POLYMER AND COMPOSITE MATERIALS PROCESSING

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Ch. 3. MIXING

Polymers and additives

Reasons of mixing additives

- The first is that additives are sometimes needed to alter the properties of the material, e.g. by making it harder or more flexible or cheaper.
- The second is that it is often important to prevent degradation of the polymer in service or during processing or both by means of appropriate additives.
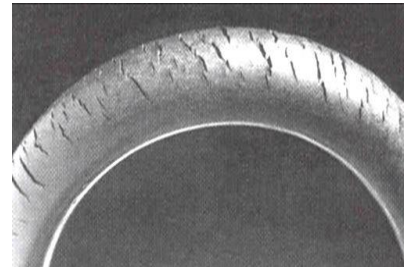
1) Modifying additives

- Reinforcing fillers are used to toughen polymers.
- Carbon black

    : The main effect is a marked improvement in abrasion resistance, which is important in many rubber applications, e.g. tyres, conveyor belting.

- Non-reinforcing fillers, or extenders

   - usually powders, added to cheapen the mix or to stiffen it or reduce its tack.

   - Commonly used materials are calcium carbonate, either as ground limestone or precipitated whiting, and china clay.

- Plasticizers

   - used in cases where it is desired to increase flexibility.

   - The outstanding example is flexible plasticized PVC.

- Liquid extenders in rubbers

   - They are hydrocarbon oils (hydrogen + carbon atoms).

- Vulcanization of rubbers

   - The rubber chains are cross-lined chemically by Sulphur.

- Chemical blowing agents

   - used to produce foamed products.

- The use of pigments or dyes to color

2) Protective additives

- Antioxidants

  - needed to prevent oxidation during processing and also to protect the polymer structure during the service life of the product.

- Heat stabilizers

  - perform a similar function in preventing degradation at high processing temperatures.

  - PVC readily degrades and darkens when heated, with the evolution of hydrogen chloride.

- Antiozonants

  - a type of specialized antioxidant used especially in rubbers.

  - prevents or retards the degradation of material by ozone (O_3)

ozone cracking in natural rubber

ozone generator by corona discharge

- Antistatic agents

  - helpful in preventing the build-up of undesirable static charges.

- Processing lubricants

  - widely used to assist the passage of the material through the processing machinery.
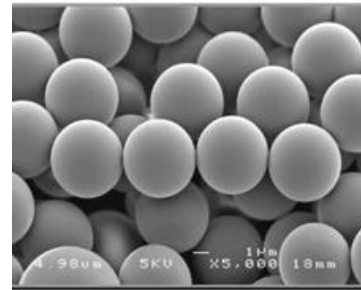
Physical form of polymer mixes

- Raw polymers are supplied in a variety of forms
  - which include large bale of solid rubber, granules, liquid medium molecular weight resin, and latex.

granule   Solid rubber   Latex particle

- In a few cases, the physical nature of the mix depends more on the additive than the polymer itself.
  - An example is the blend of powdered PVC and liquid plasticizer, termed as a *plastisol*.
 - plastisol flows as a liquid and can be poured into a mold

Plastisol used as a dip-coating

Types of mixing process

- We can identify two basic mixing functions:

    – Extensive mixing
    – Blending
    – Mixing
    – Distributive mixing

    – Intensive mixing
    – Compounding
    – Dispersion
    – Dispersive mixing

- Extensive or distributive mixing or blending

  - Distributive mixing consists of essentially of stirring together the ingredients.
  - Often this will mean the blending of a number of solids, e.g. polypropylene powder, pigment, antioxidant.
  - Small proportions of liquids can be added.

- Intensive or dispersive mixing or compounding

  - Dispersive mixing involves the more intimate dispersion of the additives into the matrix of the polymer.
    - A physical change in the components
    - High shear forces to bring about the change
    - The polymer to be in the molten or rubbery state during mixing
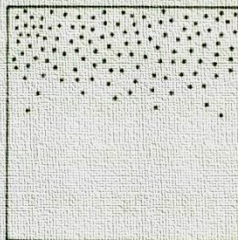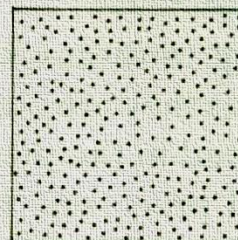   - → More vigorous mixing way than blending
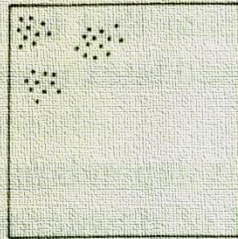
Poorly distributed
Poorly dispersed
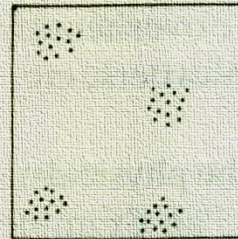
Well distributed
Poorly dispersed

Poorly distributed
Well dispersed

Well distributed
Well dispersed

Fig. 3.2 Diagrammatic representation of distributive and dispersive mixing.

