Powder Consolidation and Forming of Ceramics

The common methods for the consolidation of ceramic powders are described in this chapter. We recall that the microstructure of the green body has a significant effect on the subsequent firing stage. If severe variations in packing density occur in the green body, the fired body will, in general, contain heterogeneities that will limit the engineering properties. The *homogeneous packing* of particles in the green body is the desired goal of the consolidation step. Since the packing density controls the amount of shrinkage during firing, the achievement of high *packing density* is also desirable. Geometrical particle packing concepts provide a useful basis for understanding how the structure of the consolidated powder comes about. An important practical consideration is the extent to which the parameters of the consolidation process can be manipulated to control the packing uniformity and packing density of the green body.

The colloidal techniques described in Chapter 4 provide considerable benefits for the control of the packing uniformity of the green body. The production of green bodies with uniform microstructure from a fully stabilized colloidal suspension of spherical, fine, monodisperse particles has not been incorporated into industrial applications where mass production is desired and fabrication cost is a serious consideration. Colloidal techniques, however, play an important role in the low-cost forming methods of *slip casting* and *tape casting*, as well as in the less commonly used methods of *eletrophoretic deposition* and *gel casting*.

Mechanical compaction of dry or semidry powders in a die is one of the most widely used forming operations in the ceramic industry. In general the applied pressure is not transmitted uniformly because of friction between the particles and the die walls as well as between the particles themselves. The stress variations lead to density variations in the green body, thereby placing considerable limits on the degree of packing uniformity that can be achieved. Although the density variations can be reduced significantly by *isostatic pressing*, mechanical compaction provides far less control in the manipulation of the green body microstructure than the casting methods.

Plastic forming methods in which a mixture of the ceramic powder and additives is deformed plastically through a nozzle or in a die provide a convenient route for the mass production of ceramic green bodies. *Extrusion* is used extensively in the traditional ceramics industry and to a lesser extent in the advanced ceramics sector. *Injection molding* has been the subject of intense investigation in recent years, but it has not yet made any significant inroads in the forming of ceramics for industrial applications.

The common forming methods are summarized in Table 6.1.

Table 6.1 Feed Materials and Shapes of the Green Body for the Common Ceramic Forming Methods

Forming method	Feed material	Shape of green body
Dry or semidry pressing		
Die compaction	Powder or free-flowing granules	Small simple shapes
Isostatic pressing	Powder or fragile granules	Larger, more intricate shapes
Casting of a slurry		
Slip casting	Free-flowing slurry with low binder content	Thin intricate shapes
Tape casting	Free-flowing slurry with high binder content	Thin sheets
Deformation of a plastic mass		
Extrusion	Moist mixture of powder and binder solution	Elongated shapes with uniform cross section
Injection molding	Granulated mixture of powder and solid binder	Small intricate shapes

PACKING OF PARTICLES

The packing of particles is treated in texts by German (1) and Cumberland and Crawford (2). Particle packing is commonly divided into two types: (1) *regular* (or ordered) packing and (2) *random* packing. The commonly used ceramic forming methods produce random packing arrangements, but regular packing is typically the first structure encountered in models, partly because of their similarity to crystalline atomic structure. Several parameters can be used to characterize the packing arrangement, but two of the most widely used are

1. *Packing density* (also referred to as the packing fraction or the fractional solids content), defined as

$$\text{Packing density} = \frac{\text{volume of solids}}{\text{total volume of the arrangement}\left(\text{solids} + \text{voids}\right)} \quad (6.1)$$

2. *Coordination number*, which is the number of particles in contact with any given particle.

The packing density is an easily measured parameter that provides much insight about the behavior of a powder.

Regular Packing of Monosize Spheres

The reader would be familiar with the packing of atoms in crystalline solids to produce regular, repeating, three-dimensional patterns such as the simple cubic, body-centered cubic, face-centered cubic, and hexagonal close-packed structures. The packing density and coordination number of these crystal structures for a pure metal are listed in Table 6.2.

TABLE 6.2 Packing Density and Coordination Number of Some Common Crystal Structures for a Pure Metal

Crystal structure	Packing density	Coordination number
Simple cubic	0.524	6
Body-centered cubic	0.680	8
Face-centered cubic	0.740	12
Hexagonal close-packed	0.740	12

Random Packing of Particles

Two different states of random packing have been distinguished. If the particles are poured into a container that is then vibrated to settle the particles, the resulting packing arrangement reaches a state of highest packing density (or minimum porosity) referred to as *dense random packing*. On the other hand, if the particles are simply poured into the container so that they are not allowed to rearrange and settle into as favorable a position as possible, the resulting packing arrangement is referred to as *loose random packing*. An infinite number of packing arrangements may exist between these two limits. The packing densities of a powder after pouring and after being vibrated are commonly referred to as the *poured density* and the *tap density*, respectively.

