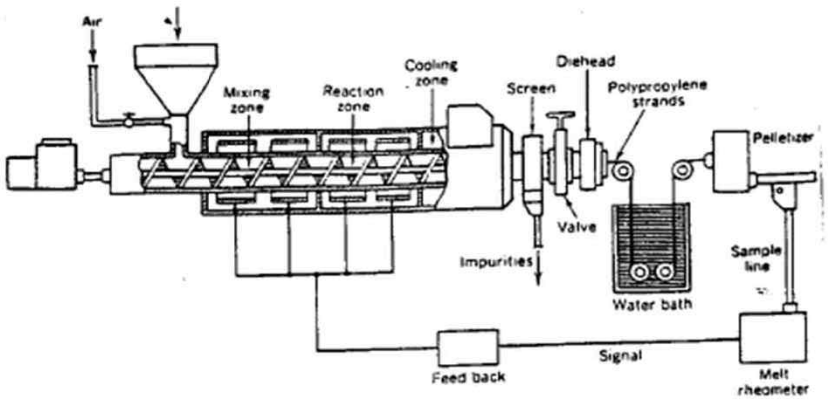
1. Heat generation during *in-situ* polymerization reaction : reaction thermodynamics should be clearly understood.
2. Exact metering of reactants : use liquid (melt) instead of solid (powder).
3. Fast mixing of the reactants: mostly a HPIM (high pressure impingement mixer) is used.
4. Realtime monitoring of the process (thermodynamically and rheologically) is required.

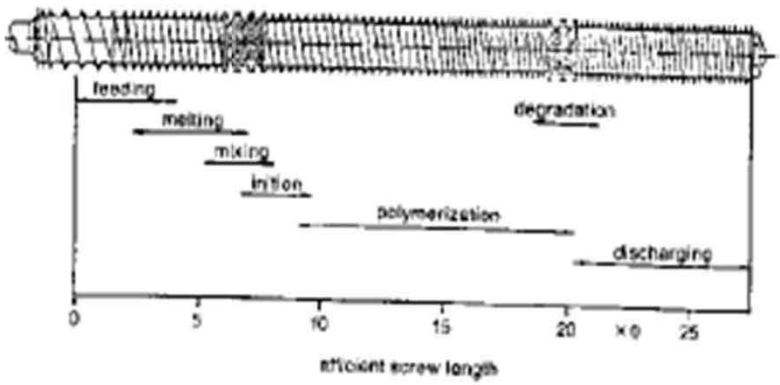
Reactive Extrusion (REX) (1)

1. Reactor : single or multiscrew extruders specially designed for chemical reaction. The single screw extruder is inadequate in reactive extrusion because of inefficient mixing action. However, a single screw with special mixing section and a multistage single screw extruder capable of devolatilization are used. A corrotating twin screw extruder is commonly used.

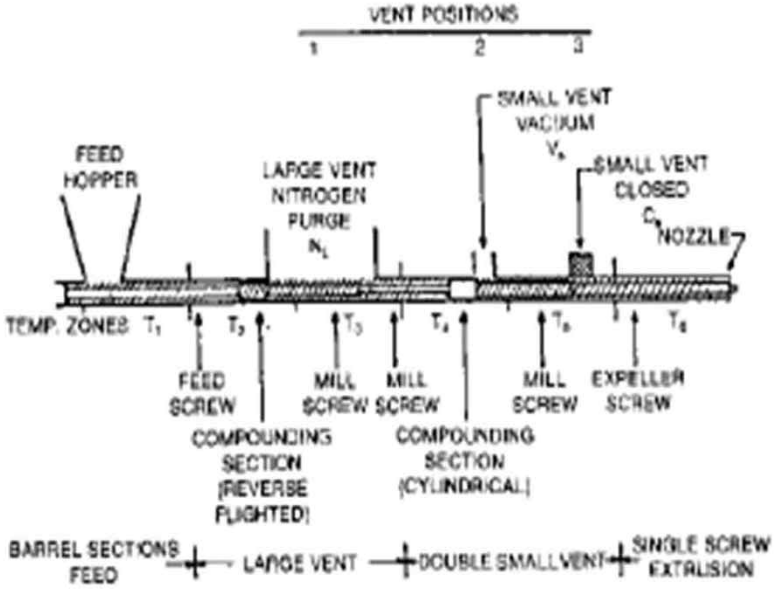
2. Application fields of REX
(1) Bulk polymerization
(2) Graft reactions
(3) Interchain copolymer formation
(4) Coupling/crosslinking reactions
(5) Controlled degradation
(6) Functionalization and modification of functional group

