## Chapter 12

# Dispersion of Small Particles in Plastics

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## Introduction

The incorporation of small particles into thermoplastics is non-trivial, both in concept and in practice. Conceptually, there are certain similarities between dispersing particles in molten plastics and dispersing cocoa powder into milk to make chocolate milk, a process familiar to many [1]. In the latter process, solid fat particles (cocoa) must be suspended in water. Because the hydrophobic surfaces of the fat particles are incompatible with the polar water molecules, these particles are not wetted by the water and water does not penetrate into the gaps within particle agglomerates. This results in the initial formation of large powder pockets or capsules that, though wetted on their exterior, are completely dry in their interior.

Stirring the mixture with a spoon will eventually break the capsules apart, producing individual particles that are then dispersed throughout the liquid. Capsule disruption can be difficult when the concentration of the capsules is small—stirring simply moves the capsules through the milk without breaking them apart. However, at higher concentrations, the capsules collide with and experience shear from one

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another, which disintegrates them into individual particles. Wetting and dispersion can be accelerated by smearing a capsule that is trapped between the spoon and cup wall. This efficiently generates a region of high shear within the capsule. The application of these factors to the dispersion of particles into liquid paints was discussed in Chap. 11.

The dispersion of particles in plastics is similar. In this case, however, it is the particles that are often hydrophilic and the liquid phase that is hydrophobic. However, the effect of this incompatibility on dispersion is the same. Particles tend to form relatively large capsules that resist infiltration by the liquid. At low concentrations, the addition of mechanical energy results primarily in the mixing of intact capsules, rather than in their disintegration. Regions or zones of high shear can be highly effective at breaking the capsules apart.

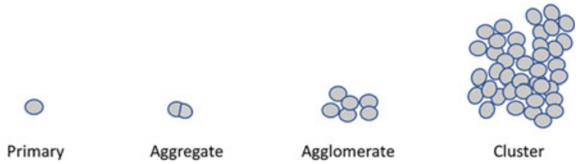
While wetting and separation are critical to particle dispersion in both polymer melts and liquid paints, there are some aspects of dispersion that are unique to each situation. One is that particles dispersed in liquid paints must be stabilized against flocculation, while those in a thermoplastic are frozen in place once the plastic solidifies. A second is that for thermoplastics the liquid medium must be created as part of the dispersion process through heat melting. For optimum efficiency, both in terms of energy and time, the transformation of mechanical energy must be properly balanced between the melting and dispersion processes.

## Particle–Particle Attractive Forces

The degree of particle dispersion of particles within a polymer can have a large effect on many optical, physical, and mechanical properties of the polymer. Pockets of undispersed filler particles such as calcium carbonate, can concentrate stress weak points that are exposed as the polymer matrix experiences mechanical forces (e.g., stretching, twisting, pinching, compression, etc.). Their presence leads to poor tensile and impact strengths, resulting in the polymer becoming brittle and prone to shattering. Poorly dispersed white or color pigment particles interact inefficiently with light. This leads to the need for greater particle concentrations to achieve the same appearance effect as is seen for well-dispersed pigment particles. Finally, surface appearance properties such as gloss and distinctness of image, as well as opacity and durability against ultraviolet radiation, are all degraded by poor particle dispersion.

As was the case with the particle groups encountered in dispersion into liquid paints, it is convenient to classify those encountered in dispersion into molten polymer based on their size and the strength of the forces holding these groups together. The smallest unit of these groups is the individual, or primary particles (see Fig. 12.1). Aggregates are small groups of primary particles that are held together so strongly that they are not separated during the dispersion process. This is most commonly seen with inorganic particles that are formed at high temperatures. Agglomerates, too, are relatively small groups of primary particles, but in this case, the bonds between the particles are weak enough to be broken during dispersion. Finally, clusters are very

**Fig. 12.1** Particle groups relevant to dispersion in polymer melts



large groups of particles that are weakly held together. These are analogous to flocculates that form when particles in liquid paints are inadequately stabilized. Because they are so large and held together so weakly, clusters are the most susceptible of the particle groups to disintegration by shear forces.

Note that the distinction between aggregates and agglomerates is not absolute. Instead, it depends on the type of disperser and the time (and energy) spent on the dispersion process. That is, some particle groups will attrit (break apart into smaller sizes) under some dispersion conditions but not under others. Obviously, the intent of any dispersion process should be to break apart as many small groups of particles into even smaller groups. Since most particle size measurements quantify the size of the particle groups, this is equivalent to saying that the dispersion process should produce the smallest average particle size, and the narrowest size distribution, that is possible.

Note also that there is no sharp delineation between agglomerate and cluster. This is, instead, a matter of definition. However, we can generalize by saying that agglomerates are groups of no more than a few tens of primary particles, while clusters can contain many thousands of primary particles. Solid particles are to be dispersed as primaries within a thermoplastic, but they usually start in a cluster or agglomerate structure in the dry powder form. The dispersion process converts the dry agglomerates into wet primaries and aggregates.

The dispersion process involves two distinct phases. First, the particle size is reduced to the greatest extent possible, moving from right to left in Fig. 12.1. Next, the particles must be distributed as uniformly as possible throughout the polymer matrix.

