MKR1153
Polymer Technology II

CH1 POLYMER MIXING

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Mixing

- Polymer and Additives
  - Usually, polymers are mixed with added ingredients (serve a variety of purposes)
- 2 types of additives
  - Modifying additives
  - Protective additives

Modifying Additives

- Alter the properties of the polymer
- Types of additive
  i. Reinforcing fillers- to toughen polymers. e.g. carbon black added to rubber; improvement in abrasion resistance
  ii. Non-reinforcing fillers- are in powder, added to cheapen the mix (usually these additives do not enhance the properties). e.g. calcium carbonate.

Modifying Additives

Types of additives

iii. Plasticizer- usually non-volatile liquids, desired to increase the flexibility. e.g. flexible plasticized PVC
iv. Liquid extender- often used in rubber, they are hyrocarbon oils, cheapen the mix (without enhancing properties)
v. Chemical additives- changes in properties (widely used for cross-linking). e.g. the ‘vulcanization’ of rubber- rubber chains are cross-linked chemically by sulphur.

Modifying Additives

Types of additive

vi. Chemical Blowing Agent – to produced foam product. e.g. in sponge or ‘Sorbo’ rubber, sodium bicarbonate is used as blowing agent
vii. Pigments/dyes- used to colour the product

Protective Additives

- Very large number of additives in this classification
- Antioxidant- used to protect polymer against atmospheric oxidation & protect the polymer structure during the service life of the product.
- Heat stabilizer- prevent degradation at high processing temperatures

Protective Additives

- Anti-ozonants - a type of specialized antioxidant used especially in rubbers. e.g. unsaturated double bonds in rubber molecules are very susceptible to attack by ozone.
- UV stabilizer - often work in conjunction with antioxidant. Starting an oxidation reaction- attack at the reactive site on the polymer by UV radiation, in sunlight.
- Anti-static agents - prevent the build-up of undesirable static charges- create a potential dangerous spark in some cases.

Protective Additives

- Processing Lubricant- widely used to assist the passage of the material through the processing machinery.
  - Internal lubricant- lubricate the polymer granules, and those of other additives during processing. These materials are often at least partially miscible with the polymer melt
  - External lubricants- essentially immiscible, lubricate the mix against the processing machinery-allow the correct degree of friction

Types of Mixing Process

Based on 2 basic mixing functions;

1. Blending
2. Compounding

1. Blending

- Blending mixing is used when the fabrication process will be followed by compounding process (pigments must be mix into granules/powder followed by injection molding process), thermosetting powders and fillers are often blends which disperse upon fusion of the resin during molding

1. Blending

- Stirring together/blending of a number of solids, e.g. polypropylene powder, pigment, antioxidant, etc.
- The results is a mixture of powders; the individual powder remain and can be separated (in principle)