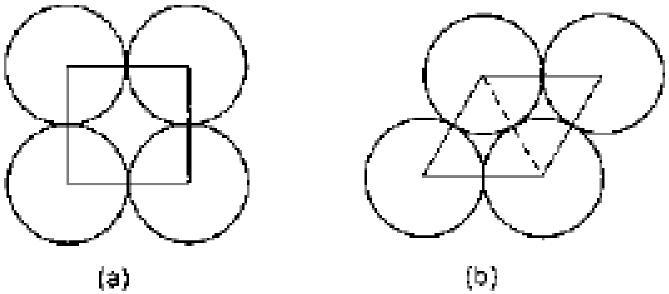


FIGURE 6.1 Two types of layers for the regular packing of monosize spheres: (a) square and (b) rhombic or triangular.

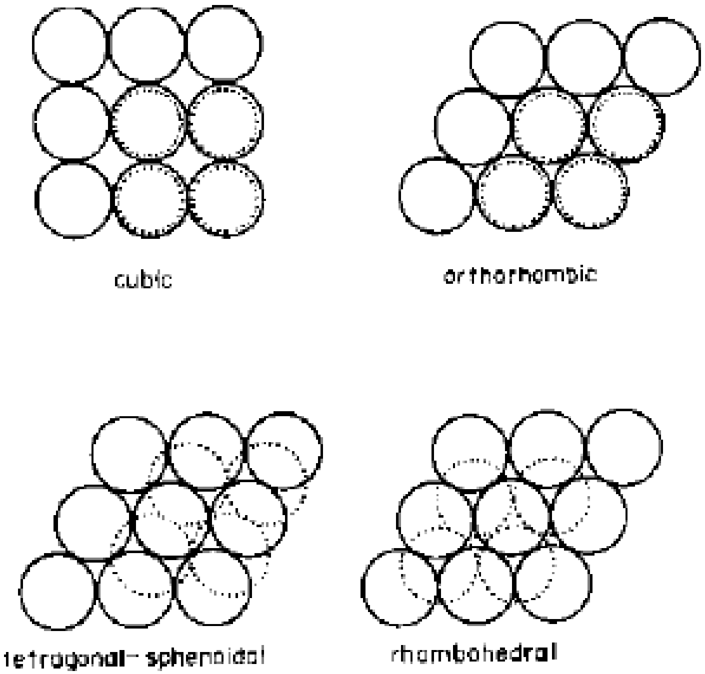


FIGURE 6.2 The four packing arrangements produced by stacking square and triangular layers of monosize spheres.

TABLE 6.3 Packing Density and Coordination Number for Regular Packing of Monosize Spheres

Packing arrangement	Packing density	Coordination number
Cubic	0.524	6
Orthorhombic	0.605	8
Tetragonal-sphenoidal	0.698	10
Rhombohedral	0.740	12

Monosize Particles

Dense random packing of *monosized spheres* has been studied experimentally by shaking hard spheres in a container. The upper limit of the packing density consistently ranges from 0.635 to 0.640 (4). Computer simulations give a value of 0.637 (5). The maximum packing density for random packing of monosize spheres is predicted to be independent of the sphere size, and this prediction has been verified experimentally. For loose random packing of monosize spheres, theoretical simulations as well as experiments give values in the range 0.57–0.61 for the packing density.

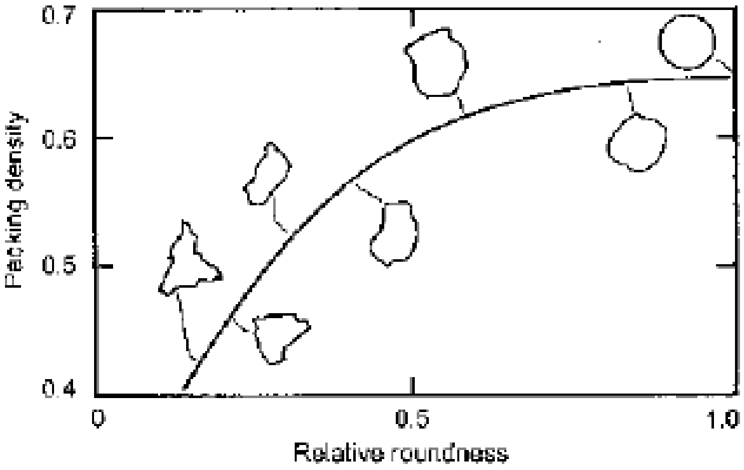


FIGURE 6.4 Packing density versus relative roundness for randomly packed monosized particles. (From Ref. 1.)