The dispersion process can involve three means of cluster and agglomerate size reduction. These are erosion, rupture, and shattering (Fig. 12.2). Erosion is the gradual shearing of small fragments from the surface regions of clusters or agglomerates. These fragments are typically no larger than 10% of the original cluster [2]. Rupture is the splitting of clusters or agglomerates into fragments of comparable size to one another. Shattering is the separation of agglomerates and clusters into their constituent components in a single event or collision.

The main differences between the three processes are the number of events needed for the complete disintegration of the initial cluster and the amount of energy required for each event. A shattering event is the most energetic of the three, but it results in the most size reduction. Erosion and rupture are more gradual processes requiring many more events and greater times than shattering.

Besides the energy and time differences between these means of attrition, the intermediate particle size distributions resulting from each are different. Erosion leads

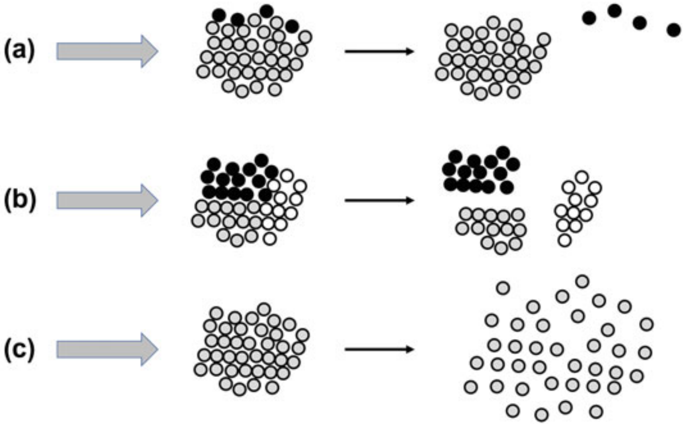


**Fig. 12.2** Disruption of agglomerates. Gray arrows denote force on the agglomerate. Particles are shaded for identification purposes only and are otherwise identical. **a** Erosion. **b** Rupture. **c** Shattering

to a bimodal distribution consisting of individual particles or small agglomerates, [2] which grow in number over time, and agglomerates or clusters, which reduce in size and number over time. Rupture leads to a monomodal distribution that shifts to lower sizes over time. This distribution can be described by a power law equation (Eq. 12.1) [3].

$$Y = kX^{\alpha} \tag{12.1}$$

where

Y is the fraction of particles with a certain diameter,

X is that diameter, and

k and $\alpha$ are constants.

The energy required to fragment clusters and agglomerates and to provide dispersive and distributive mixing must have a source. Compressive loads are the most common means for dispersive mixing. Particle–particle collisions and particle–wall impacts are examples of these compressive loads. Additional forces, such as those of a hydrodynamic nature, provide another source of energy for agglomerate fragmentation in thermoplastic dispersions. These forces are of a shear, rather than impact, nature. The magnitude of hydrodynamic forces is determined by the viscous shear stress.

For shear grinding, the ease with which particles will disperse is determined by the balance of the shear forces pulling them apart (the viscous shear stress) and the attractive forces holding them together (typically van der Waals forces). This balance is quantified by the fragmentation constant, $F_a$, which is simply the ratio of the two forces [4]. For agglomerate disruption to occur, the viscous shear force must be greater than the cohesive strength of the particles within the agglomerate, i.e., $F_a$ must be greater than unity.

Cohesive strength is not an absolute property of a material, such as melting point or color, but instead varies depending on the internal structure or packing of the particles, the density of the packing, and the interparticle attractions due to electrostatic charges, van der Waals forces or capillary forces arising from moisture condensed between the particles [5–8]. In most agglomerates, the cohesive force is dominated by van der Waals attractions. In this case, the particle–particle interactions can be described by the Hamaker constant, H [9]. The cohesive strength between particles can be calculated as the ratio of the Hamaker constant between two surfaces with a certain particle radius, at a defined separation distance, and with a defined solids volume fraction as shown in Eq. 12.2.

$$S_c = \frac{H}{a \bullet z^2 \bullet \rho} \tag{12.2}$$

where

$S_c$ is the cohesive strength,

H is the Hamaker constant,

a is the radius of the primary particle,

z is the equilibrium separation distance between the two-particle surfaces, and

$\rho$ is the solids volume fraction.

Reduction of the Hamaker constant is an effective means of decreasing interparticle cohesive strength and reducing the energy needed to grind agglomerates. The Hamaker constant can be reduced by decreasing the polarity of the particle surfaces [10]. This is typically done by coating the particles with a dispersing aid (see also Chap. 11) [11, 12]. Organic surface treatments are commonly used for this purpose, [13, 14] although the inorganic surface treatments applied to $TiO_2$ particles also enhance dispersibility (Chap. 7). The organic surface treatments are not to be confused with surface treatments for adhesion promotion [15]. Although the latter type of surface modification can supply "wet-in" capabilities, their primary functions are to protect solid particles, especially those with a non-unity aspect ratio, from fracture during processing, and to strengthen the adhesive bond at the solid particle–matrix interface (see also Chap. 9).

Particle dispersion into a plastic occurs through a well-defined sequence of steps, with some steps involving a number of stages. We will discuss these steps in order, beginning with the dry blending of the solid ingredients.

## Dry Blending

The first step in particle dispersion is to intimately mix the powder particles with polymer pellets, a process known as dry blending. When done properly, dry blending reduces dispersion time and energy; the more intimate this mixing, the greater the reduction of the magnitude of these process parameters.