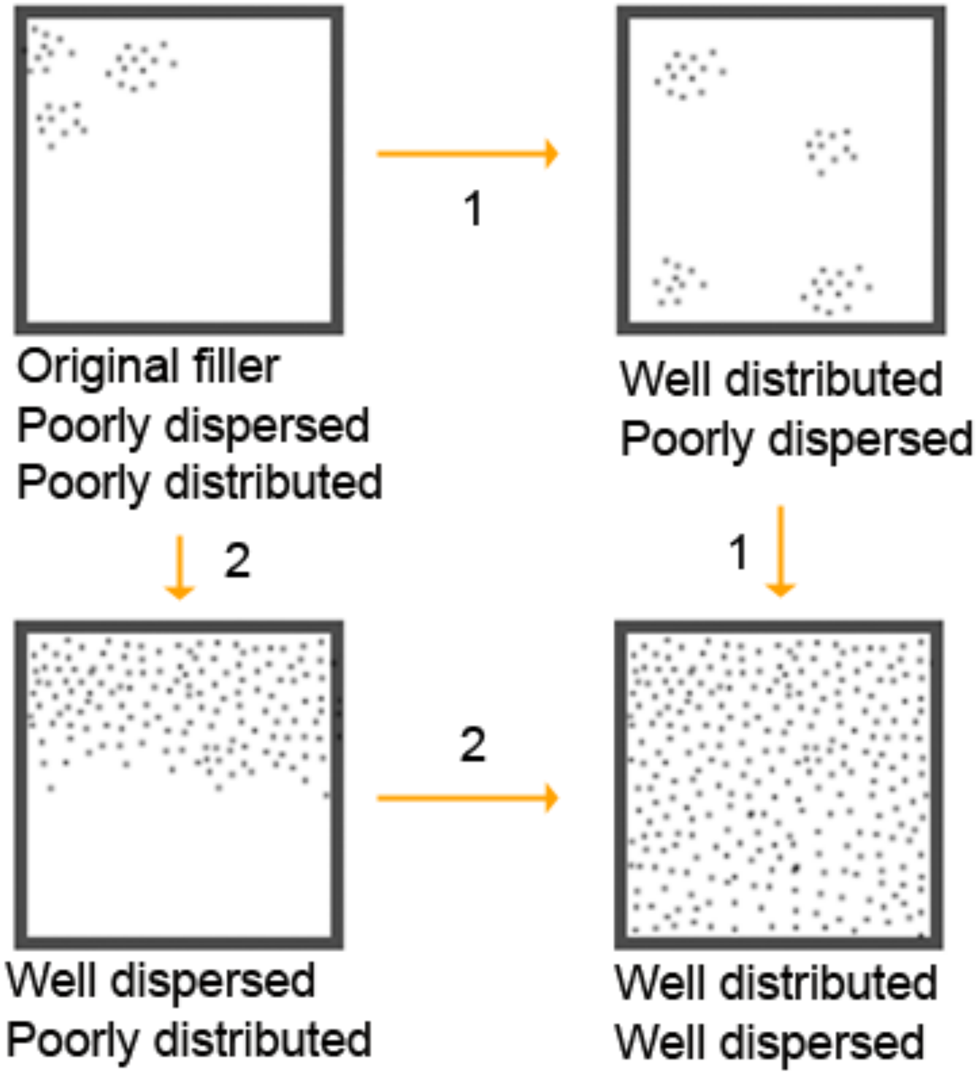
2. Compounding

- Compounding mixing is used when accurate distribution & dispersion of ingredients is required (e.g. in rubber compounding, 4-5 additives have to act together for efficient cross-linking of the rubber)

2. Compounding

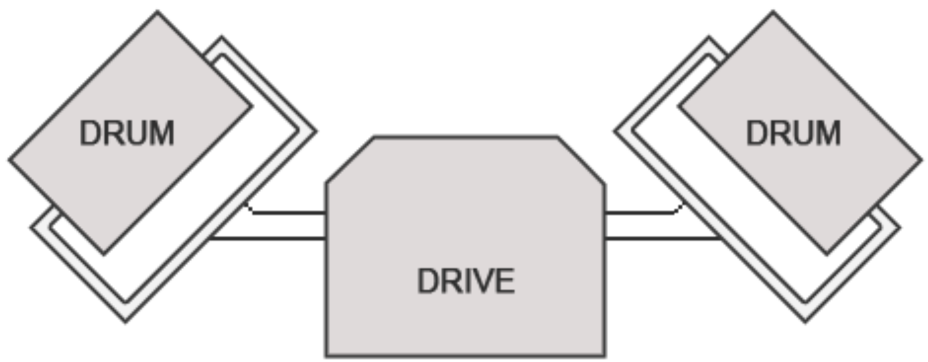
- Involves more intimate dispersion of the additives into the polymeric matrix
- It requires;
  - A physical change in the component
  - High shear force to bring about the change
  - The polymer to be in the molted or rubbery state during mixing

Dispersion vs. Distribution



Some Processes and Machine (Blending)