TABLE 6.4 Dense Random Packing Density for Various Particle Shapes

Particle shape	Aspect ratio	Packing density
Sphere	1	0.64
Cube	1	0.75
Rectangle	2:5:10	0.51
Plate	1:4:4	0.67
Plate	1:8:8	0.59
Cylinder	5	0.52
Cylinder	15	0.28
Cylinder	60	0.09
Disk	0.5	0.63
Tetrahedron	1	0.5

Source: Ref. 1.

Bimodal Mixtures of Spheres

The packing density of an arrangement of spheres in dense random packing can be increased by filling the interstitial holes with spheres that are smaller than those of the original structure (Fig. 6.5a). For this type of random packing of a binary mixture of spheres, the packing density is a function of (1) the ratio of the sphere diameters and (2) the fraction of the large (or small) spheres in the mixture.

By filling the interstitial holes with a large number of very fine spheres, we can maximize the packing density of the binary mixture.

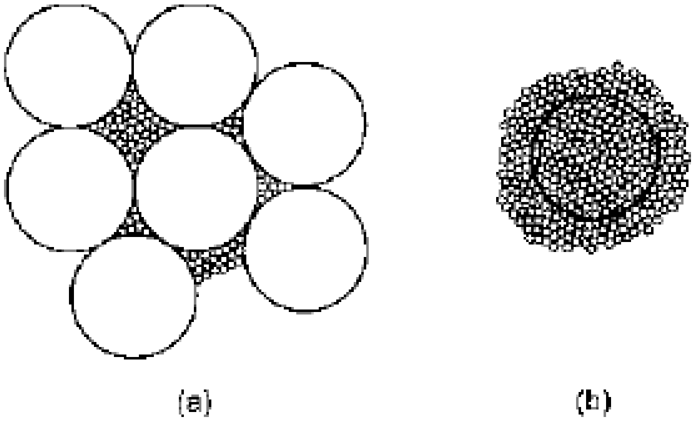


FIGURE 6.5 Increase in packing density achieved by (a) filling the interstices between large spheres with small spheres and (b) replacing small spheres and their interstitial porosity by large spheres.

ADDITIVES AND CERAMIC FORMING

In the forming of ceramics, the use of certain additives, sometimes in concentrations as low as a fraction of a percent by weight, is often vital for controlling the characteristics of the feed material, for achieving the desired shape, and for controlling the packing uniformity of the green body. In methods such as tape casting and injection molding, the selection of suitable additives forms one of the most vital parts of the forming process. The additives are either *organic* or *inorganic* in composition. Organic additives, which can be *synthetic* or *natural* in origin, find greater use in the forming of advanced ceramics because they can be removed almost completely (e.g., by pyrolysis) prior to the sintering step. Therefore the presence of residues that can degrade the microstructure of the final product is largely eliminated. Organic additives can also be synthesized with a wide variety of compositions so they provide a large number of chemicals for specialized applications. Inorganic additives cannot generally be removed after the forming step and are used in applications, particularly in the traditional ceramics industry, where the residues do not have an adverse effect on the properties of the final product.

The additives serve a variety of specialized functions, which may be divided into four main categories: (1) solvents, (2) dispersants (also referred to as deflocculants), (3) binders, and (4) plasticizers.

1 Solvents

Liquids serve two major functions:

1. Provide fluidity for the powder during forming.
2. Serve as solvents for dissolving the additives to be incorporated into the powder, thereby providing a means for uniformly dispersing the additives throughout the powder.

