The strength of packed particles is dominated by the fractional density. Wetting fluids improve the interparticle cohesion and increase the resistance to shear. The variation in strength with fractional density and particle size can be approximated as:

\[ \sigma = K \times N_c \times \frac{F_c}{D^2} \]

where \( \sigma \) is the tensile strength, \( K \) is a factor dependent on the particle shape, \( \Phi \) is the fractional density, \( N_c \) is the packing coordination, \( F_c \) is the cohesive bond strength between particles, and \( D \) is particle diameter. The fractional density is the ratio of the actual density to the theoretical density. As \( \Phi \) increases, \( \sigma \) also increases (Figure).
A simple technique for deagglomerating a coarse powder is to lightly mill it in a dry atmosphere. The impact breaks apart the agglomerates. Jar mills with balls, cylinders, or rods are appropriate for many powders.

For smaller particles, it is more effective to use surface active agents to induce repulsive forces. Some common additives are polyvinyl alcohol, stearic acid, sodium oleate, glycerine, and oleic acid.

**Particle Site, Shape, and Purity Modifications**

Interparticle friction can arise from irregularities on the particle surface. The greater the surface roughness or the more irregular the particle shape, the lower the packing density and slower the powder flow. The highest density is associated with smooth spherical particles. The use of vibration or lubricants can help to have high packing density. Oxidation of a metal powder is effective in reducing interparticle friction (Figure).
Many impurities are segregated to the surface of a metal powder, reflecting the solidification events and adsorption of contaminants during handling. To avoid carrying these contaminants into the final compact, the surface needs to be removed prior to consolidation. This can be performed using surface chemical or ultrasonic treatments. Oxides can be reduced by heating in hydrogen, dissociated ammonia, or carbon monoxide as a part of an annealing treatment to soften the powder for easier compaction. The addition of a halide (chlorine or fluorine) to the process gas is effective in removing surface films.

Chemical dissolution in acid is not widely employed, but it can result in significant dissolution of the powder surface.

Ultrasonic agitation in a fluid proves effective in removing surface films.
Particle Packing Modifications

Packing Structures: Particle packing is important in most forming processes. Random packing structures are typical of PM processing. While the fractional density is btw 0.60 and 0.64 for monosized spheres, the actual density depends on the powder characteristics such as site and shape, and factors including the adsorbed moisture. For common PM powders the packing density ranges from 30 to 65% of theoretical density; the lower value is representative irregular and sponge powders.

Interparticle friction arises from particle surface irregularities. The greater the surface roughness or more irregular the particle shape, the lower the packing density. For particles of the same size but different shapes, the packing density will decrease as the shape departs from equiaxed (fig.1).

![Bar Chart](image)

fractional density

increasing particle roughness
Figure plots the fractional packing density vs. the length to diameter ratio for fibers, showing that fractional densities as low as 0.10 result from the random packing of fibers. Obviously, packing improves as the particles approach a smooth, equiaxed shape.

**Improved Packing Technique:** To overcome the inherent packing limits of a powder, it is possible to tailor the particle size distribution for a higher packing density.

Bimodal particle blends can pack to higher densities than monosized particles. Small particles are selected to fit the interstices between large particles without forcing the large particles apart. Even smaller particles can be selected to fit into the remaining pores.
The optimum composition in terms of weight fraction of large particles $X^*$ depends on the amount of void space between large particles, which equals $1-\delta_L$, where $\delta_L$ is the fractional packing density of large particles; 

$$X^* = \frac{\delta_L}{\delta^*}$$

with the packing density at the optimal composition, $\delta^*$ given as:

$$\delta^* = \delta_L + \delta_s (1-\delta_L)$$

$\delta_s$: fractional packing density for small particles.

Figure illustrates how the packing density increases with the particle size ratio (large dia./small dia.). Note the dramatic change in behavior at the particle size ratio corresponding to one particle filling the triangular pores between the large particles at roughly a 7:1 size ratio.
The ideas developed for bimodal mixtures can be extended to multimodal systems. At least a 7:1 particle size ratio is needed for optimal packing. For a trimodal packing, that corresponds to a size ratio of 49:7:1.