In addition to simply bringing the different components together, dry blending can reduce the size and number of large particle clusters. These clusters form during powder handling prior to use (e.g., pneumatic conveying, screw conveying, intentional compression to increase bulk density, subjection to a load, etc.) and are dependent on the nature of the particles themselves (e.g., particle size, surface area, geometry, surface polarity, etc.) [16–19]. This nature is often described by non-technical but very descriptive terms such as "clumpy", "lumpy", "chunky" or "dusty".

Cluster formation and growth can occur when the powder is subjected to relatively low intensity agitation. Under these conditions, agglomerates that collide have insufficient energy to attrit one another. Instead, the collision process brings agglomerate surfaces into close contact. When the attractive forces between particles on different agglomerates are strong enough, the agglomerates themselves agglomerate, forming large clusters. Similarly, if an agglomerate encounters a single particle, this particle can be incorporated into the agglomerate (Fig. 12.3). These clusters can grow further by settling under gravity (Fig. 12.4).

In addition to cluster formation during handling, clusters can also form during dry blending [20]. Since the ultimate goal of dispersion is to completely disintegrate agglomerates and clusters, care should be taken to avoid this. One means for doing this is to provide sufficient shear during dry blending, especially if the subsequent

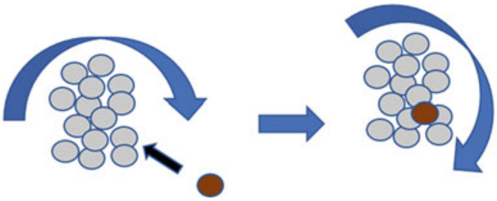


**Fig. 12.3** Growth of an agglomerate during low intensity mixing

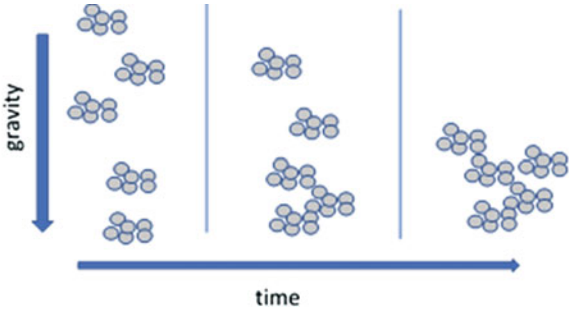


**Fig. 12.4** Cluster formation during powder settling

processing step is “flood feeding”. Flood feeding is when the feed hopper sits atop the compounder’s mouth and feeds the dry blend into the compounding equipment—that is, the compounding equipment regulates the feed rate. Here adequate mixing of the solids in the dry blend step is critical, particularly for downstream compounding processes that function by melting and pumping the polymer into a die with minimal mixing and devolatilization.

Minimization of agglomerate and cluster growth during dry blending can also be addressed by adding various materials during this process. The solid particles are often combined with dispersants (typically fatty acid/glycerol derivatives), other additives (typically phenolic-based anti-oxidants), and polymers during dry blending. Dispersants moderate the stickiness of solid particles and can reduce static charges that bind the agglomerates together. Other additives are mixed into the solids at this time to assure thermal stability in the subsequent processing steps, which involve melting and shearing the compound components.

Certain particles in the dry blends can stick to equipment. Friction on the wall surfaces, such as the hopper walls, varies with the solid additive as well as the roughness and frictional coefficient of both the solid and wall surfaces. In addition, some particles cannot be introduced in dry blending due to their sensitivity to processing. In particular, hollow glass microspheres, alumina flakes, and carbon or glass fibers are not recommended for dry blending as excessive shear stress can result in significant damage to the particles and a resulting loss of functionality. Finally, consideration must be given to particles with high densities, such as metallic fillers, as these can segregate in the dry blend based on their weight.

Dry blending is crucial for many plastics processes, but it is not an exact science. In general, the dry blend process and equipment must be carefully chosen to be compatible with the needs of a particular set of ingredients. Low shear, low-temperature blenders, such as tumble blenders, V-cone blenders, and ribbon blenders are often used when the formulation has only one type of solid particle and it is present at relatively high concentrations.

High-speed blenders are much more shear intensive and often require cooling to keep the pre-blend mixture below the resin melting point. These blenders are quite common in the polyvinylchloride (PVC) industry, where the dry blend mixture consists of half a dozen or more ingredients. High-speed and high shear blenders are essential for PVC compounding because the PVC resin must be softened with heat during the mixing process. During intensive blending, solid particles are often suspended in a bed of PVC using liquid ingredients (e.g., lubricants, plasticizers, liquid colorants, etc.). After cooling, the free flowing, homogenized PVC pre-blend is ready for the next step in compounding.

## Particle Wetting

As was discussed in the context of paints (Chap. 11), the first step in the dispersion process is wetting. Wetting refers to the replacement of air and other materials, such as moisture, from the particle surfaces and from the voids between them, with the melted thermoplastic resin (Fig. 12.5). This process can be likened to the burning of a candle. Wax that has been melted by the flame soaks into the porous cotton wick, where it provides the fuel needed to sustain the flame. The melted wax represents the polymer resin melt, and the candle wick represents the porous particle agglomerates.