- When are 'blending' and 'compounding' used?

  - In most cases, it is necessary to achieve both good distribution and good dispersion for a satisfactory product.
  - Blending or distributive mixing is used:
    – When the fabrication process to follow offers some compounding actions (=rough mixing initially).
    – Thermosetting powders are often blends of powdered resin and fillers which disperse upon fusion of the resin during molding. (why? Simply mix with stirrer or hand)
    – As a preliminary to a separate compounding process.
  - Compounding or dispersive mixing is needed:
    – When accurate distribution and dispersion of interactive ingredient is required.
    – When large amounts of modifying ingredients, e.g,, fillers, plasticizers, other polymer, etc., are being used.
    – When the fabricating process offers little or insufficient compounding action.
    – Compounder is needed rather than simple mixer or stirrer
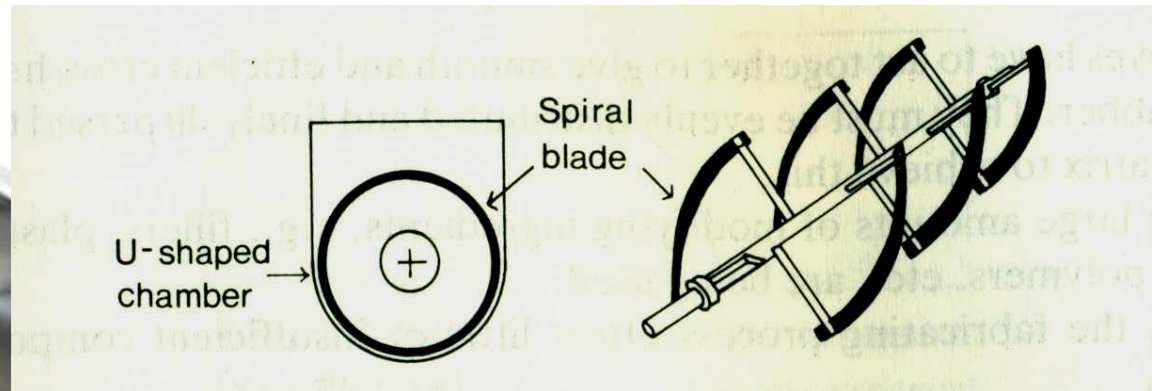
Some processes and machines

- Blending
    - Processes for blending vary from the simplest to sophisticated high speed machines.
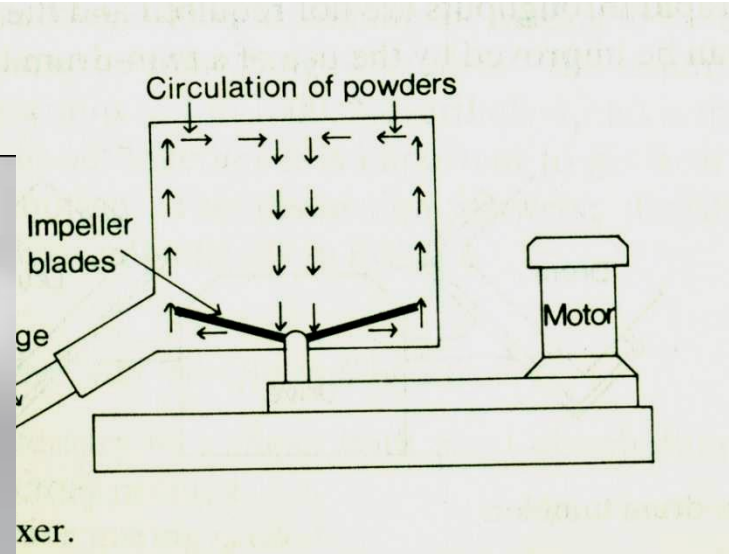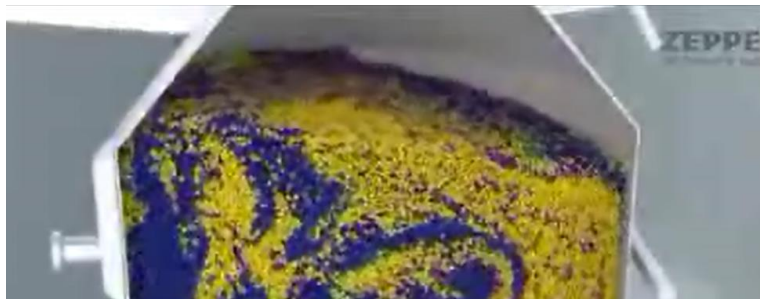   - The simplest is to tumble together dry ingredients.