REX (2) : Examples of Equipment

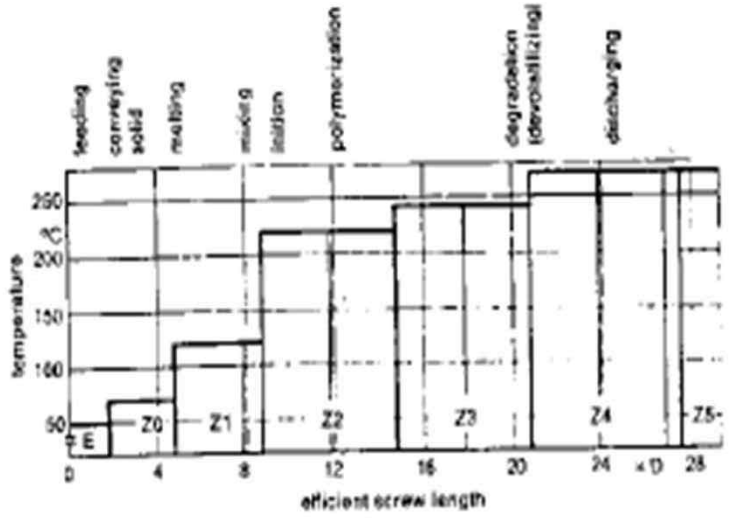




e 4.7 Screw design for polyamide synthesis (Bartilla et al. 1986). Reprodu



4.4 Extruder reactor for synthesis of polyester (Gouinlock et al.,1968). I



4.8 Temperature profile across extruder for polyamide synthesis (Barti

REX (3)

1. Considerations in operation:

(1) The difference of temperatures between neighboring barrels < 100°C.

(2) Pressure; 0 to 50MPa (0 to 7,250psi).

(3) Retention time can be extended by successive combination of extruders.

(4) Heat-sensitive additives should be incorporated near the die.

2. Process advantages [(1)-(6)] and limitations [(7)-(8)]:

1) Increased surface/volume ratio promotes reaction, mixing, and heat transfer; improved thermal history control by reducing residence time (30 sec to 30 min) due to constant surface renewal.

2) Solventless polymerization due to ability to handle ultrahigh viscosity; no solvent recovery process and no contamination by solvent.

3) The shear heat can be used as chemical reaction energy, and the heat of reactions (e.g., exotherms of polymerization) can be used as well.

4) Sequential reaction initiation is possible; an intended reaction can be initiated at the intended position.

5) Ready-to-use polymer is obtained.

6) Easy removal of unreacted monomer and by-product.

7) Difficult to handle large heats of reaction.

8) High cost for long reaction times.

Reaction Injection Molding (RIM)

1. Some important reaction injection molding (RIM) processes

(1) Urethane RIM system demands exact stoichiometry

(2) Non-urethane RIM systems: nylons, polyureas, polyesters, epoxies, and polydicyclopentadienes

2. Advantages:

(1) Low energy consumption and low tooling cost

(2) Large part size and complex part capability

(3) Faster cycle time

3. Equipments consist of high pressure metering, impingement mixing mixing, and a self-cleaning mix head.

(1) Precise metering of the amount of pumping: lance displacement pump

(2) Fast mixing: impingement mixer

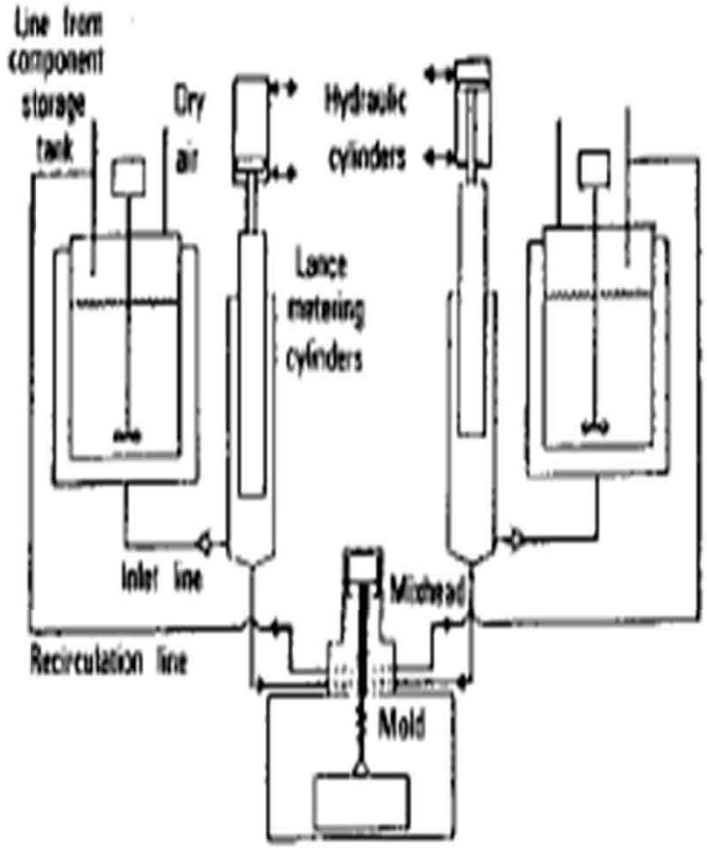
4. Process: injection of monomers or oligomers into a mold, followed by a fast polymerization reaction in the mold.

(1) Mold for RIM should be pore-free and tightly sealed.