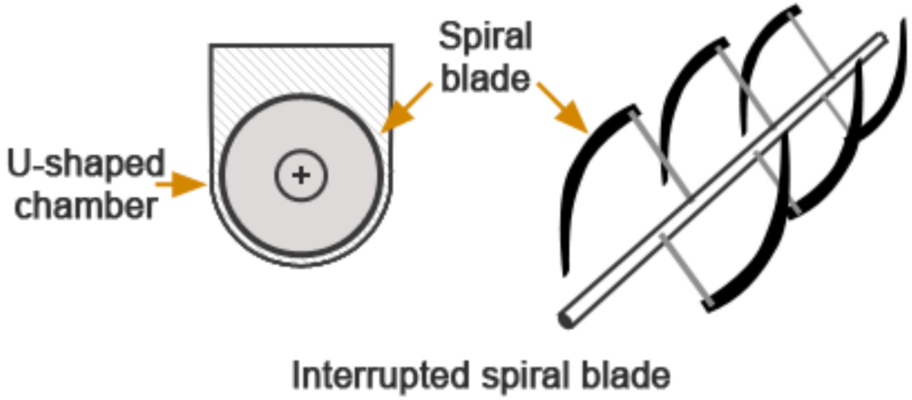
- Vary from the simplest to sophisticated high speed machine
- The simplest- is to tumble together dry ingredients, e.g. using a twin-drum tumbler

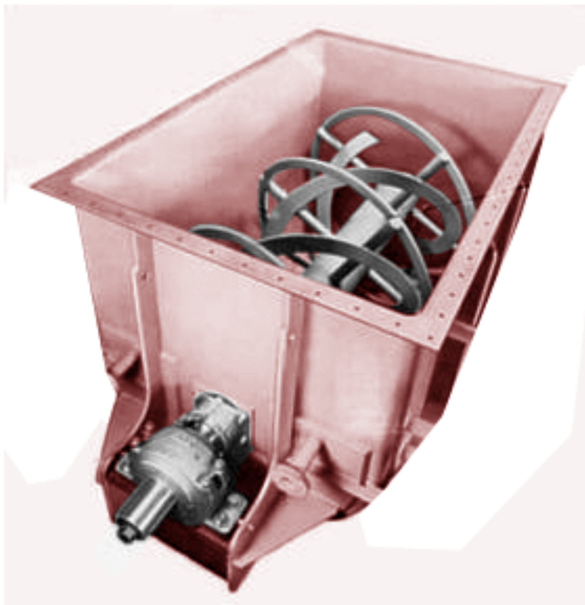


Twin-drum tumbler

Some Processes and Machine (Blending)

- Ribbon-blender
  - A tumbling action takes place
  - The chamber is stationary and the ribbons rotate constantly scooping the material from the outside to the centre