Fig. 3.3 Twin-drum tumbler.
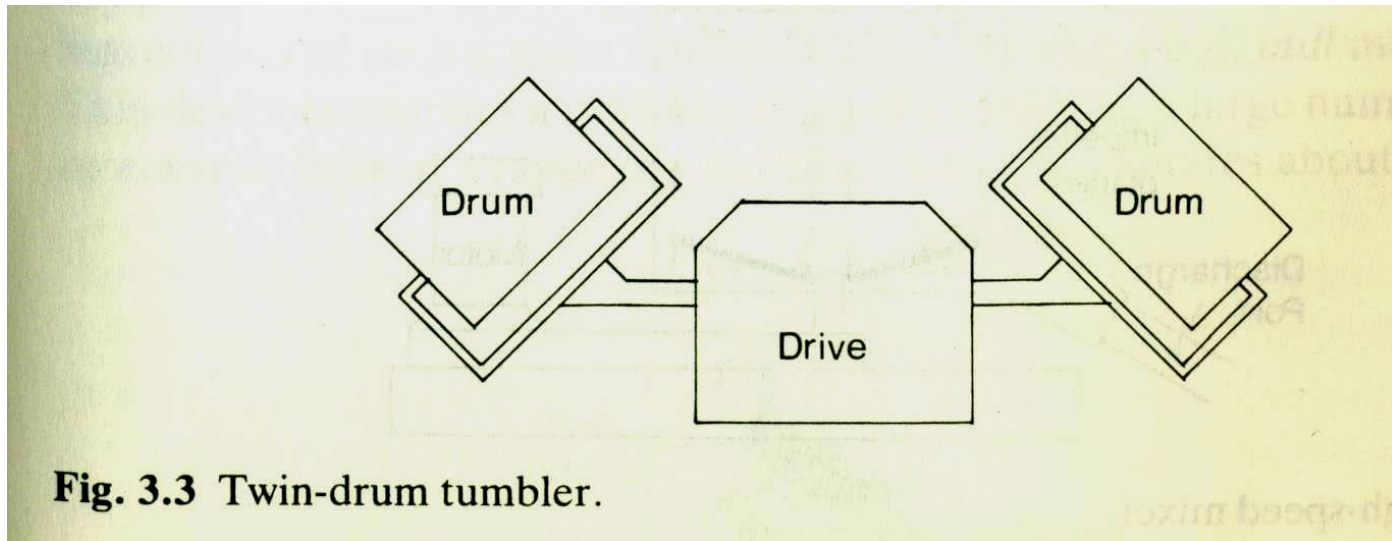
– Ribbon-blender

- The chamber is stationary and the ribbons rotate.

Spiral
blade

U-shaped
chamber
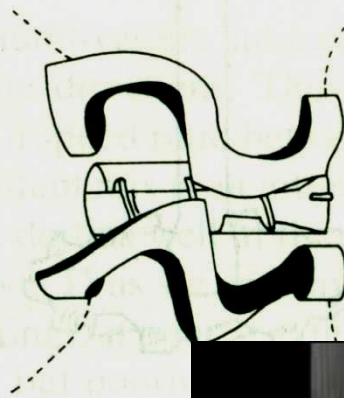
– High speed mixer (Henschel mixer)

- PVC dry blends
- External heating is unnecessary.
- Very high speed mixing and easy sample acquisition