<table>
<thead>
<tr>
<th># of components</th>
<th>size ratio</th>
<th>weight %</th>
<th>packing fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>100</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>7:1</td>
<td>73:27</td>
<td>0.86</td>
</tr>
<tr>
<td>3</td>
<td>49:7:1</td>
<td>75:14:11</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>343:49:7:1</td>
<td>73:14:10:3</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Mixing and Blending Homogeneous Feedstock:

Mixing and blending are necessary to prepare unique particle size distributions, combine powders to generate new alloys during sintering, add lubricants for compaction, and to prepare a powder-binder mixture for shaping.
A major reason for blending powders is to remove segregation, typically induced by vibration in transport. (larger particles at the top, leading uneven compaction and sintering)

Although there are 3 causes of segregation: (i) difference in particle size, (ii) density, and (iii) shape), size segregation is dominant. For ex, a powder will segregate by size if the small particles can pass through the voids btw the large particles. One consequence of size segregation is that there will be a point-to-point density variation.

The degree of segregation can be calculated; (Cs: segregation coefficient)

\[ C_s = \frac{X_t - X_b}{X_t + X_b} \]

where:
- \( X_t \): fraction of large particles in the top half of container
- \( X_b \): fraction of large particles in the bottom half of container

An irregular particle shape will inhibit size segregation. Likewise, less size segregation occurs with particle sizes below approx. 100µm because of larger interparticle friction.

Some simple rules to prevent segregation:

1) reblend a dry powder after transport.
2) do not vibrate a dry powder.
3) do not feed a dry powder through a free-fall where sizes can segregate.
4) minimize unnecessary shear for a powder-binder mixture.
Dry Powder Mixing: The mechanisms of powder mixing are diffusion, convection, and shear as shown in the figure. Diffusional mixing in a rotating drum, convective mixing in a screw mixer, and shear mixing in a blade mixer.

Most metal powder mixing and blending is performed using rotating containers (figure). The interior of such mixing devices is important in determining the mixing efficiency. Chambers, intensifiers (spinning blades), and dividers are possible internal additions which enhance intermixing.

The volume of powder in the mixer determines the mixing efficiency. As the mixer becomes filled with powder, the relative motion of the powder is inhibited.
A powder volume between 20 and 40% of the mixer capacity is usually optimal as shown in Figure. It shows the rate of mixing vs. the volume of fill and speed for a cylindrical mixer, measured in rotations per minute (RPM). The rotation speed has also a large effect on mixing efficiency. A slow rotation will prolong the time necessary to obtain adequate mixing, but rapid rotation will impart a centrifugal force to the powder which interferes with flow.

The optimal rotational speed $N_0$ (in RPM) for a cylindrical mixer can be estimated as:

$$N_0 = \frac{32}{\sqrt{d}}$$

where $d$ is the drum diameter in meters. Accordingly, a cylinder with a 1-meter-diameter will have an optimal speed of 32 RPM.
Mixing with Binders and Lubricants

Mixing is the first step in the preparation of a powder-binder feedstock for shaping. The quality of the mixture is important, since mixing deficiencies cannot be corrected by subsequent processing. Uniform quantities of the particles and binder are needed in all portions of the mixtures used in PM shaping.

The inhomogeneities in a mixture occur in 2 main forms:

- Separation of the binder from the powder and
- Segregation according to particle size within the binders.

The separation of particles by size (or shape or density) leads to uneven packing densities and distortion of the final product. Small or irregular shaped particles require longer mixing times to attain homogeneity. In the presence of agglomeration, uniform mixing is difficult. Polar molecule coatings on the particles can provide repulsive force to reduce agglomeration and interparticle friction, thereby improving packing. This is most important with submicron particles.
Mixture Homogeneity

The intensity of segregation is measured by the compositional fluctuation from point-to-point. The measure of uniformity can be based on sample density, heat capacity, electrical conductivity, or microscopic examinations.

As shown in the figure, 3 levels of homogeneity exist, ranging from stratified mixtures with large scale segregation, to agglomerated structures with partial homogenization, to the ideal of a dispersed homogenous structure. A mixture homogeneity index is generated based on the variance in powder concentration between samples $S$, the variance anticipated for perfectly mixed but random samples $S_r$, and the variance for the initial segregated mixture $S_0$:

$$ M = (S_0^2 - S^2) / (S_0^2 - S_r^2) $$

where the homogeneity index $M$ varies from 0 to 1.0, unity represents homogeneity/homogenous mixture.
The powder-binder mixture starts as a totally segregated system with an initial variance as follows: 

\[ S^2_0 = X_p (1-X_p) \]

where \( X_p \) is the concentration of the major powder component. The final variance for a fully-mixed, randomly sampled system should approach zero, accordingly \( S^2_r = 0 \). Hence, \( M = 1 - \frac{S^2_r}{S^2_0} \) for the general case.