The surface tension of the polymer melt must be lower than the surface energy of the particles in the agglomerate if the polymer melt is to wick between the particles. This condition can be achieved in two ways. First, the polymer melt surface tension can be lowered by using lubricating agents. These are analogous to the wetting agents used in the dispersion of particles into a liquid paint. Second, and more commonly, the particle surfaces can be coated with a treating agent that reduces surface energy. These agents were discussed earlier for $TiO_2$ particles in Chap. 7 and extender particles in Chap. 9.

Intuitively, we might expect the replacement of air in the voids within an agglomerate by molten resin to occur from the outside in. That is, a front of molten resin would uniformly flow through all of the outer voids, into the agglomerate interior, filling the inner voids as it progresses. However, infiltration of the molten resin into the agglomerate proceeds through a different process. This is because the pores connecting the intra-agglomerate voids have a size distribution, and liquid flow through any particular pore will be controlled by the diameter of that pore. In particular, the flow becomes hindered as the pore diameter, or cross-sectional area, decreases.

Rather than flowing uniformly into the agglomerate, the molten resin follows the path of least flow resistance, as indicated by the black line in Fig. 12.6. This is typically through the widest pores, or channels. When the particle surfaces can be

**Fig. 12.5** Wetting of a particulate agglomerate by polymer resin

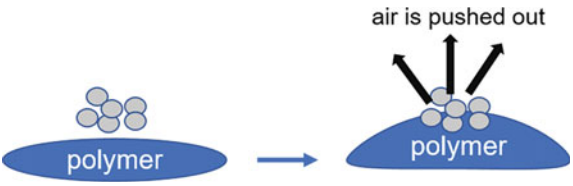
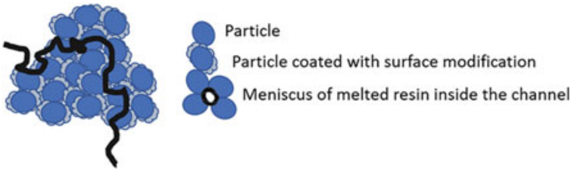


**Fig. 12.6** Flow of molten polymer into a particle agglomerate



wetted by the resin, the gaps between them do not necessarily fill initially. Instead, the resin coats the particle surfaces, and a meniscus is formed at the interface of the molten resin and air remaining within the pore [21].

Once the molten resin has infiltrated the agglomerate through the paths of least resistance, it enters into the narrower, more resistant, pores. This process proceeds primarily from the inside out—that is, resin deep within the agglomerate enters the narrower pores that connect to the larger channels [22]. This resin is replaced by additional resin from outside the agglomerate that travels along the paths of least resistance. This sets up a flow system in which the molten resin is, in effect, pumped into reservoirs within the agglomerate, and then is redistributed from these reservoirs into small pores that reside deep within the agglomerate.

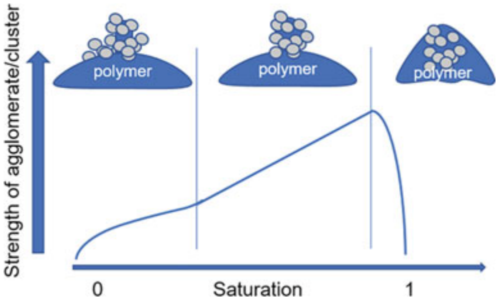
The initial layers of resin on the particle surfaces create cohesive bridges between the particles, and the resulting capillary pressure actually adds to the cohesive strength of the agglomerate [23]. Figure 12.7 shows the strength of an agglomerate with the saturation of the agglomerate voids. Once saturation is reached, the structure collapses as a flood of the polymer flows from the inside to the outside. Agglomerates, therefore, do not break apart during the wetting process, but rather at its conclusion.

Many physical factors affect the facility with which the agglomerates are wetted and the strength of the agglomerates during this process. High polymer melt viscosity increases both the agglomerate strength and the time needed for complete flow into the agglomerate. Particle size and shape also affect the flow rate of the molten polymer.

The effect of particle size can be complex. In general, smaller particles have greater surface areas, and so require more resin to saturate the surface before the voids can be filled. In addition, pore size, up to a point, decreases with decreasing particle size, and this affects the velocity of the molten polymer through the pore.

However, the trend of decreasing pore size with decreasing particle size only applies when the particles pack uniformly. Once a certain size minimum is reached, this trend is reversed because, as was shown in Chap. 1, small particles pack in small groups, these groups pack together into larger groups, and so on. Large pores form between the particle groups. The sizes of these larger pores are consistent with the sizes of the particle groups. In addition, the void volume increases substantially as smaller groups of particles nestle together into large groups, and this results in the need for higher amounts of resin to saturate the agglomerate. Finally, the lower

**Fig. 12.7** Polymer saturation relationship with agglomerate/cluster strength



density of agglomerates of small particles decreases the cohesive strength of the agglomerates, which also affects the time necessary to completely wet the agglomerates. This situation is often encountered with carbon blacks and nanoscale fillers [24].

An additional complication is seen when the wetting process alters either the particle packing structure or the overall size of the agglomerate. This can occur when capillary forces from the molten resin pull the particles closer together. This is seen in clusters of nanoparticles, which are typically diffuse and fragile, and can collapse when wetted. In other situations, the cluster size can be reduced when the exterior of the particle becomes fully wetted and sheds from the partially dry interior. This process can repeat several times, depending on the size and structure of the agglomerate. This slows the kinetics of cluster wetting and has been reported for calcium carbonate clusters of one micron or larger [25].