Circulation of powders

Impeller blades

Motor

– Z-blade mixer

- Dough molding compound (DMC).
- The two Z-shaped blades counter-rotate to distribute the solid fillers into the liquid base.
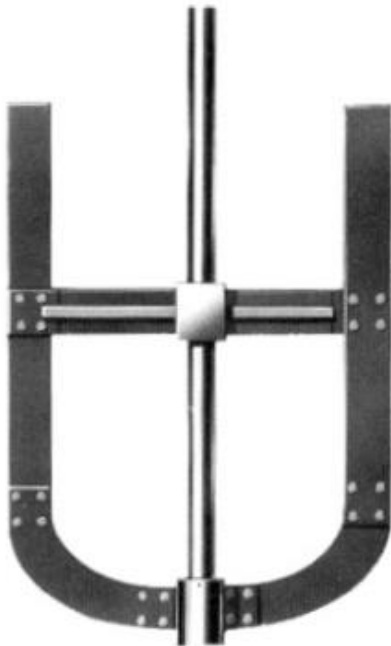- Food processing industry
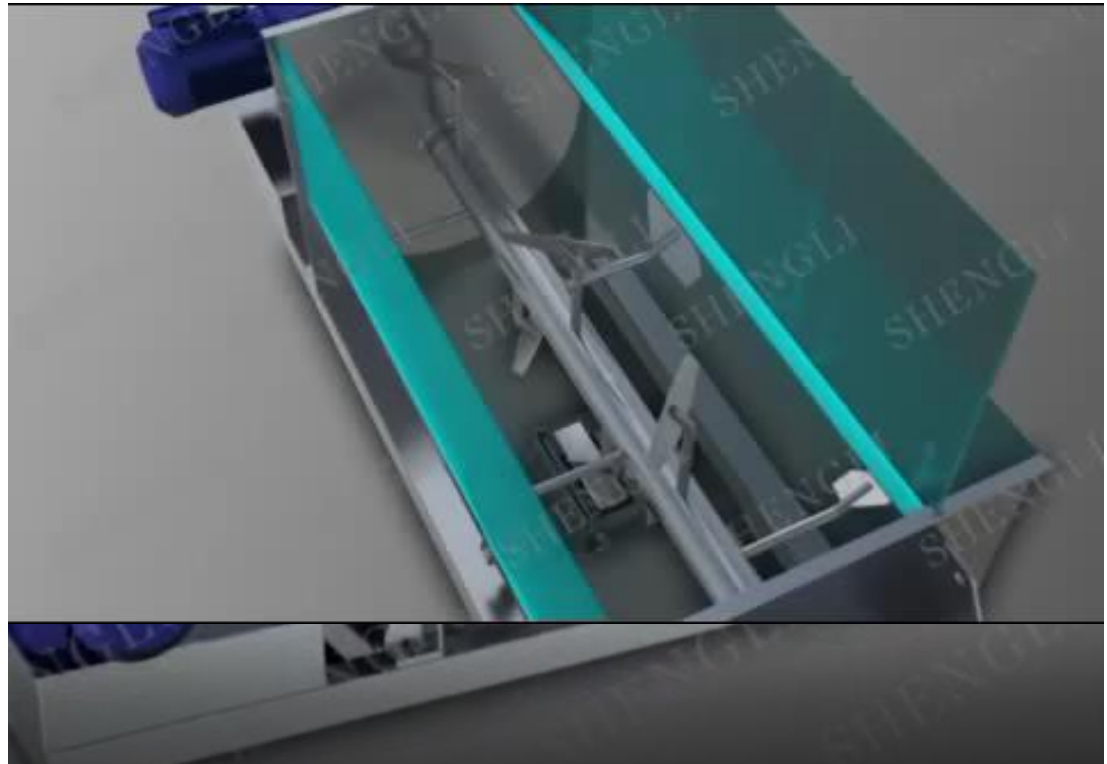

Fig. 3.6 Z-blade mixer.

– Paddle mixer (similar to anchor mixer)

- Paints and the paint-like plastisols are prepared.
- Scaled-up domestic food mixer
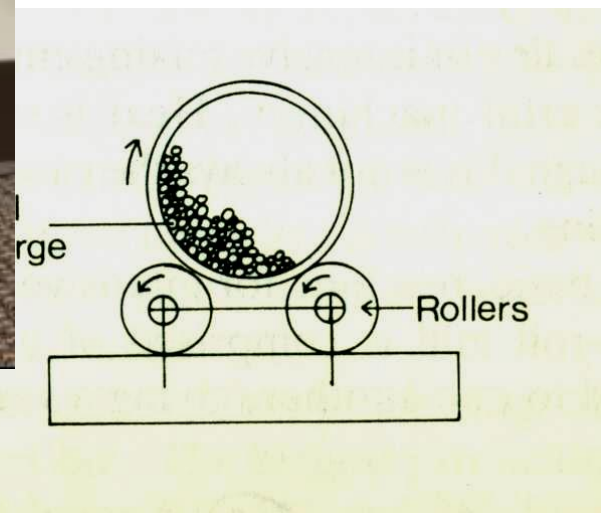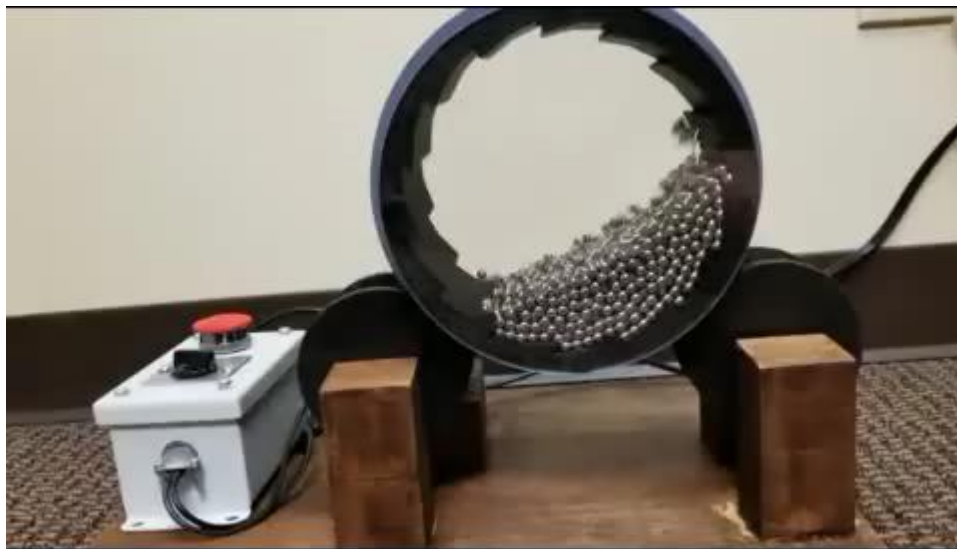- The viscosity is low enough for these relatively low-powered machines to be effective.