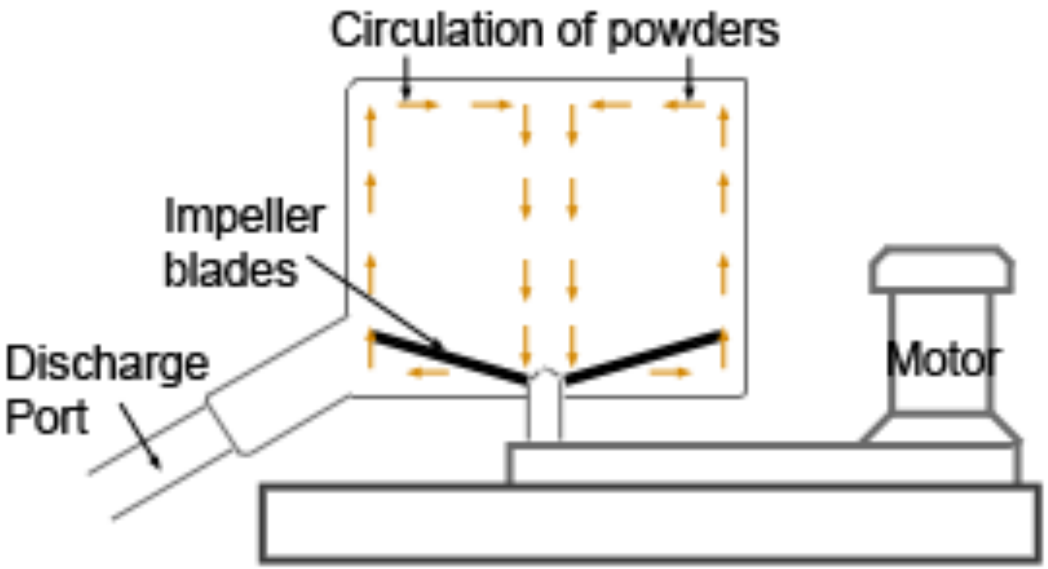


Ribbon blender

Some Processes and Machine (Blending)

- High speed mixer
  - More sophisticated & rapid machine for blending
  - Widely used for PVC dry blends, drying, incorporated pigments, antioxidant, etc.
  - Run at several thousand rpm, and form a circulating powders which becomes heated by friction (150-200ºC)
  - Mixing tank can be single wall or jacketted for temp. control

High Speed Mixer

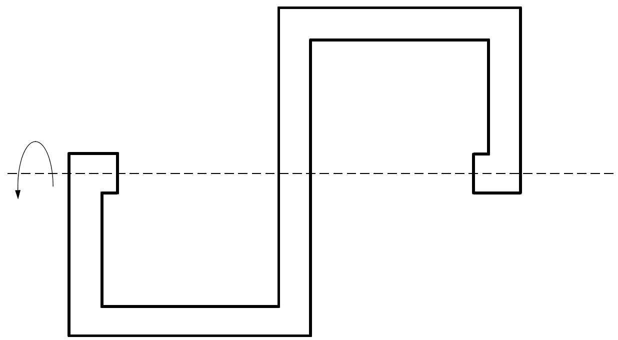


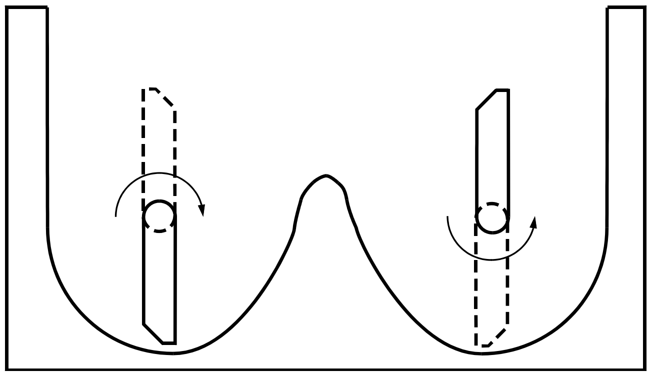
High Speed Mixer

Mixing tank

Some Processes and Machine (Blending)

- Dough Moulding Compound
  - Dough-like blend, e.g. DMC are made in Z-blade (The name comes from the shape of the mixing blade)
  - The mixer itself comprises twin stainless steel bowls in each of which is a mixing blade. The blades rotate in opposite directions (and rarely at different speeds).





Dough Moulding Compound

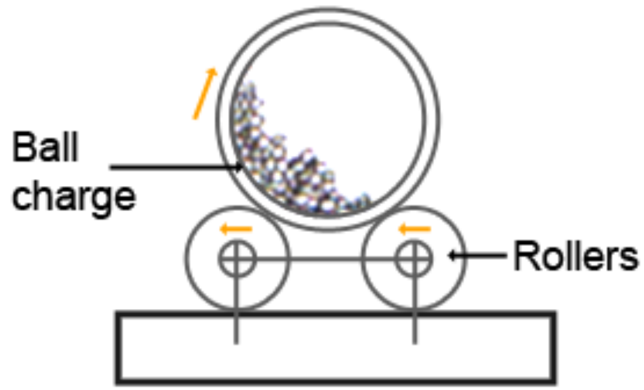
- The powders are charged first and blended for about a minute.
- The resin (containing catalyst) and shrinkage control additive are added and mixing is continued for between 15 and 30 minutes.
- During this time the mixer is stopped occasionally and the walls of the bowl scraped clean.
- Once the slurry is homogeneous the reinforcing fibres are added gradually. These are blended into the slurry until they are just distributed throughout the mix - a time of about 5 minutes, typically.