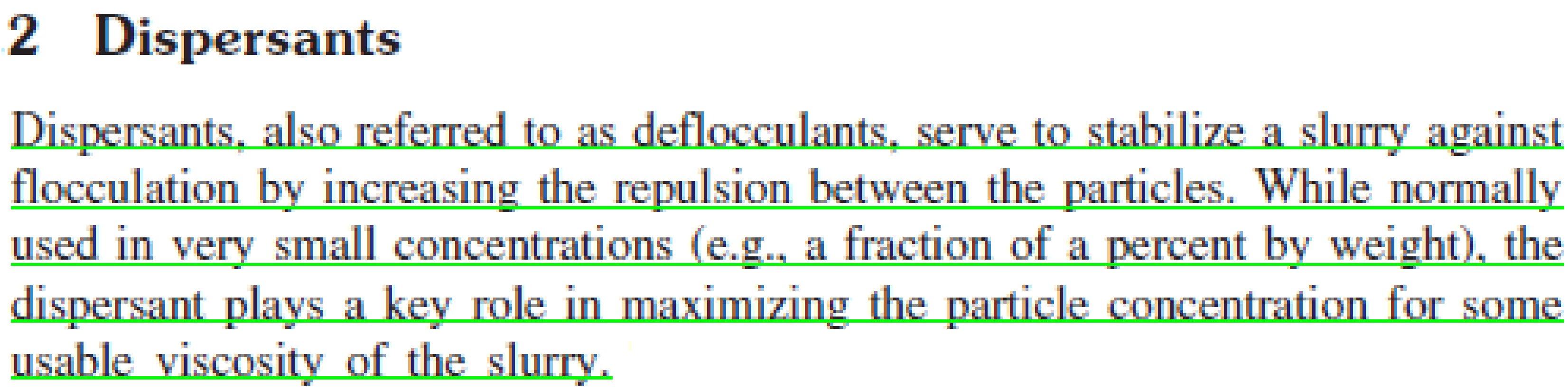
The selection of a solvent involves basically a choice between water and an organic liquid. Organic solvents generally have higher vapor pressure, lower latent heat of vaporization, lower boiling point, and lower surface tension than water, due in a large part to the strong hydrogen bonding of the water molecules (Table 6.6). Several common organic solvents also have a lower viscosity than water. The actual choice of a liquid for a given application often involves the consideration of a combination of several properties from the following list: (1) the ability to dissolve other additives, (2) evaporation rate, (3) ability to wet the powder, (4) viscosity, (5) reactivity towards the powder, (6) safety, and (7) cost.

Generally, solubility of the solid in the liquid is enhanced if the chemicals have similar functional groups [e.g., poly(vinyl alcohol) and water, which contain OH groups] or similar molecular polarity [e.g., poly(vinyl butyral) and ethanol]. Evaporation rate is an important factor in industrial tape casting where the tape is often cast, dried, peeled off from the carrier film, and rolled up for storage in a continuous operation. Fast drying solvents such as toluene and methyl ethyl ketone (2-butanone) are commonly used for tape casting, particularly for thick tapes. Water is used occasionally for thin tapes. The evaporation rate of a liquid is determined by its latent heat of vaporization, but the boiling point is sometimes used as a rough guide. A mixture of solvents (e.g., trichloroethylene and ethanol) is sometimes used in tape casting to control the solubility and evaporation rate.

Wetting of a solid by a liquid is defined in terms of the contact angle θ (see Fig. 5.19), given by

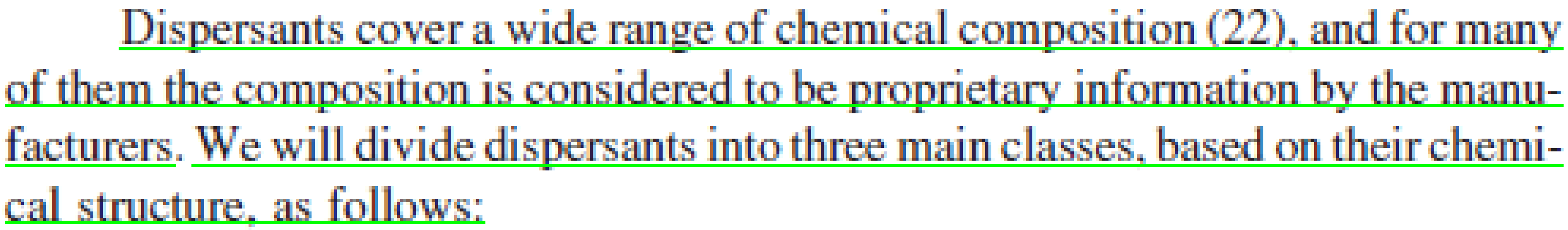
$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{6.6}$$

where γ_{SV}, γ_{SL}, and γ_{LV} are the surface tensions of the solid–vapor, solid–liquid, and liquid–vapor interfaces, respectively. Good wetting (low θ) is desirable in practice and, according to Eq. (6.6), is promoted by a low value of γ_{LV} (if γ_{SL} is not changed considerably). This is often achieved by using an organic solvent (low γ_{LV}) or by adding a *surfactant* (or *wetting agent*) to water to reduce its surface tension.