The initial action is to break apart large clusters of particles by shear. With continued mixing, the cluster size decreases as binder becomes dispersed in the interparticle pores. Empirical examinations of mixing kinetics show that the homogeneity \( M \) initially varies exponentially with time:

\[ M = M_0 + \exp(kt + C) \]

\( M_0 \): initial mixture homogeneity  
\( t \): time

\( C \) and \( k \) are constants for a given situation.

During mixing, simultaneous segregation can lead to a steady-state homogeneity less than ideal. Max. homogeneity occurs when the rate of mixing equals the rate of segregation. Initially, the homogeneity increases rapidly during mixing, but in some cases it can decrease due to segregation in the mixer if the binder has a low viscosity and the powder has a wide size distribution.
Coating, Bonding, and Agglomeration of Powders

Composite Particles: A composite particle has two or more phases present in each particle. They might be coatings, dispersed internal phases, or surface agglomerates. For example, yttrium is vapor coated onto silicon carbide particles and whiskers to prevent chemical interactions during hot consolidation of metal matrix composites. Vapor techniques are also used to put nickel onto graphite particles for use as conductive fillers in gaskets. Fluid bed techniques are useful for vapor coating a powder. Powder is levitated by flowing hot gas containing the coating vapor species. The critical Reynolds number \( R_n = D \rho f \sqrt{V / \eta} \) where \( D \) is particle size, \( \rho f \) is fluid density, \( V \) is fluid velocity, \( \eta \) is fluid viscosity, for achieving fluidization of powder:

\[
R_n = \frac{A \varepsilon_f^3}{(1 - \varepsilon_f)}
\]

\( \varepsilon_f \): fractional porosity of the powder bed at the onset of fluidization (~ 0.4)
A is given as: \( A = D^3 \left( \frac{S_m - S_f}{g} \right) \frac{g}{(150 \pi^2)} \) with \( D \) being the particle size, \( S_f \) the fluid density, \( S_m \) metal density, \( g \) gravitational constant, \( \eta \) fluid viscosity.

Another coating process is electrochemically deposit one metal on the surface of another for alloying during sintering; examples include Cu on W or Cu on Fe.

**Powder Lubrication**

Friction btw the die wall and powder during pressing is a fundamental problem. As the compaction pressure is increased, ejection of the powder mass from the die becomes more difficult. Consequently, lubricants are used to minimize die wear and ease ejection.

There are 2 means of lubricating a pressing; die wall and powder lubrication. Die wall lubrication is preferred in theory, but it is not easy to incorporate into automatic compaction equipment. Thus, lubricants are usually mixed with the powder as a final step before pressing. Typical concentrations are btw 0.5 and 1.5 wt%. 
For metal powders, stearate powders of Al, Zn, Li, Mg or Ca are in common use. The molecular chains contain 12 to 22 carbon atoms, and they are surface active and melt at relatively low temperatures. Common stearate sites are 10 to 30 μm. Properties of some stearates are given below.

<table>
<thead>
<tr>
<th>Name</th>
<th>Oxide</th>
<th>% Oxide</th>
<th>Softening T, °C</th>
<th>Tm °C</th>
<th>Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc stearate</td>
<td>ZnO</td>
<td>14</td>
<td>100 to 120</td>
<td>130</td>
<td>1.09</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>CaO</td>
<td>9</td>
<td>115 to 120</td>
<td>160</td>
<td>1.03</td>
</tr>
<tr>
<td>Lithium stearate</td>
<td>Li₂O</td>
<td>5</td>
<td>195 to 200</td>
<td>220</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Besides stearates, other lubricants include waxes and cellulose additives.

During deformation, the lubricant forms a fluid that lowers friction by creating a thick film of high viscosity polymer. Low viscosity fluids are not effective since they will be forced away from the friction points by the high pressures used in powder compaction.
Some of the effects of lubrication are shown below.