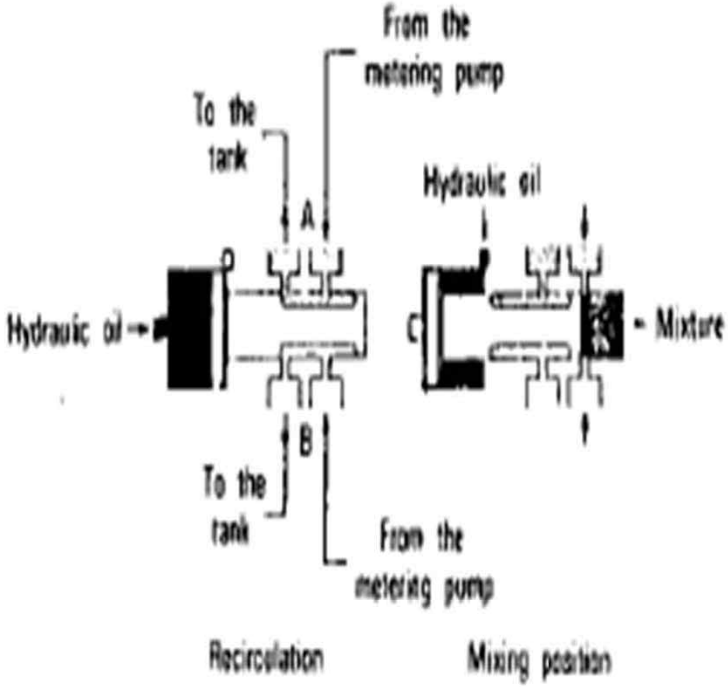
(2) Mold venting should be at the highest point in the mold.

(3) Require lower pressure and lower temperature than the conventional

Typical Equipments for RIM



Schematic diagram of RIM process.



Standard mixhead configuration.

Example : Nylon 6 RIM

1. Nylon 6 block copolymer is obtained by anionic polymerization of caprolactam (T_m=69°C) RIM process consists of high pressure metering, impingement mixing, and a self-cleaning mix head.
2. Precise metering of the amount of pumping by using lance displacement pump.

   Fast mixing : impingement mixer to the polymeric polyol prepared by using bis-acyl lactam as an initiator.
3. Preparation of polyesteramide prepolymer by reacting polyol with initiator (excessive initiator must be used to produce acyl lactam terminated prepolymer).
4. The ratio of acyl lactam to polyol determines the MW of block copolymer.
5. Anionic polymerization of caprolactam initiated by end-group of acyl lactam: caprolactam magnesium bromide (prepared by reacting caprolactam and Grignard reagent ethyl magnesium bromide) acts as a catalyst.

Part VII

Fiber Spinning

Fundamentals of Fiber Spinning

- Fiber is composed of amorphous, oriented (or mesophase), and crystalline regions. Oriented region confers anisotropic mechanical strength and crystallites act like crosslinking points to stabilize the metastable oriented structure. Thus, uniformity in size and distribution of crystallites is crucial to good mechanical properties and level dyeing.

- Instead of crystallites, strong intermolecular attractions through polar groups in the main chain or in the pendant resulting from molecular orientation can also act like weak crosslinks through hydrogen or inonic bond.

- Thus, fiber spinning should be carried out to control the inner microstructure of fiber together with the outer shape of the fiber

Elongational Rheology (1)

- Elongational (or free surface) flow vs. shear (or wall) flow

(1) Shear flow
- Mostly, rotational flow with tumbling and stretching of polymer molecules ; weak flow
  ⇒ Low orientation results
- $X_1(t) = X_1(0) + X_2 \dot{\gamma} t$