Anchor mixer

– Ball mill

- This device comprises a cylindrical vessel containing a large number of steel or ceramic balls.
- The process is slow, several hours milling usually being needed.

rge

Rollers

Fig. 3.7 Ball mill.

– Dip mixer (Cowles dissolver)

- This makes it particularly suitable for latex or emulsified mixes, which are often used as surface coatings; such colloidal dispersions are easily coagulated by high shear mixing.
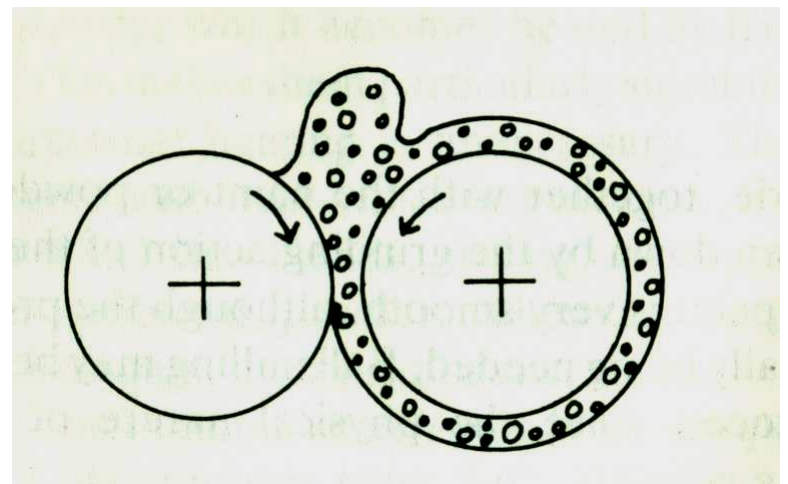
High Speed Dissolver
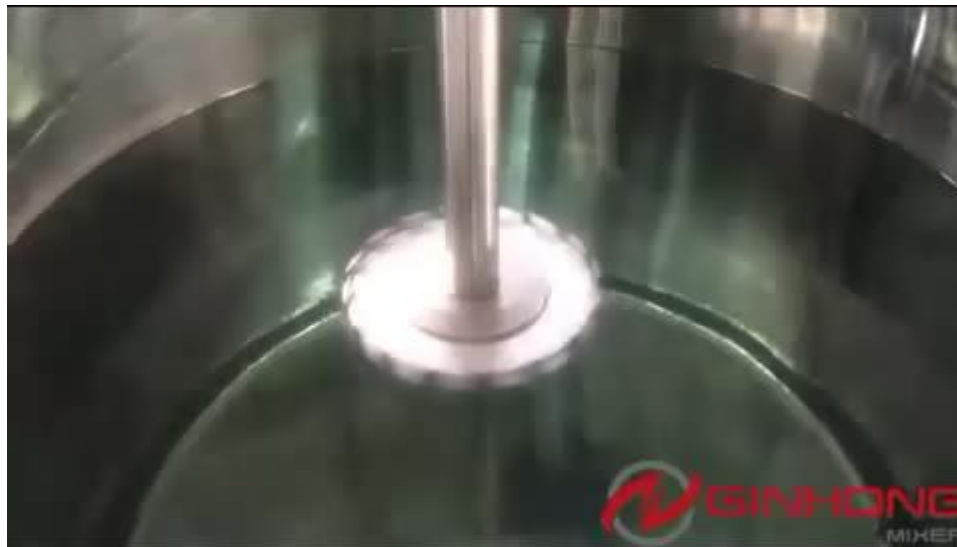
- Compounding

1) rubbers

Compounding mixing employs high shear processes and much more powerful machinery.

– Two-roll mill
 - The simplest and basic machine

- Two-roll mills do the mixing in the machine is good at intensive or dispersive mixing but poor at extensive or distributive mixing.
- Usually raw polymer, through the nip a few times until it warms up, softens and forms a smooth band round one of the rolls.
- In general, the roll is the hotter, faster one.
- The nip is adjusted, once the band is formed round the preferred roll, to give a small 'bank' of polymer rolling along the top of the nip.
- As soon as this condition is achieved, the additives can be introduced.
- Time consuming
  - It is no longer in use as a primary production process, although still widely used for laboratory scale work.

- The mill is still widely used as the receiver of materials mixed in internal mixers.
  - As a refiner of the mix
  - As cooler
  - As a convenient way of turning the large chunks into easily handled sheets.
  - For the addition of sensitive ingredients

- The Banbury mixer
  - The advent of the internal mixer revolutionized the scene and dominates the picture.
  - There is a complex flow pattern within the mixer, with elongational flow as material enters the nip between the rotors and shearing flow as it leaves it.