- Flow time, s
  - lithium stearate
    - wt.% 0.50
    - wt.% 0.75
    - wt.% 1.00
  - stainless steel

- Green density, g/cm³
  - compaction pressure, MPa
    - 828
    - 414
    - 207
  - sponge iron

- Ejection pressure, MPa
  - sponge iron
  - compaction pressure, MPa
    - 828
    - 414
    - 207

- Weight % zinc stearate
  - Apparent density, g/cm³
    - lithium stearate
      - wt.% 0.50
      - wt.% 0.75
      - wt.% 1.00
    - stainless steel
  - 60 vol. %, 50 RPM
  - mixing time, min.

- Weight % zinc stearate
  - 0.50
  - 0.75
  - 1.00

- Mixing time, min.
  - 0
  - 20
  - 40
  - 60
Powder Agglomeration

The small, hard particles such as the ceramics (e.g., Alumina), intermetallics (NiAl), refractory metals (W and Mo), and other compounds (WC, TiB₂), are not free flowing and have low apparent densities. Such powders prove difficult to press. Furthermore, the high inter-particle friction of these fine powders makes handling difficult. Consequently, large agglomerates are formed to aid flow. The powder is mixed with an organic and a volatile agent to form a slurry. The slurry is sprayed or centrifugally atomized into heated free-fall chamber where surface tension forms spherical agglomerates.

Heating during free-fall causes vaporization of the volatile agent, giving a hard, dense-packed agglomerate. Water-based solutions with PVA, cellulose, or PEG are common agglomeration mixtures. The typical agglomerate size is 200 μm.
Shaping and Compaction

Most applications for PM dictate high densities in the final product. Powder densification can be achieved through one of three methods; (i) sinter densify a low density preform; (ii) press to a high density followed by sintering, or (iii) simultaneously press and sinter.

 Powders that exhibit good sintering densificaion can be shaped using low pressures, often with the aid of an organic binder. Injection molding is an example of that process. Compaction relies on an external source for deforming the powders into a high density component.

 In shaping, binders are used to hold particles in place for transport with subsequent densification in a sintering furnace. There are several forming methods like injection molding, tape casting, slip casting, pressure filtration, extrusion.
**Injection Molding**

Powder Injection Molding (PIM) builds on the shaping flexibility, but relies on a high particle content to form complex metallic shapes. The key steps are shown in Figure. Process begins by mixing selected powders and binders. The particles are small to aid in sintering densification, and often have average sizes below 20 μm with near spherical shapes. The binders are thermoplastic mixtures of waxes, polymers, oils, lubricants and surfactants.

The powder-binder mixture is granulated and injection molded into the desired shape. After molding, the binder is removed and the remaining powder structure sintered.
A cross-section through a typical molding operation and a conceptual outline of the molding sequence is shown below.
Formulation of a Powder-Binder Mixture

Small particles are used to aid sintom and densification. Carbonyl oxide reduced, and gas atomized powders with near spherical shapes and mean particle sizes between 0.5 to 15 μm are typical. A typical binder is composed of 70% paraffin wax and 30% polypropylene, with appropriate lubricants or wetting agents to provide binder adhesion to the powder. The binder is fully molten at ~150°C. The amount of binder tends to range near 40 vol% of the mixture, depending on the powder characteristics; for steel that corresponds to ~6 wt.% binder.

Sufficient binder is needed to fill all interparticle voids and to lubricate particle sliding during molding. Best molding success is attained with mixture viscosities below 100 Pa.s. That viscosity depends on the inherent binder viscosity, as well as the mixture temperature, shear rate, solid contact, and the type of surface wetting agents.
The viscosity of the mixture $\eta_m$ varies with the powder contact $\Phi$, also termed the solids loading, and basic binder viscosity $\eta_b$ as follows:

$$\eta_m = \eta_b \left(1 - \frac{\Phi}{\Phi_c}\right)^{-2}$$

where $\Phi_c$ is the critical solids loading which is often close to the tap density for the powder.