In general, shear stresses induced in particle structures from the dispersion process are most efficiently transferred throughout these structures when they are completely saturated with molten resin—that is, when they are fully wetted. In the absence of this, both erosion and rupture are inefficient, and extra time and energy is required to disperse the particles into their smallest units.

## Disruption of the Agglomerate Structure Using Shear

We discussed above the necessity of energy for the dispersion process and will now consider the mechanisms by which this energy is applied to and transmitted through particle agglomerates. Recall that energy must be applied both to disperse the particles and to distribute them uniformly throughout the resin mass. These two actions can be considered independently of one another.[1]

Distributive mixing addresses the rearrangement of the mixture through an ordered or random mixing process. The goal of distributive mixing is to spread agglomerates uniformly throughout the polymer melt, but not necessarily to break them apart. In addition, distributive mixing circulates regions of the dispersion mass into, and out of, zones of high shear intensity. Dispersive mixing, on the other hand, involves the rupture and erosion of the agglomerates into their constituent units through the shear that is applied in these zones. This shear must be strong enough to overcome the forces holding the wetted agglomerates together.

The size and nature of these intense shear zones are dependent on the type of dispersion equipment, as will be shown by the example below. Regardless of how these zones are created, however, the conditions within them are similar. Dispersive

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[1] The same consideration occurs in the dispersion of particles into a liquid paint (Chap. 11). In that case the balance between dispersion and mixing is controlled through the relationship between rheology and shear. More specifically, turbulent flow results in mixing while laminar flow results in dispersion.

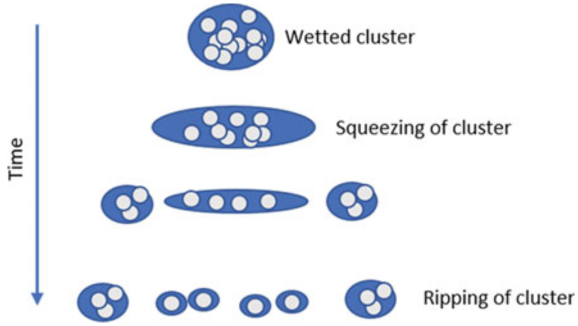


**Fig. 12.8** Squeezing and ripping of wetted clusters during dispersive mixing

mixing proceeds through repeated cycles of compression (squeezing) and rupture (ripping) of wetted clusters and agglomerates, as shown in Fig. 12.8.

There are many varieties of plastic dispersers available commercially [26–28]. The more common ones are listed in Table 12.1, along with their advantages, disadvantages, and recommended applications. For each type, there are several adjustable parameters that can be used to optimize dispersion. These include temperature, residence time, fill level, clearance between mixing elements, etc. In addition to these machine parameters, melt composition will also affect dispersion efficiency. In particular, high concentrations of solid particles will increase melt viscosity, which, in turn, raises the shear stress within the polymer (see Chap. 17).

## Examples of Particle Dispersion into Plastic Resin

Although a wide variety of equipment is used to disperse particles into the molten polymer, there are certain attributes that are common to all. Dispersive mixing and distributive mixing occur at different locations within the equipment, allowing the equipment to be configured (or reconfigured) to match an exact task. In addition, the energy required to melt the polymer is decoupled from the energy required to disperse the particles. Although frictional heat is invariably generated in the dispersion process, this amount of heat does not need to bring the temperature to exactly that which is desired. If higher temperatures are required, heat can be added through an external heater. If excess heat is created in the dispersion process, it can be removed through external coolers in much the same way.

Examples of the operations of three disperser types, a roll mill and an internal batch mixer, both of which operate in batch mode, and a screw extruder, which operates in continuous mode, are given below.

**Table 12.1** Disperser types for melt processing solid particles

| Disperser type | Advantages | Disadvantages | Typical application |
|---|---|---|---|
| Two-roll mill | • Application of shear is extremely efficient<br>• Final material is two-dimensional, i.e., a film sheet | • Successful processing is dependent on the skill of the operator<br>• Limited dispersion efficacy for particles with non-unity aspect ratios (platelets or needles)<br>• Final material is two-dimensional, i.e., a film sheet | • Flexible PVC<br>• Rubber |
| Internal mixer | • Very energy efficient (fewer kW per kg)<br>• Simplified operations<br>• Processes a wide range and combination of ingredients, from pliable to extremely rigid materials, without changes to machine parts as might be required for screw extruders | • Insufficient pressure for extrusion or pelletizing operations<br>• Batch charging and discharging which can affect productivity and product consistency<br>• Precise control of melting and mixing is difficult | • Rubber |
| Continuous mixer | • Very energy efficient (fewer kW per kg)<br>• Less shear compared to twin- screw extruders | • Insufficient pressure for extrusion or pelletizing operations<br>• Higher capital cost compared to screw extruders<br>• Sustaining a starved condition requires balance between orifice setting, rotor speed and temperature controls | • Color concentrates, masterbatches and mineral-filled concentrates |
| Single- screw extruder | • More economical based material of construction<br>• Less shear compared to twin- screw extruders<br>• Operational flexibility for a wide range of different types of materials | • Limited feed performance<br>• Limited capability for dispersive mixing<br>• Lower productivity compared to similarly powered twin-screw extruders, especially under high-pressure conditions | • Melt polymers requiring pressure (e.g., injection/blow molding, cast/blown film) |