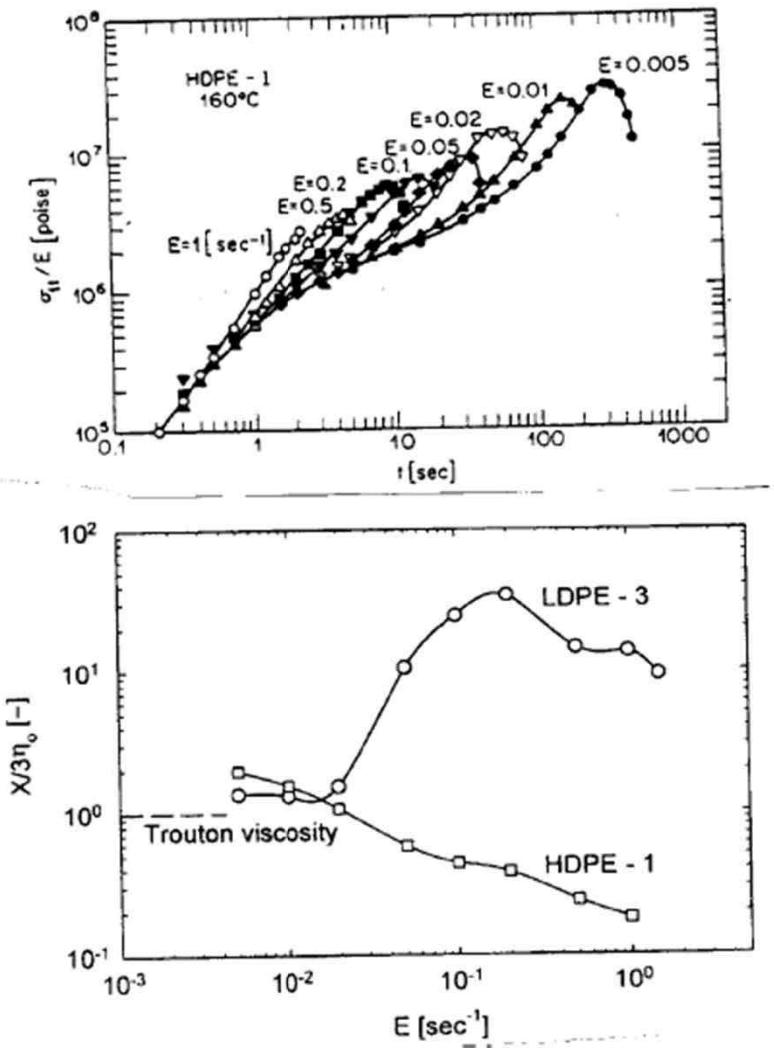
(2) Elongational flow
- Irrotational flow : Strong flow
  ⇒ High orientation results (Effective mixing)
- $L(t) = L_0 e^{\dot{\varepsilon} t}$, where, $\dot{\varepsilon} = d\ln L/dt$

  ※ Hencky strain : $\varepsilon = \ln(L/L_0) = \ln\lambda$

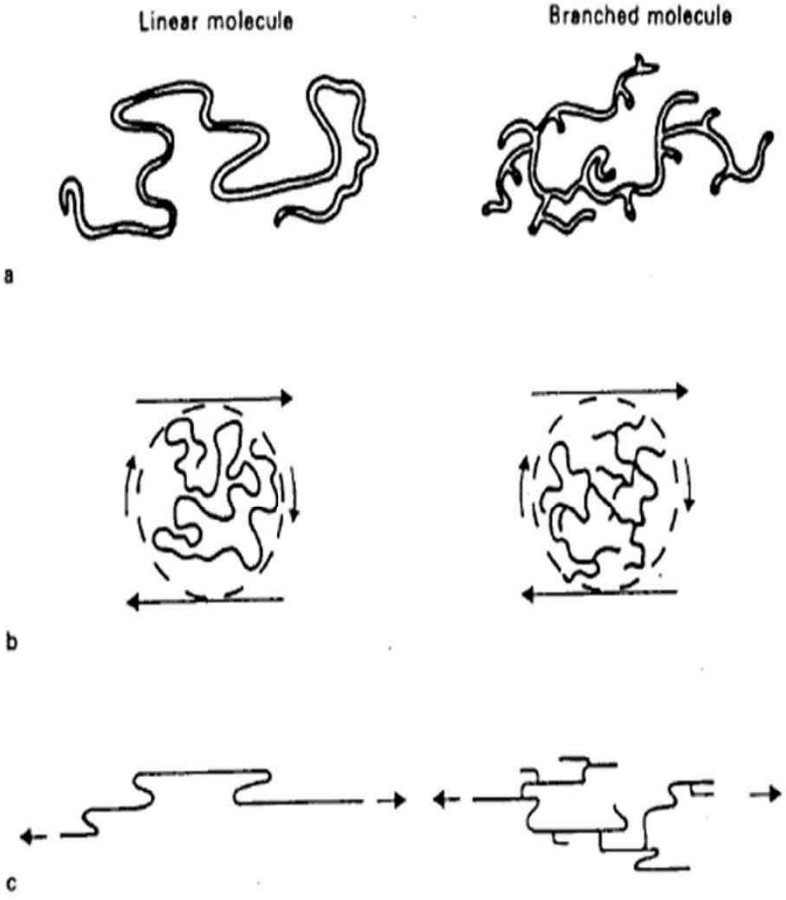
Elongational Rheology (2)

Elongational viscosity (η_E) is sensitive to rate of elongation and molecular structure

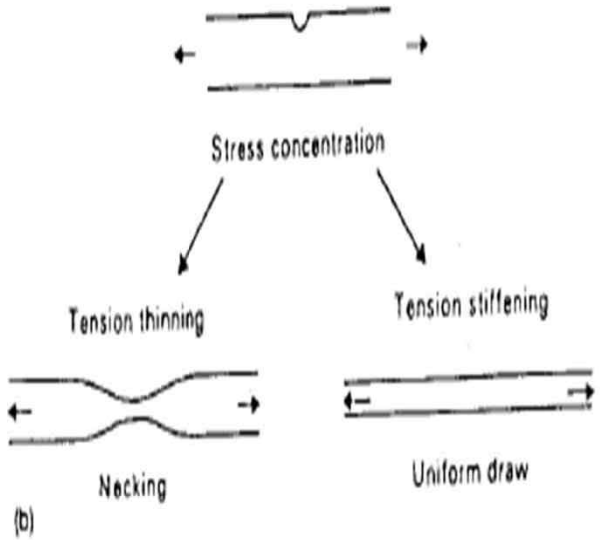
1. Troutonian: η_E does not vary with elongatinal rate(e). E.g., linear polymer with bulky pendant group.
2. Tension-stiffening(-hardening, or -thickening): η_E increases with e. E.g., LDPE.
3. Tension-thinning(-softening,-weakening): linear polymers such as HDPE and PP.