At high solids loadings near the critical level, the viscosity undergoes a large change (figure). At the critical solids loading the particles are in point contact with no lubricating binder layer.
Shaping Process

The mixture is heated in the barrel of the molding machine (actually an extruder) to temperatures btw 130 and 190°C. The actual molding impact occurs with a forward pushing of the screw in the barrel to inject a preset volume of molten feedstock into the die. The feedstock flows from the nozzle at the end of the barrel through the sprue, runner, and gate prior to filling the die cavity (figure). The tooling is cooler than the feedstock, thus there is a progressive viscosity increase during mold filling cycle. The increasing flow resistance during mold filling requires a pressure increase until the cavity is filled.
The actual molding pressures are dependent on the die geometry, binder, and powder characteristics, but may be as high as 60 MPa.

The mass flow rate in mold filling \( \dot{Q} \) depends on the applied pressure \( P \) and mixture viscosity \( \eta_m \) as follows: \( \dot{Q} = \frac{P}{(\eta_m K)} \) where flow resistance \( K \) depends on the mold geometry.

For a cylindrical shape; \( K = \frac{128 L}{(\pi d^4)} \) where \( L \) is the length and \( d \) is the diameter.

For a rectangle of width \( W \) and thickness \( t \), \( K = \frac{L}{(W t^3)} \)

* Small diameters or thicknesses pose the greatest difficulty in mold filling. Successful molding requires high pressures or low viscosities. The molding machine limits available pressure, and temperature governs the viscosity. Consequently, temperature and pressure provide the primary control parameters in molding.
After molding, the binder is removed from the compact by a process termed debinding. There are several options for debinding, including thermal, solvent, and capillary extraction methods. For metals, thermal debinding is used frequently, where the compact is heated slowly to 600°C in air to decompose the binder and oxidize the particles. The oxidation process provides handling strength to the compact before sintering.

An alternative is to immerse the compact in a solvent that dissolves one of the binder constituents, leaving some polymer behind to hold the particles in place.

The next step is sintering, which can be incorporated directly into the debinding cycle. Sintering provides strong interparticle bonds and removes the void space by densification.
Other Binder Assisted Processing

Slurry Techniques: Large shapes are formed using slurry techniques in which the molding pressures are low. That is why many PIM components are relatively small. Tape casting and extrusion are used to generate homogeneous log, thin structures such as filter tubes, and catalytic substrates; product size and shape influence process selection.

Many of the characteristics of the binder and powder are the same as those encountered in PIM. Further, after molding, the debinding and sintering steps are essentially the same as for PIM.

In slip casting, small particles are dispersed in a low viscosity binder composed of water and a gelation component. The powder-water-binder mixture is poured into a porous mold. To maintain a low viscosity in the mixture, the binder is selected to have an inherently low viscosity and the solids loading in the slip is far below that encountered in PIM.
By using a porous mold, the binder is adsorbed by capillary action into the pores and the viscosity of the mixture increases. A typical porous mold is formed from plaster of Paris (hydrated calcium sulfate), with pores of approx. 0.1 μm size. After drying, the compact is removed from the mold and sintered. The drying step can take several days for large compacts.

Slip casting is slow, but the tooling is inexpensive and the final compacts can be relatively large. A mixture of water, alginate, and surfactants is a typical binder. Other binder systems rely on water solutions of cellulose or polyvinyl alcohol (PVA), or on polymers dissolved in common solvents.

All of those binders include surface active agents to keep the particles dispersed and deagglomerated. In the water-based systems, the acidity is controlled to minimize the slip viscosity. A target viscosity for the mixture during molding is 10 Pa·s.
Variations on the slip casting approach include pressure filtration, freeze casting, centrifugal casting, and tape casting. In tape casting, the powder-binder or slurry is fed onto a moving paper or plastic sheet that passes through a controlled opening. A blade (or blade) levels the slurry to form a continuous thin sheet. Subsequently, one constituent of the binder is evaporated, leaving bands of binder behind to provide strength during separation of the tape from the substrate before sintering. Binders for tape casting are acrylics, waxes, polyvinyl alcohol, and polyvinyl butyral. Dispersants are a key to minimizing powder agglomeration in all of these slurry forming processes.

**Extrusion**

Extrusion is most appropriate method for generating long, thin structures such as tubes and rods. The powder-binder mixture is placed in a plunger or screw type extruder equipped with a sized nozzle. The mixture is forced under pressure through the nozzle, giving a long and constant-cross section product.