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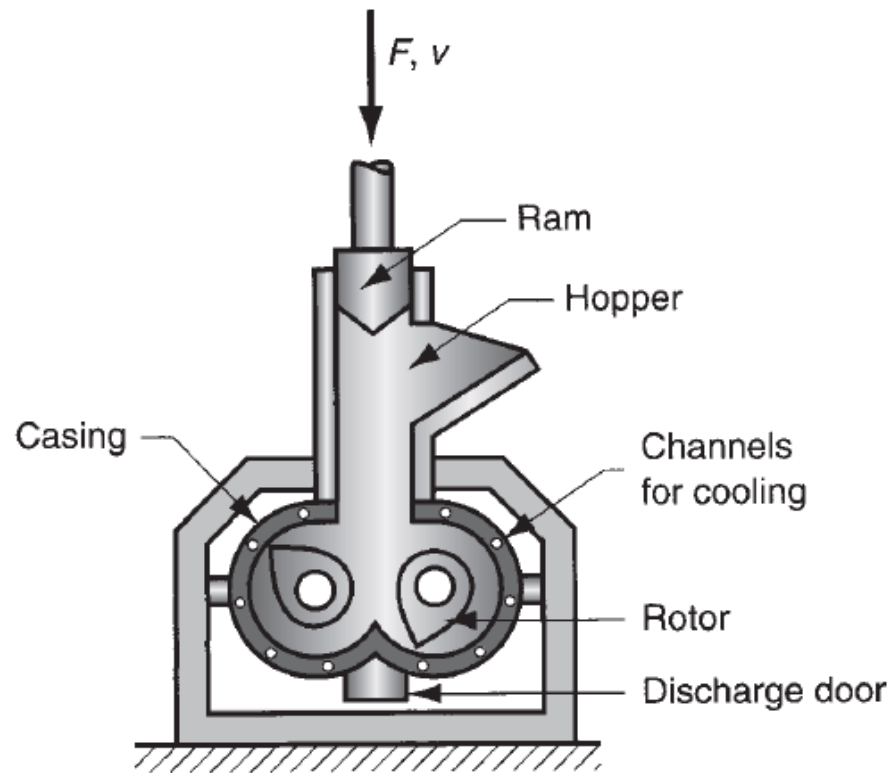
– Strong points of the internal mixers
  • They vastly increases the rate of throughput, and properly run, the regularity of the product.

– For usual polymers,
  • Viscous dissipation (heat generated) does benefits to the mixing

– For common rubbers,
  • The operation with water cooling is necessary.
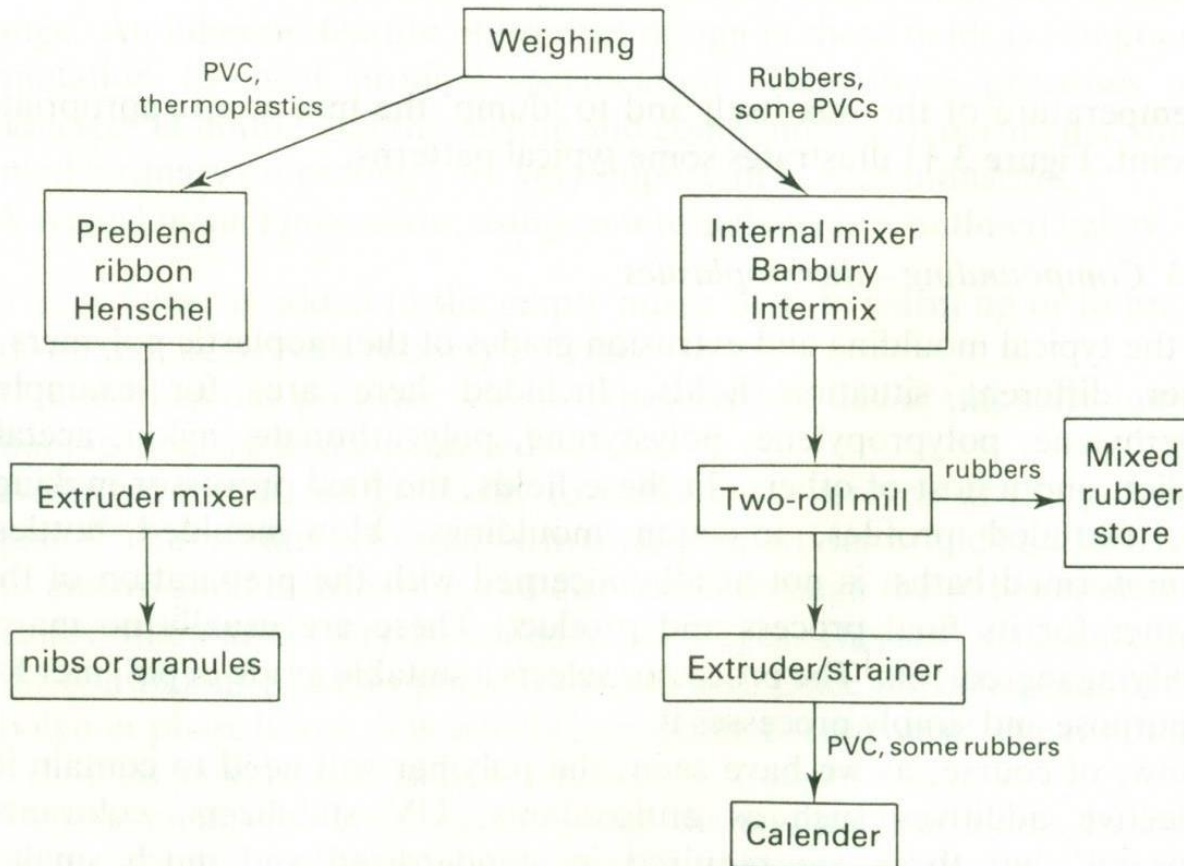
- Compounding