(continued)

**Table 12.1** (continued)

| Disperser type | Advantages | Disadvantages | Typical application |
|---|---|---|---|
| Twin screw extruder | • High pumping efficiency<br>• Lower dependence on the flow properties of the material<br>• Higher mixing efficiency<br>• Heat exchange rate from barrel surface to the material is faster and more uniform | • High cost<br>• Heat generated in the barrel is low, requiring external heating of the barrel | • Rigid PVC<br>• Compounding with solid particles |

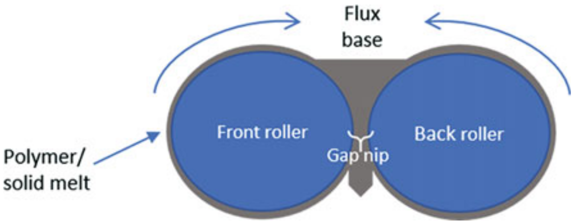
## *Dispersive/Distributive Mixing with a Two-roll Mill*

The two-roll mill is perhaps the simplest disperser. It consists of two heated (or cooled) cylinders (also called drums or rolls) that rotate at high speeds in opposite directions, that is, toward one another (Fig. 12.9). Dispersion occurs in the space between them, termed the nip gap, or simply gap, [29] in a manner similar to the three roll mill discussed in Chap. 11. The gap is the zone of high shear where dispersion takes place. The polymer melt adheres to one of the heated cylinders as a blanket and passes through the gap. In batch processing, the blanket is then rotated back into the gap several times, while in continuous processing, it is separated as a sheet from the roller.

The rotational speeds and the gap clearance are both controlled in this process. Shear rates within the gap are typically adjusted to between $10^2$ and $10^5$ $s^{-1}$. One cylinder is normally rotated at a higher speed than the other. This increases the friction that the melt experiences, and higher rotational speed differences give greater melt heating. The ratio of the peripheral speeds is referred to as the friction ratio, and a typical value would be 1:1.25.

The mix of polymer melt and solid particles is referred to as the flux. The viscosity of this flux is low enough to allow for flow when pressure is applied to it. As the flux enters the gap, the high shear rips it apart. During passage through the gap, the flux is squeezed. Mixing is accomplished through a lateral cross motion or a folding motion. This reduces the formation of streaks within the flux. Two-roll milling is a highly

**Fig. 12.9** Operation of a two-roll mill



effective means of dispersing solid particles since the shear rate can be controlled over a wide range of values [30, 31].

## *Dispersive/Distributive Mixing with an Internal Batch Mixer*

The second disperser that we will discuss is the internal batch mixer, which is the oldest mixing device used for polymers and dates back to the 1820s [32]. As was true for the two-roll mill, these devices disperse particles into the resin by passing the mix through a zone of high shear. The internal batch mixer operates by the addition of a blend of the polymer and solid particles into a heated mixing chamber. Two parallel, cylindrical blades in this chamber rotate at fixed speeds (usually slightly different from one another), while the power to the blade rotors is monitored. A typical curve of power as a function of time is shown in Fig. 12.10 [33].

The consistency of the polymer changes during processing, proceeding through four phases:

(1) Freshly introduced solid pellets
(2) De-formable solid pellets
(3) Flux (i.e., a dough-like suspension of solid particles in resin)
(4) Viscoelastic fluid

The progression of these phases and their relationship to the power curve are shown in Fig. 12.11.

**Fig. 12.10** Evolution of power over time in an internal batch mixer

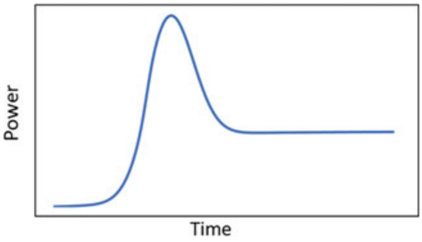
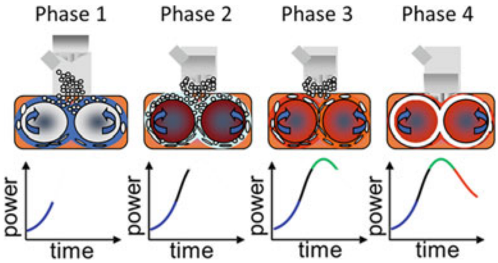


**Fig. 12.11** Progression of phases in the internal batch mixer



In the first phase, the ingredients are placed in the chamber with blades rotating. The ingredients are pushed into the chamber with a piston ram. Pressure from this piston squeezes the resin pellets, increasing the power needed to maintain a constant rotor speed. In the second phase, compression of the resin pellets is complete, and the temperature begins to increase.

Next, the polymer pellets deform, and dispersive mixing reaches its peak. In the third phase, the combination of pressure and heat causes the resin to soften. This lowers the viscosity of the mixture, which, in turn, decreases the power required to turn the rotors. At this point, the resin is completely melted and the flux of resin and solid particles is distributed throughout the chamber. Finally, in the fourth phase, the solid particles are dispersed within the flux. At the completion of this process, the melt is typically discharged into a two-roll mill or a screw extruder for further cooling and to convert the solidified material into the desired form (sheets, pellets or chunks).