Component	PHR	Note
Resin	100	High reactivity resin having a maleic : phthalic ratio around 2 : 1 and an alkyd : styrene ratio of about 70 : 30 by weight. The resin viscosity is in the order of 10Pas.
Shrinkage Control Additive	40-65	Also called a low profile additive. The material is a solution of a thermoplastic polymer such as polystyrene, polymethyl methacrylate, polyvinyl acetate or polycaprolactone in styrene. The solution contains about 30% polymer by weight. Used at ratios of 40:60 or 30:70 by weight on the host resin.
Fillers	150–250	General purpose fillers include calcites and dolomites. Effects fillers include alumina trihydrate. The mean particle size of all fillers used in DMC is in the range 5mm-20mm with an oil absorption between 20-30. Exceptionally larger fillers or fillers having higher oil absorptions (up to 45) are used but at relatively lower levels.
Lubricant	3–5	Zinc Stearate, Calcium Stearate
Catalyst	1–2	A relatively stable peroxide having a half-life of a few minutes in the temperature range 100^{o}C - 130^{o}C is used. Commonest materials are t-butyl perbenzoate, peroctoate or dicumyl peroxide. Combinations of peroxides are used to fine-tune the rate of crosslinking.
Pigment	5–10	

Some Processes and Machine (Blending)

- Ball Mill
  - Comprises of cylindrical vessel containing large number of steel or ceramic balls
  - It rotates, the balls tumble inside together with the powder
  - Agglomerates of powder are broken down by the grinding action of the tumbling balls

Ball Mill



Some Processes and Machine (Compounding)

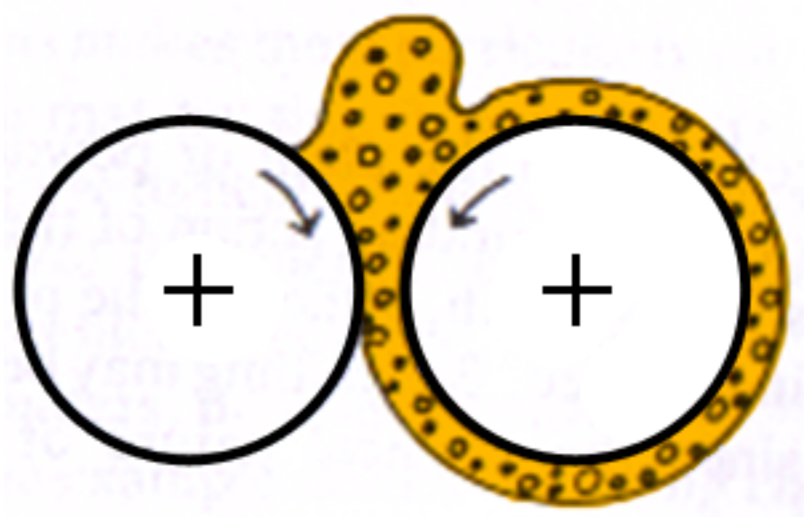
- Involve high shear process & much more powerful machinery
- The simplest technique is two-roll mill

Two-roll mill

- Pair of rollers with a vertical ‘nips’ between them
- The polymer and additives are subjected to high shear in the nip as the rolls rotate in opposite directions
- Two-roll mill mixing started with rubber processing, now exist for various function
- Mixing on two-roll mill is time consuming, 2 h for a 200 kg mix on a 84” wide mill, and depends on the skill of mill operator