2) thermoplastics

- The easiest way to achieve all this is to use an extruder as a mixer.
- Often the extruder is itself fed with a blend from a Henschel-type high speed mixer.
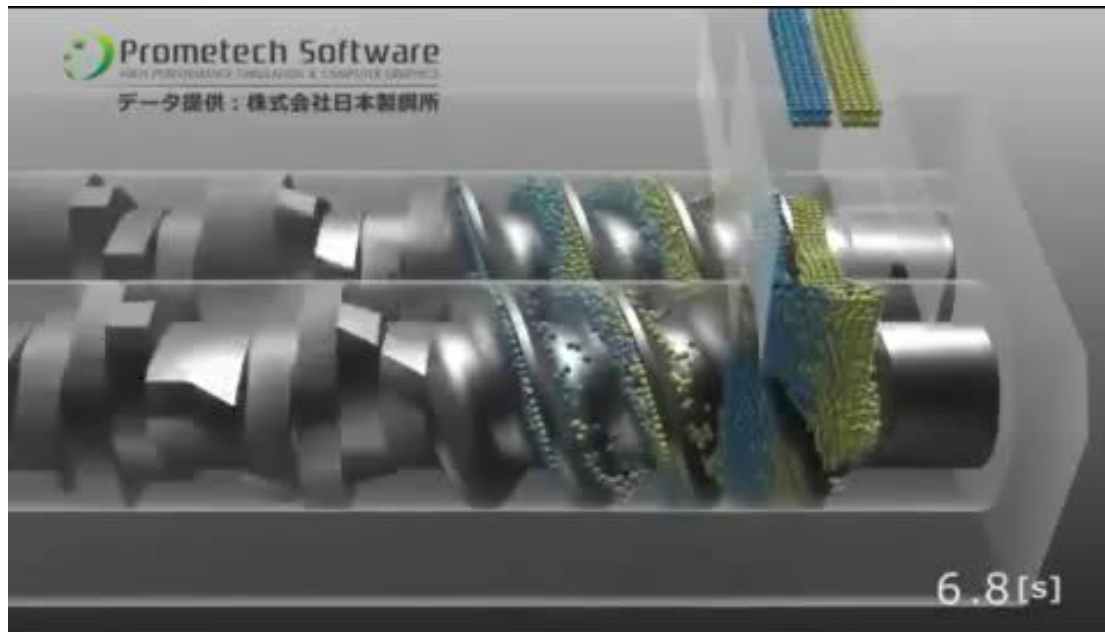
- Mixing processes – summary

Figure 3.12 summarizes in diagrammatic form the various routes for mixing and compounding discussed in more detail above.

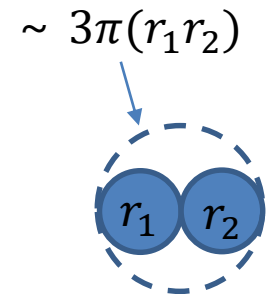Fig. 3.12 Mixing schemes for different classes of material.

- Some relations in mixing

1) Forces in mixing

: how is the force transmitted to break down agglomerates of additive particles?