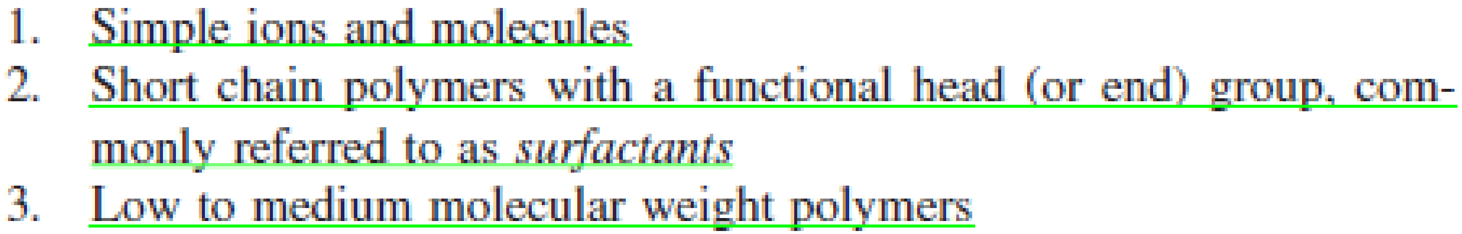


2 Dispersants

Dispersants, also referred to as deflocculants, serve to stabilize a slurry against flocculation by increasing the repulsion between the particles. While normally used in very small concentrations (e.g., a fraction of a percent by weight), the dispersant plays a key role in maximizing the particle concentration for some usable viscosity of the slurry.



Dispersants cover a wide range of chemical composition (22), and for many of them the composition is considered to be proprietary information by the manufacturers. We will divide dispersants into three main classes, based on their chemical structure, as follows:



1. Simple ions and molecules
2. Short chain polymers with a functional head (or end) group, commonly referred to as *surfactants*
3. Low to medium molecular weight polymers

2.1 Simple Inorganic Ions and Molecules

Dispersants consisting of simple ions and molecules are effective in aqueous solvents. They are formed by dissociation of dissolved inorganic compounds such as salts, acids, and bases, often referred to as electrolytes. Examples are sodium silicate (Na_2SiO_3) commonly used for clays, tetrasodium pyrophosphate ($Na_4P_2O_7$), sodium hexametaphosphate ($Na_6P_6O_{18}$), sodium carbonate (Na_2CO_3), and hydrochloric acid (HCl) for oxides.

Sodium silicate forms one of the most effective dispersants for clays. As illustrated in Fig. 6.13, replacement of bivalent Ca^{2+} ions (or Mg^{2+} ions) more commonly present on the clay particle surfaces by monovalent Na^+ ions produces less screening of the surface charge and, hence, to a greater repulsion between the clay particles.

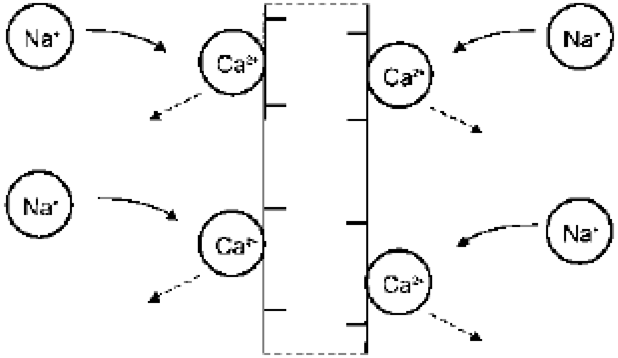


FIGURE 6.13 Schematic illustrating the stabilization of clay particles with sodium silicate.

2.2 Short-Chain Polymers with a Functional Head Group (Surfactants)

Surfactants contain a short-chain organic tail (containing up to 50–100 carbon atoms) and a functional head group that is nonionic or ionic in nature (Fig. 6.14a). For *nonionic surfactants*, the head group may be polar but does not ionize to produce charged species, so nonionic surfactants are commonly effective in *organic* solvents. Adsorption onto the particle surfaces occurs either by van der Waals attraction or, more effectively, by stronger coordinate bonding. As illustrated in Fig. 6.14b, using the Lewis acid-base concept, an atom in the surfactant functional group which has an unshared pair of electrons (e.g., N or O) may act as a Lewis base and form a coordinate bond with an atom (e.g., Al) on the particle surface which has an incomplete shell of electrons (Lewis acid). Stabilization most likely occurs by steric repulsion between the organic tails or micelles that are stretched out in the organic solvent (Fig. 6.14c and d). Examples of some commonly used nonionic surfactants are given in Fig. 6.15.