Two-roll mill

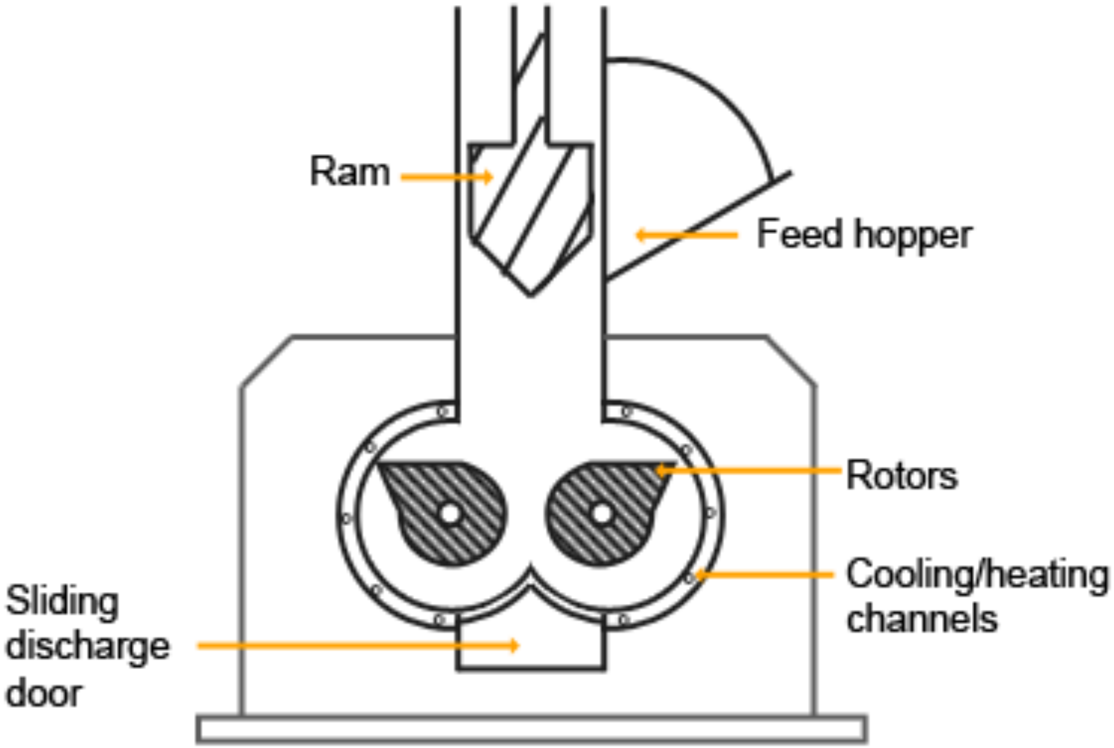
- Schematic illustration of a two-roll mill



Banbury Mixer

- 2 rotors-counter-rotating within a chamber
- Each has two or four ‘blades’ which mix by smearing the materials against the chamber wall
- A weighted ram keeps the mix in place inside the chamber

Banbury Mixer



Banbury Machine	Mill size (in.)	Capacity (kg)
No. 11	84	350
No. 9	84 0r 60	200
No. 3	36	80

Banbury Mixer vs. Two-roll Mill

- The rate of output (200 kg batch of rubber compound would take 2 h- two-roll mill. A number 11 Banbury mixer produce 350 kg in 15 min or less)

Compounding

- Additives used in Thermoplastics (PP, PE, PS, PC, nylon, etc) much smaller proportions compared to rubber.
- Normally polymer resin manufacturer or some specialist compounding companies will produce and supply polymers with appropriate additives.