→ by fluid mechanical stress in the mixer　　$\sim 3\pi(r_1 r_2)$

$$stress\ \tau = \frac{force}{area} = \frac{F}{a}$$

area a (for the two agglomerate particles) $\sim 3\pi(r_1 r_2)$

$$F = 3\pi\tau(r_1 r_2)$$

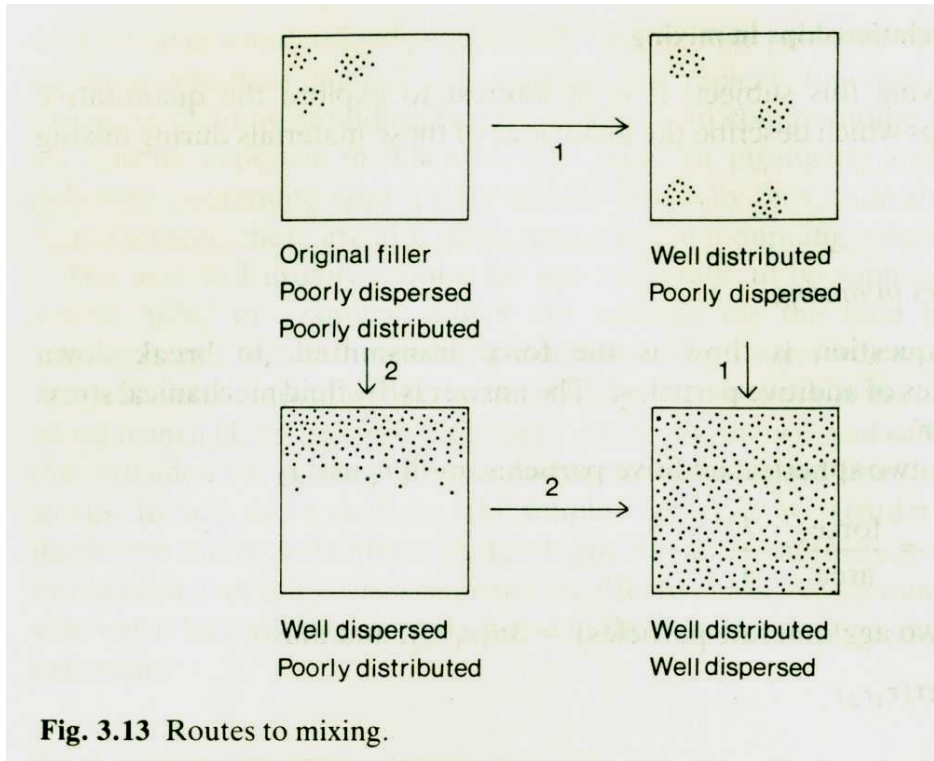Since $\tau = \eta\dot{\gamma}$ (Constitutive equation)　→　$F = 3\pi\eta\dot{\gamma}(r_1 r_2)$

Energy dissipated per unit volume,　$P = \eta\dot{\gamma}^2$

Thus,　$P = \dfrac{F^2}{9\pi^2 r_1{}^2 r_1{}^2 \eta}$

Less energy is needed under high viscosity conditions to achieve good dispersion!

2) Routes for mixing

- Route 1 will entail lower viscosity than Route 2, which means that
  Route 1 will require more energy than Route 2.
  → Pre-blending is needed to achieve route 2.

- Reynold's number: boundary between laminar flow to turbulent flow
- Distributive mixing is very difficult in polymer melt
  why? → Re is very low (since η is very high)

Fig. 3.13 Routes to mixing.

Original filler
Poorly dispersed
Poorly distributed

Well distributed
Poorly dispersed

Well dispersed
Poorly distributed

Well distributed
Well dispersed

$$Re = \frac{\rho V D}{\eta}$$

D: diameter of channel
V: velocity of fluid
ρ: density of fluid
η : viscosity of fluid

Reynolds Number (R_e)
explained

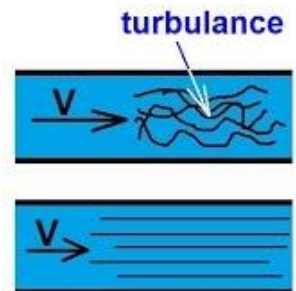$$R_e = \frac{\text{" inertial force"}}{\text{"viscous force"}} = \frac{\rho v L}{\mu}$$

turbulance

$$\rho \rightarrow [\frac{kg}{m^3}]$$

$$v \rightarrow [\frac{m}{s}]$$

$$L \rightarrow [m]$$

$$R_e = \frac{\rho v L}{\mu} \text{ (units?)}$$

→ Here, $L \sim D$

- Reynolds number, *Re*

: dimensionless number
   must exceed about 2000 to achieve turbulence (2000 is easily attained in low viscosity systems with normal stirring speeds)

e.g. $Re = \dfrac{\rho V D}{\eta}$ $D = 0.5\ cm = 0.005\ m$

$\eta = 150\ Pa \cdot s$

$\rho = 1000 kg/m^3$

$Q = 250 cm^3/s$

$V = \dfrac{Q}{A} = \dfrac{2.5e - 4}{1.96e - 5} = 12.7 m/s$

$\therefore Re = 0.42$

In such a case, turbulent flow cannot occur in polymer melts.
→ Distribution cannot be made by this *Re*.

1) At very low viscosity, turbulence results in efficient distribution
2) At high viscosity (for most polymer melts), turbulence cannot occur and distribution is poor, although dispersion (by less energy dissipation) is quite efficient.
3) At very high viscosity (for rubbers), there is sufficient shear to break down agglomerates, and efficient distribution and dispersion can occur in a single process.

- Reynolds number in Navier-Stokes equation

  - By non-dimensionalization of N-S equation, we can derive *Re* number.

  → Homework!

- Microfluidics for mixing