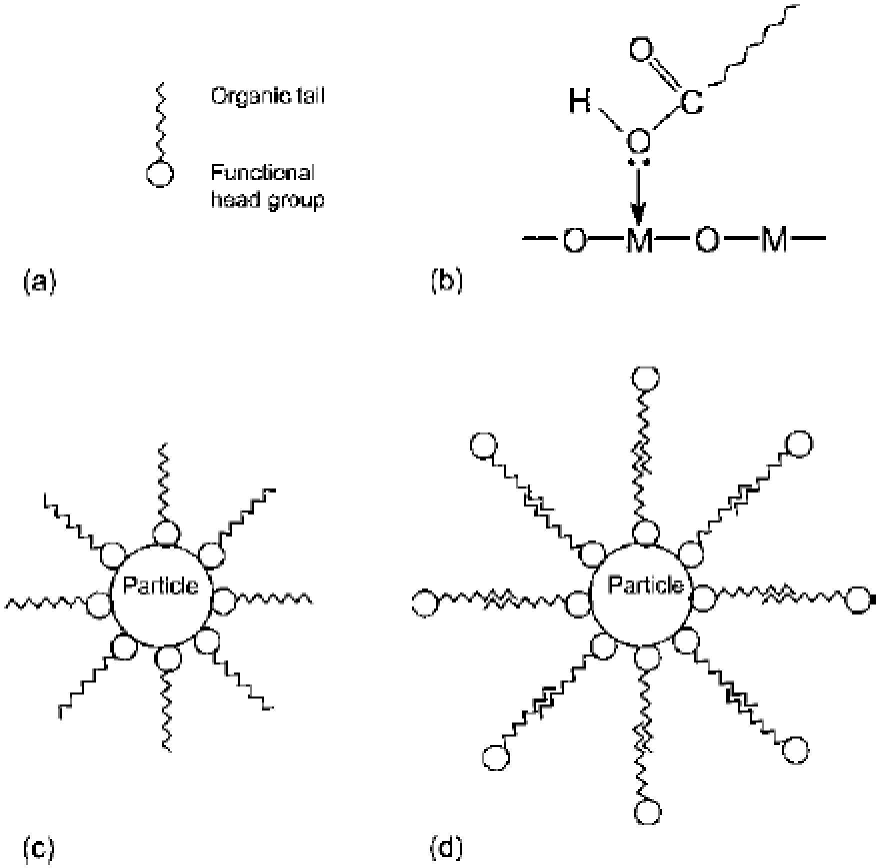
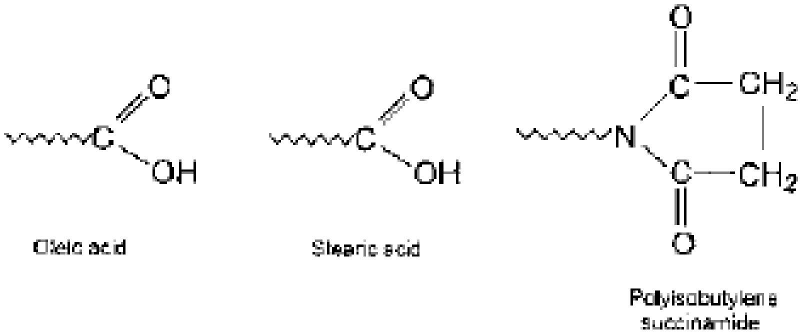
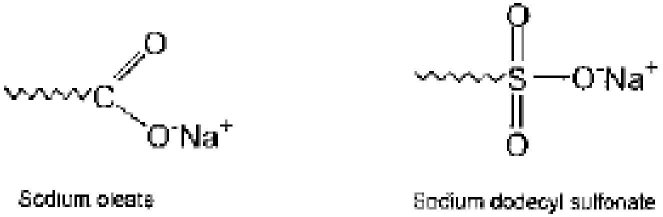


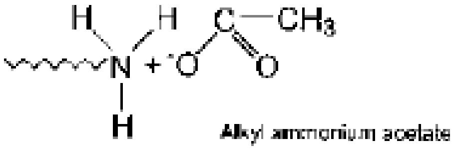
FIGURE 6.14 (a) Schematic of a surfactant molecule. (b) Illustration of surfactant adsorption onto an oxide particle surface by coordinate bonding. (c) Stabilization by steric repulsion between organic tails of the surfactant molecules. (d) Stabilization by micelles.



(a) Nonionic surfactants soluble in organic solvents



(b) Anionic surfactants soluble in aqueous solvents



(c) Cationic surfactant soluble in aqueous solvents

FIGURE 6.15 Functional head groups of some common surfactants.

Ionic surfactants are described as either *anionic*, when the functional head group ionizes to form a negatively charged species, or *cationic*, when a positively charged head group is formed (Fig. 6.16a). They are effective in *aqueous* solvents.