Figure 12.12 shows the interplay of squeezing and ripping over the course of this process. During the initial squeezing, the solid particles embed themselves into the polymer pellets. The extent of this embedding is dependent on particle hardness. Continued application of pressure causes the softened pellets to deform. As the heat and pressure build, the lower melting point material will flow into the particle agglomerates and clusters, wetting them and forming capillary bridges with other resin pellets. The capillary bridges are then pulled apart by mechanical forces, creating smaller agglomerates that then repeat the process.

Dispersive mixing occurs in the internal batch mixer as the thermoplastic resin melts, completely or partially, and passes through the nip region of the disperser (Fig. 12.13). In this process, the nip region is the clearance between the chamber wall and rotor tip. In Fig. 12.13, as the mix of polymer and solid powder is squeezed by the clockwise rotation of the rotor, it becomes deformed. As the wetted agglomerates pass through the nip, they are pulled apart.

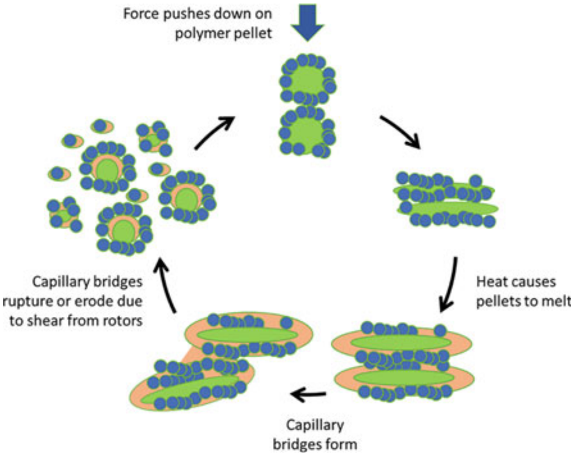


**Fig. 12.12** The cycle of squeezing resin (green) and solid particles (blue) into flux, followed by shearing the flux

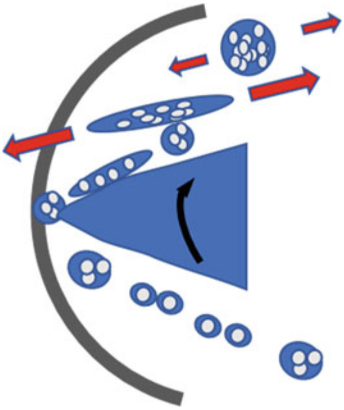


**Fig. 12.13** Nip region between the blade and wall of an internal batch mixer

After passing through the nip, the unmelted polymer is added to the flux and the process is repeated during the next rotational cycle. This sequence of squeezing and ripping provides the dispersive mixing required for compounding. Simultaneous with this dispersive mixing, distributive mixing occurs as the wetted particle agglomerate moves from one side of the chamber to the other. During this time, the consistency (viscosity) of the flux changes, with a concomitant change in the power draw of the rotors.

The shape of the rotor blades and their orientation with respect to one another ensures that all fluid particles undergo highly intensive shear forces (dispersive mixing) in the nip region [34]. The flow patterns between the rotors promote efficient laminar (distributive) mixing [35]. Figure 12.14 shows the rotors turning in the chamber as they stir the mixture of polymer and particles. The red dots show the highest-pressure zone, which is immediately in front of the face of the rotating blade. The pale blue regions in this figure represent the volume occupied by the mixture of resin and particles, and the dark blue regions represent the chamber walls and the piston ram.

The pressure within the high-pressure zones (the red dots in Fig. 12.14) depends on the blade orientation, and so changes during rotation. The greatest pressure occurs when the blades sweep past the inner wall of the chamber. This is seen in Fig. 12.14 for the left rotor in positions 3 and 4 and for the right rotor in positions 1 and 2. As

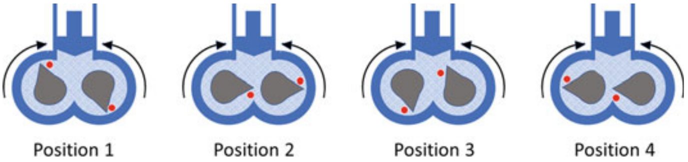


**Fig. 12.14** Side on view of internal batch mixer rotors during rotation

the red dots move into the intersection zone of the two-chamber sections, distributive mixing occurs as material is exchanged between the two rotors.

Although they are configured differently, the underlying principles of the two-roll mill and the internal batch mixer are similar. Both dispersers operate by repeatedly passing the mixture of resin and particles through regions of high shear stress, followed by intimately mixing the sheared material. The two operations differ in the location of the high shear zone (the nip). In the two-roll mill, the nip is located between the rotating drums, while in the internal batch mixer, the high shear zone is the small clearance between the rotors and the chamber wall.

Because of torque and heat transfer limitations in the internal mixer, only a small portion of the compound is subjected to high stress at any given time. However, the overall rotor configuration ensures that the entire compound mixes freely between the high stress regions, since during the rotation, one rotor blade pushes material across the intersection zone and into the path of the other rotor blade. In a two-roll mill, mixing of this kind is accomplished by manually cutting the melt off the roller and then placing the cut sections into the feed.

## *Dispersive/Distributive Mixing with a Single-Screw Extruder*

Both the two-roll mill and internal batch mixers operate in batch mode, meaning that a set quantity of material is charged into the disperser, the disperser runs to the desired degree of dispersion, and the material is discharged, leaving the disperser ready to accept a new charge. Plastics can also be dispersed in a continuous process that involves the screw conveyance of the material through a tube, or barrel, with the mixing and dispersive steps occurring in different regions of the barrel. The dispersed material, still in the molten state, is then extruded through a die for further processing.