Engineering Significance of Elongational Flow Behavior of Branched Polymers



a Branched and linear molecules
b Shear flow
c Stretching flow



(a) The dependence of λ, the elongational viscosity, on tensile stress for branched and linear polyethylene. At stresses below 10^3 Pa, both polymers approach Newtonian behaviour (λ independent of σ). Non-Newtonian behaviour occurs above 10^3 Pa: branched PE tension-stiffens; linear PE tension-thins.

(b) Illustration of the way in which tension-stiffening liquids may be drawn without necking: the higher stress at the incipient neck (an adventitious small reduction in cross-section) is neutralized by λ increasing at that point owing to the stress increase

Melt Instability during Spinning

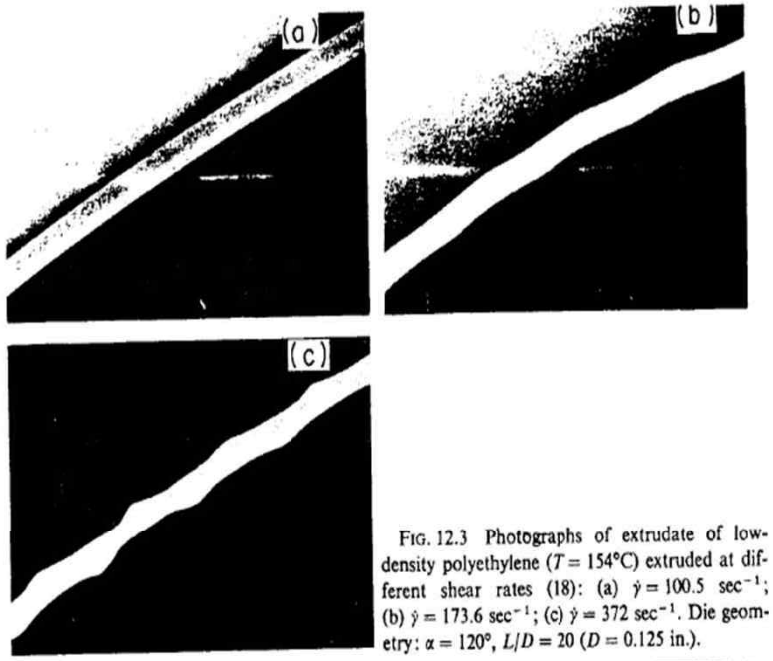


FIG. 12.3 Photographs of extrudate of low-density polyethylene ($T = 154°C$) extruded at different shear rates (18): (a) $\dot{\gamma} = 100.5\ sec^{-1}$; (b) $\dot{\gamma} = 173.6\ sec^{-1}$; (c) $\dot{\gamma} = 372\ sec^{-1}$. Die geometry: $\alpha = 120°$, $L/D = 20$ ($D = 0.125$ in.).