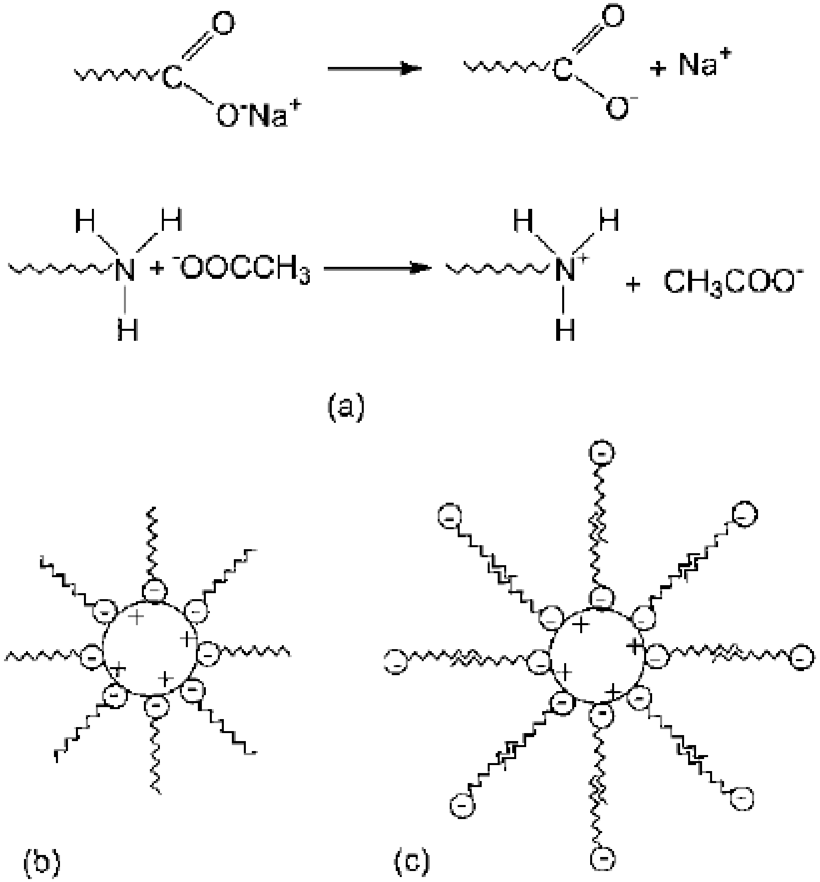


Figure 6.16 (a) Dissociation of anionic and cationic surfactants to form negatively charged and positively charged head groups, respectively. (b) Stabilization by negatively charged surfactant. (c) Stabilization by negatively charged micelles.

2.3 Low to Medium Molecular Weight Polymers

These dispersants, with a molecular weight in the range of several hundred to several thousand, are also classified into nonionic and ionic types. Common *nonionic* polymeric dispersants are poly(ethylene oxide) (PEO), or poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), polystyrene (PS), and block copolymers of PEO/PS. With a higher molecular weight, many of these polymers are effective as binders; their chemical compositions are given in the next section (see Fig. 6.18).

3 Binders

Binders are typically long chain polymers that serve the primary function of providing strength to the green body by forming bridges between the particles. In some forming methods (e.g., injection molding), they also provide plasticity to the feed material to aid the forming process. A large number of organic substances can be utilized as binders, some of which are soluble in water, while others are soluble in organic liquids. The monomer formulas of some common *synthetic* binders are shown in Fig. 6.18. They include the vinyls, acrylics, and the ethylene oxides (glycols).

The selection of a binder for a given forming process involves the consideration of several factors that include (1) binder burnout characteristics, (2) molecular weight, (3) glass transition temperature, (4) compatibility with the dispersant, (5) effect on the viscosity of the solvent, (6) solubility in the solvent, and (7) cost. It is clear that low cost is a key consideration in industry.

The binder as well as the other additives used to aid the forming of the green body must normally be removed as completely as possible (commonly by pyrolysis) prior to sintering. The concentration of the binder is commonly much greater that that of the other additives, so the burnout characteristics is of primary importance in the selection of the binder. As discussed in detail later, the burnout characteristics depend primarily on the binder chemistry and the atmosphere (oxidizing or nonoxidizing).