Both single-screw and twin-screw extruders are quite common in the plastics industry. As the names imply, these differ in the number of screws used. In the twin-screw extruder, screws are placed parallel to one another, with their flights either inter-meshed or not, and rotated either concurrently or counter-currently. In the simpler single-screw extruder, a single screw with a tapered shaft is employed.

The principles of screw extrusion can be demonstrated with a single-screw extruder, with the understanding that the operations of a twin-screw extruder are more complex and have more ability to be modified for different materials. A schematic of a typical single-screw extruder is shown in Fig. 12.15. The extruder consists of

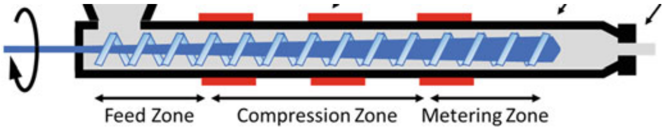


**Fig. 12.15** Single-screw extruder

a metal barrel into which the screw is centered. The barrel is typically heated at different positions along its length (the red bars in this firgure), with the ability to create a temperature gradient through it. A feed mixture is dropped into the barrel through a hopper, and the final dispersed material is extruded through a die at the end of the barrel.

The extruder can be configured in a number of ways so as to be optimized for any mixture of resin and particles. Among the most important of these is the screw itself. The shaft of the screw is tapered while the flights are not. The shaft is narrowest at the feed end of the barrel, allowing for maximum feed rates. As the material is conveyed along the barrel, the shaft gradually widens, compressing the material as it is conveyed through the barrel. At the end of the extruder the shaft thickness remains constant so as to convey the material through the die. This portion of the extruder is called the metering zone.

Material is moved through the extruder by the back pressure that develops within the barrel. The magnitude of this pressure is determined by the dimensions of the barrel and the screw, and screws are typically designed specifically for a given polymer and particle mix. Screw parameters that can be adjusted include the diameter of the shaft, the reach of the flights, and the distance between the flights. In addition to providing the force necessary to convey the material through the extruder, the back pressure also determines the degree of shear in the different regions of the barrel.

Without going into excessive detail, we can describe some ways in which twin-screw extruders are similar to and different from single-screw extruders. Twin-screw extruders are, understandably, more complex. The screws themselves are configured with multiple zones along the barrel, and by proper screw design, the material can be added into different regions along the barrel. This allows materials that are temperature or shear sensitive to be incorporated into the melt under less stressful conditions, the latter of which is particularly important because twin-screw extruders generate significantly higher shear than their single-screw counterparts (this is beneficial for mixing efficiency). In addition, the configuration along the barrel of the extruder can be more extensively modified than is the case for single-screw extruders. This is done by using modular screw and heating elements.

## Summary

Dispersion of particles and additives into polymeric resins relies on many of the same principles as dispersion of particles into liquid paint. Dispersion proceeds through the initial (and complete) wetting of particle clusters and agglomerates, followed by the disruption of these clusters and agglomerates into the smallest particle unit (primary particles or aggregates) and their intimate mixing into the dispersion medium.

Successful particle dispersion within a polymer melt requires that the viscous shear stress be greater than the cohesive forces within particle agglomerates. There are two strategies for doing this: maximizing the viscous shear stress that is applied to the agglomerates, or minimizing the cohesive forces that hold the agglomerates together. Viscous force maximization is addressed through equipment design, and many different types of dispersers are used in the plastics industry, with each type optimized for specific end-use. Alternatively, cohesive forces can be decreased by altering the polarity of the particle surfaces. This is typically accomplished by coating the particles with an organic surface treatment. These treatments also improve the compatibility of inorganic particles with the organic polymer matrix.

Particle wetting can be complex because the viscous polymer melt does not flow uniformly through a particle cluster or agglomerate. Instead, the polymer initially flows through the largest pores within the cluster, which represent the path of least resistance. Once filled, these pores, and the larger voids connected by them, act as resin reservoirs for the filling of nearby smaller pores and voids. In the early stages of wetting, the capillary forces within the agglomerates increase their cohesive strength. At the final stage of wetting, however, the cohesive strength decreases to a value lower than in the original dry agglomerate.

Dispersion is done primarily through shear. Large agglomerates can either erode from the shearing process, or can be ruptured by it. The primary difference between these is the size of the reduced agglomerates after shearing. Erosion leads to a bimodal distribution of particle sizes, with populations of primary particles or aggregates and large agglomerates, whereas rupture leads to a monomodal size distribution that shifts to lower values as the shearing process continues.

Dispersion in plastics can be done using either batch or continuous operations. Batch dispersers include the two-roll mill and internal batch mixers. These operate under the principle of having zones, or regions, of high shear, in which the agglomerates undergo dispersive mixing, and regions of low shear, in which the material undergoes distributive mixing. The zones of high shear are created by sweeping one surface closely past another.

Continuous dispersers include both single- and twin-screw extruders. In this equipment, the material to be dispersed is conveyed through a barrel using one or two screws. Zones are present along the length of the barrel where the mix can be sequentially heated, melted, dispersed, and mixed. This equipment can be easily reconfigured for different types of polymers (which may melt at different temperatures) and combinations of particles and additives.

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