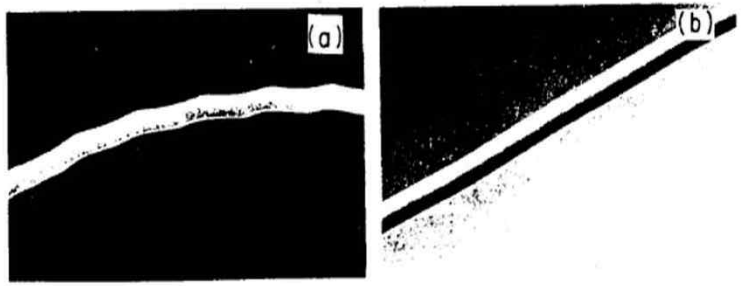
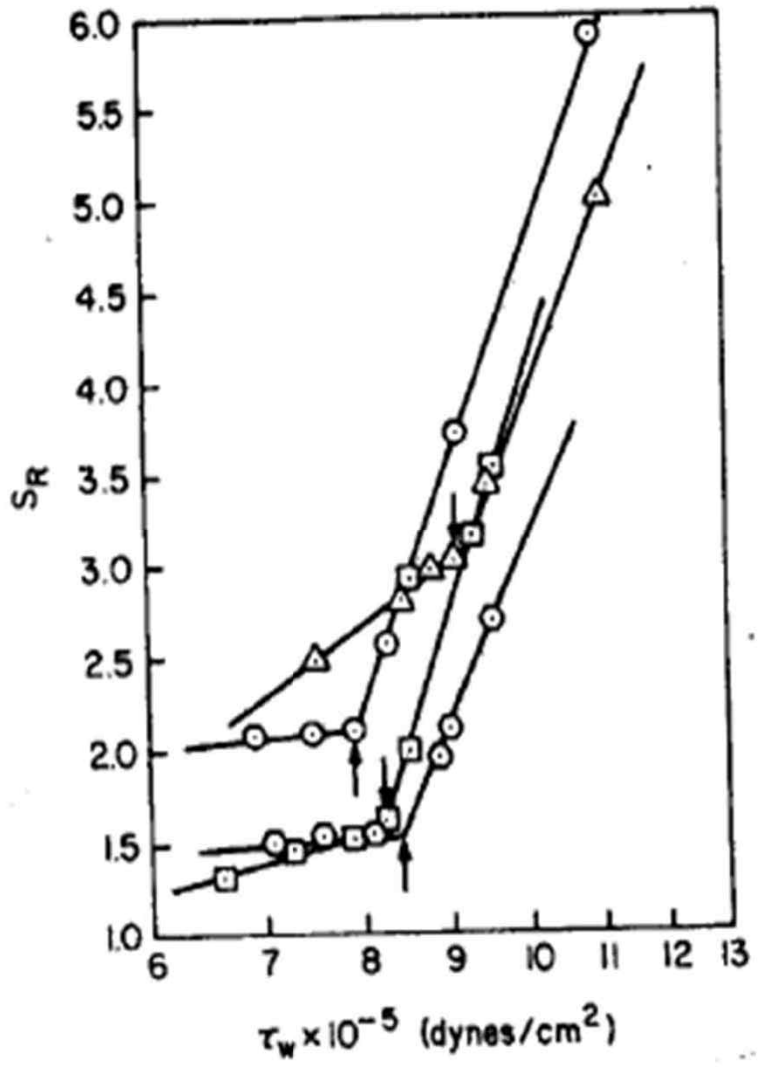
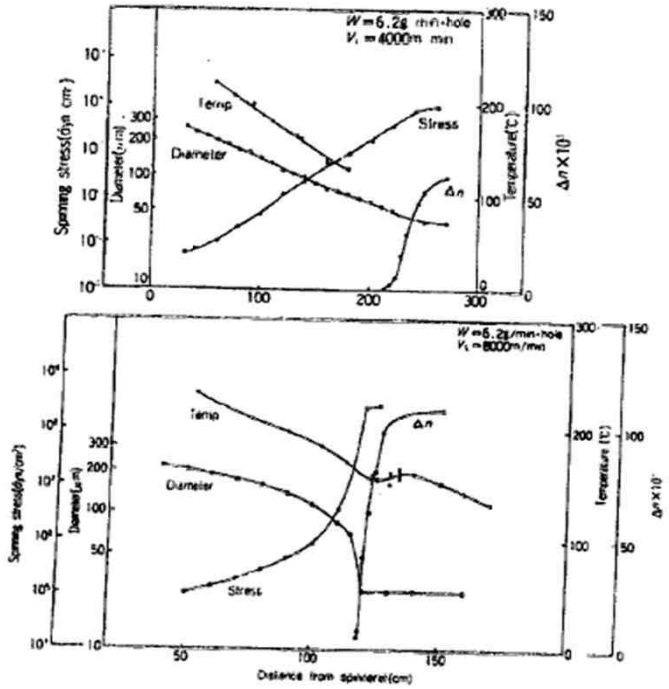


FIG. 12.4 Photographs of extrudate of low-density polyethylene ($T = 154°C$) extruded through dies having different L/D ratios (17): (a) $L/D = 4$; (b) $L/D = 20$. Shear rate in both cases is $356\ sec^{-1}$.