Forces in Mixing

- How the force transmitted, to break down agglomerates of additive particles?
  - By fluid mechanical stress in the mixer

- Consider two spherical additive particles, radius r1 and r2, the stress is

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

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For the two agglomerate particles

$$a = 3\pi r_1 r_2$$

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

Since $\tau = \eta\dot{\gamma}$

$$F = \eta\dot{\gamma}3\pi r_1 r_2$$

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

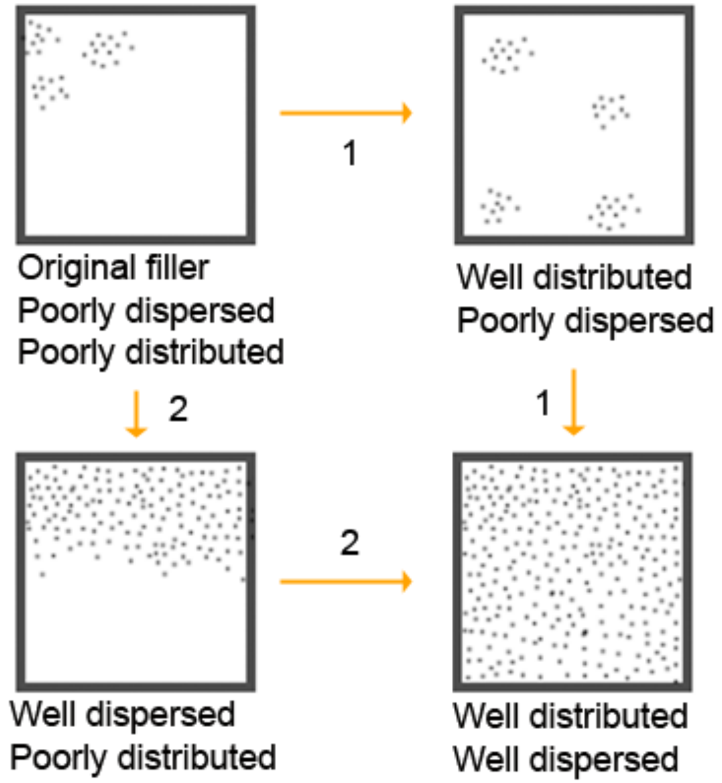
Thus,

$$P = \frac{F^2}{9\pi^2 r_1^2 r_2^2 \eta}$$

Less energy is needed
Under high viscosity conditions
To achieve good dispersion
WHY?

Routes for Mixing

- Route 1: with well distributed but poorly dispersed additive, will entail lower viscosity than route 2.
- Previous equation suggest that Route 1 will require more energy than Route 2



Group Discussions

1. Why distributive mixing is difficult to achieve in melts?

2. For example low viscosity system exhibits turbulent mixing

Turbulent flow in melt?

- The boundary between laminar flow and turbulent flow is described by Reynolds equation

$$Re = \frac{DV\varrho}{\eta}$$

V= velocity of the fluid, ρ= density, η = viscosity, D = diameter of circular channel

- Reynolds Number must exceed 2000 for turbulent flow

Consider a channel where, D = 0.5 cm = 0.005 m, η= 150 Pas, ρ= 1000 kg m^{-3}, and Q = 250 cm^3 s^{-1}

(Q is the amount of materials put through a process / volume throughput)

Find velocity from the volume throughput

$$\pi r^2 = \pi(0.0025)^2 = 1.96x10^{-5}m^2$$

$$V = \frac{Q}{A} = \frac{2.5x10^{-4}}{1.96x10^{-5}} = 12.7ms^{-1}$$

$$Re = \frac{0.005x12.7x1000}{150} = 0.42$$

Low value of Re indicates that turbulent flow Cannot occur in polymer melts.

$$Re = \frac{DV\varrho}{\eta}$$

- Based on Reynold's equation, three viscosity regimes are seen to be;
  - At low viscosity, turbulence results in efficient distribution
  - At high viscosity (as found in polymer melts), turbulence cannot occur & dispersion is poor
  - At very high viscosity (as in rubber), there is sufficient shear to break down agglomerates & efficient distribution and dispersion can occur.

End of Chapter 1

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