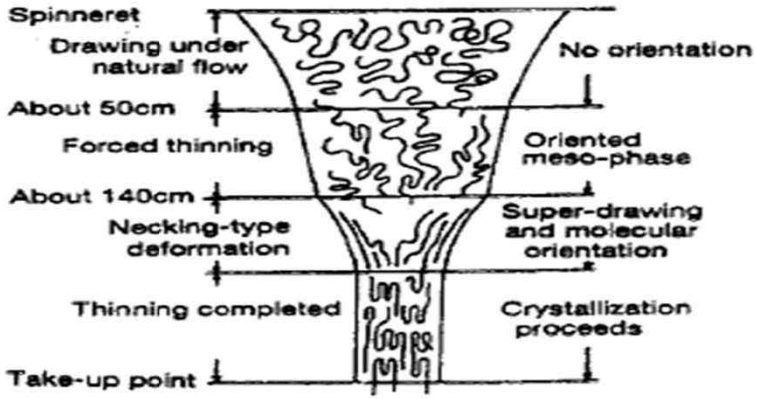


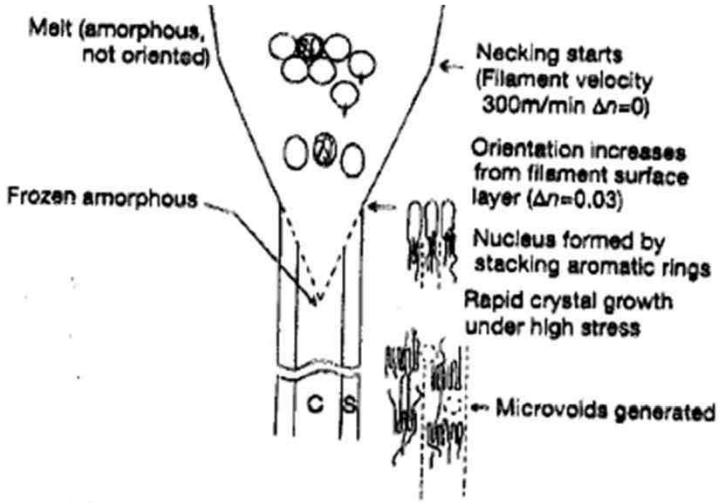
High Speed Spinning



Filament velocity, deformation rate, spinning stress, elongational viscosity and filament temperature at the onset of necking

Take-up velocity (m/min)	Fiber velocity (m/min)	dv/dx (sec^{-1})	σ (dyn/cm^2)	λ (poise)	Temp. (°C)
6000	2014	111	1.8×10^{7}	1.6×10^{3}	125
7000	928	164	5.2×10^{3}	3.2×10^{4}	150
8000	887	119	3.7×10^{7}	3.1×10^{4}	180
9000	493	65	1.1×10^{7}	1.7×10^{4}	199
10000	288	18	3.5×10^{7}	1.9×10^{4}	221





Air-gap Spinning

1. Dry jet-wet (Liquid-crystalline) spinning

Anisotropic phase has fast stress relaxation but has slow orientation relaxation.

High stretching at the air gap

→ High fiber orientation

→ High tensile properties

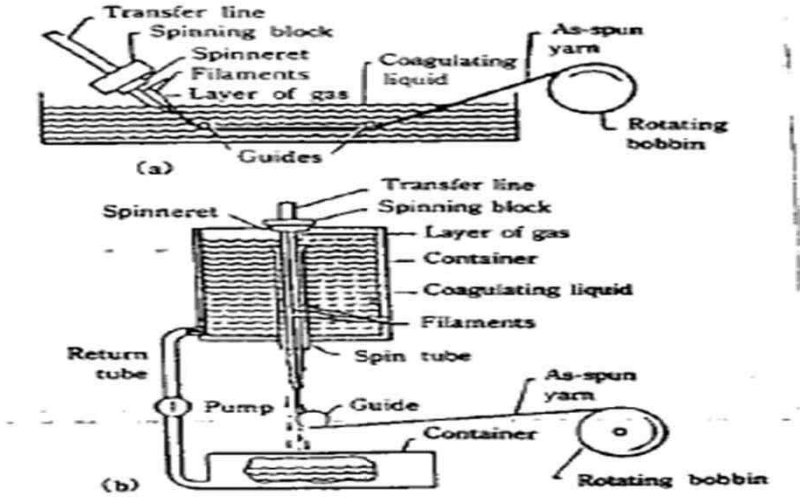


Fig. Schematic representation of dry-jet wet spinning process : (a) without spin tube, (b) with spin tube

2. Gel spinning process

UHMWPE solution dope with least molecular entanglements

→ High orientation with least defect (lower concentration prefers)

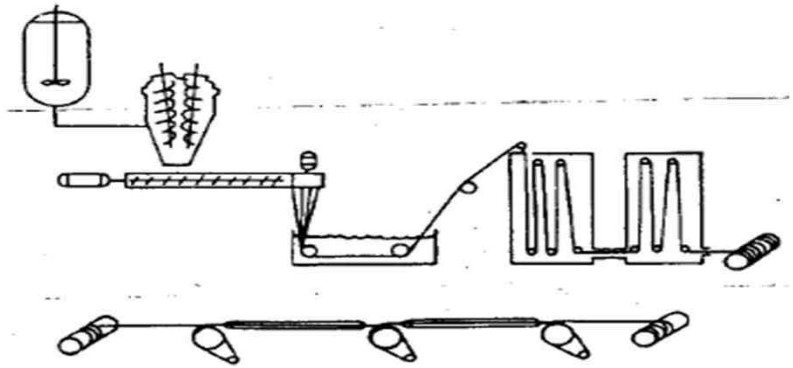
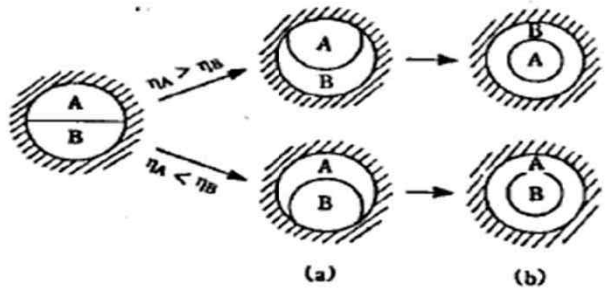


Fig. Gel-spinning apparatus

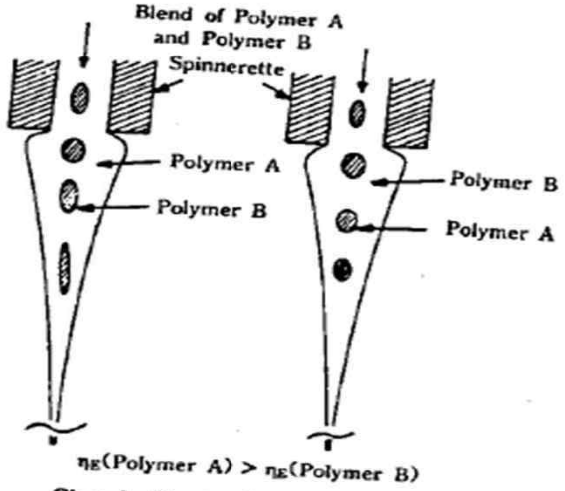
Blend Spinning

- Extrusion of **incompatible polymer blends** leading to effective **elongational deformation of the dispersed phase** if the dispersed phase has lower elongational viscosity than the matrix phase

- Theoretical background of the spinning of the **island-in-sea type fiber**



Schematic showing the evolution of the change of interface shape in side-by-side coextrusion through circular dies : (a) a small L/D ratio : (b) a sufficiently large L/D ratio.



Sketch illustrating deformation of liquid droplets suspended in another liquid medium.

Electrospinning

- Electrospinning is a powerful process to produce fibers with diameters in the range of a few tens nanometers to several microns.

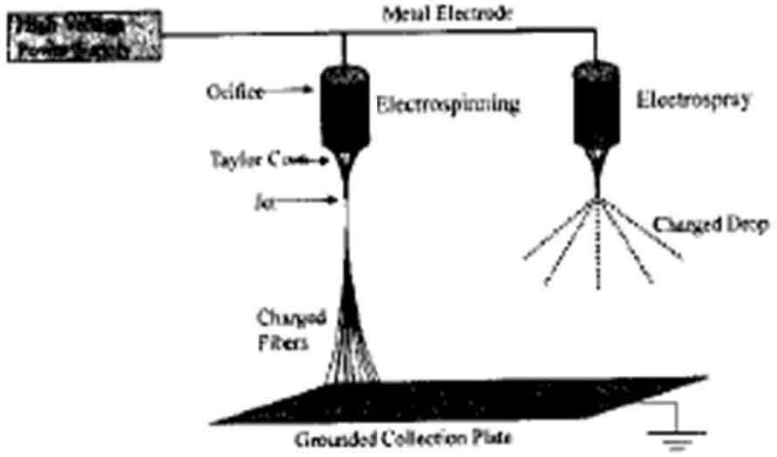


Figure 8. Schematic diagram of the electrospinning and electrospray processes.

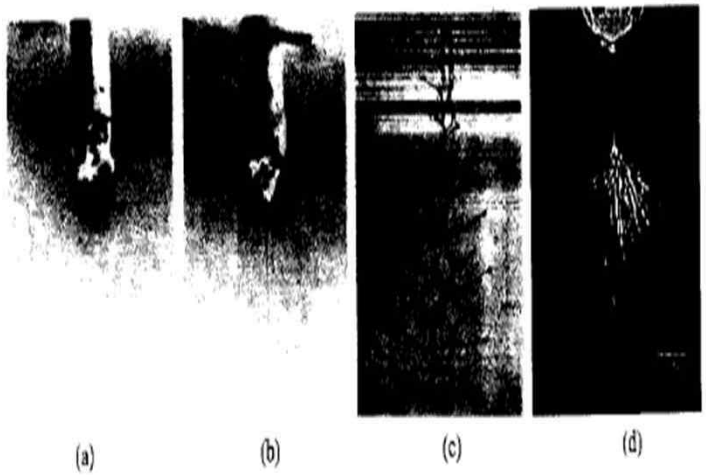


Figure 9. (a) Unperturbed droplet, (b) electrohydrodynamic con-jet, (c) electrostatic spray droplet, and (d) splaying of jet observed in electrospinning.

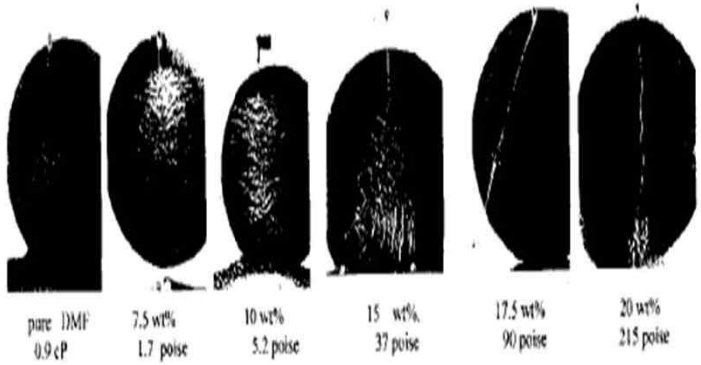


Figure 10. Microflash photographs of electrospinning of PAN solution[16].