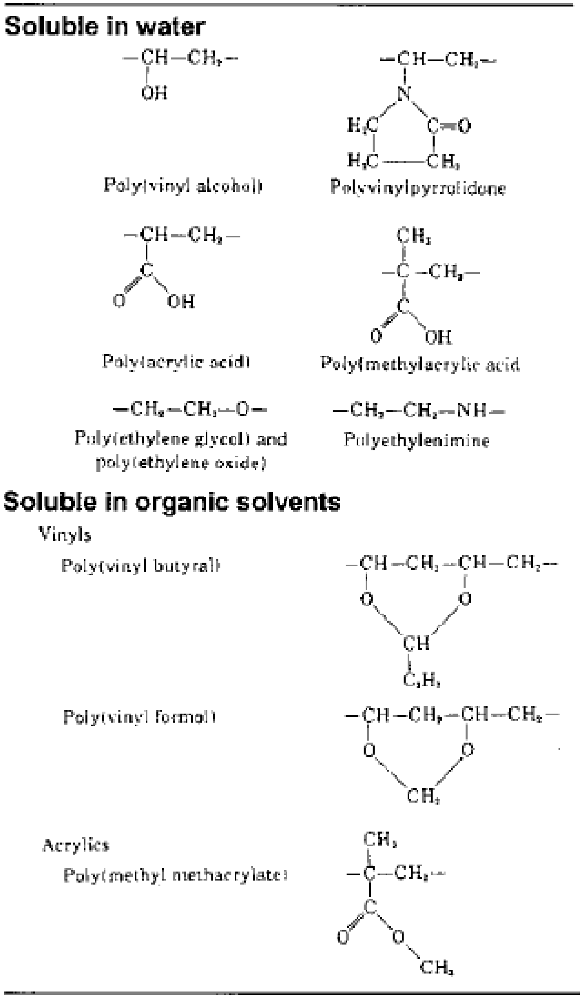


FIGURE 6.18 Monomer formulas of some synthetic binders.

The effect of the binder on the rheology of the solvent is a key consideration. Organic binders increase the viscosity and change the flow characteristics of the liquid. Some can even lead to the formation of a gel. In the casting methods (e.g., tape casting), the binder should not produce a rapid increase in the viscosity of the solvent with increasing concentration because this will limit the amount of powder that can be incorporated into the suspension for some usable viscosity. On the other hand, a rapid increase is generally desirable in extrusion to provide good green strength with a small concentration of binder.

Binders are often arbitrarily classified into low, medium, and high viscosity grades based on how effectively they increase the viscosity of the solution. The scheme shown in Fig. 6.21 has been proposed by Onoda (18) and the classification of several water-soluble binders according to this scheme is shown in Table 6.7.

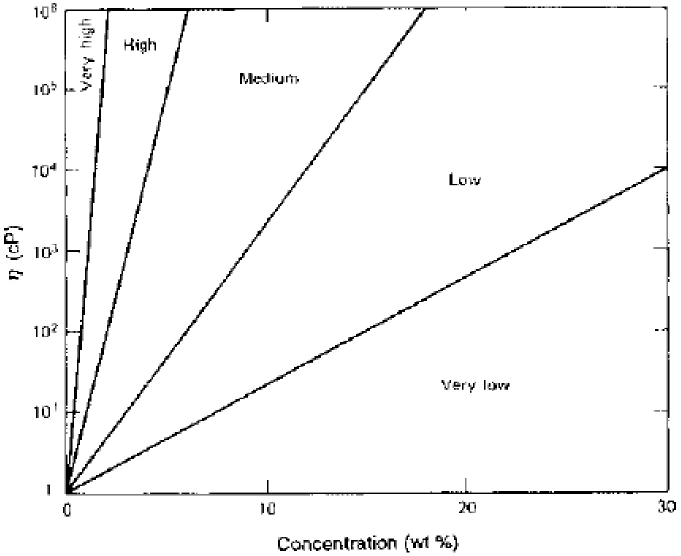


FIGURE 6.21 Criterion for viscosity grades based on viscosity–concentration relationship. (From Ref. 18.)

Table 6.7 Viscosity Grades for Some Water-Soluble Binders

	Viscosity grade				
Binder	Very low	Low	Medium	High	Very high
Gum arabic	•				
Lignosulfonates	•				
Lignin liquor	•				
Molasses	•				
Dextrins	•—•				
Polyvinylpyrrolidone	•—•				
Poly(vinyl alcohol)	•—	—	•		
Poly(ethylene oxide)		•—	•		
Starch		•—	•		
Acrylics		•—•			
Polyethylenimine (PEI)		•—	•		
Methycellulose			•—	—	•
Sodium carboxymethylcellulose			•—	—	•
Hydroxypropylmethylcellulose			•—	—	•
Hydroxyethylcellulose			•—	—	—•
Sodium alginate				•—•	
Ammonium alginate				•—	•
Polyacrylamide				•—	—•
Scleroglucan				•	
Irish moss				•	
Xanthan gum				•	
Cationic galactomanan					•
Gum tragacanth					•
Locust bean gum					•
Gum karaya					•
Guar gum					•—•

Source: Ref. 18.

4 Plasticizers

Plasticizers are generally organic substances with a lower molecular weight than the binder. The primary function of the plasticizer is to soften the binder in the dry state (i.e., reduce the T_g of the binder), thereby increasing the flexibility of the green body (e.g., tapes formed by tape casting). For forming processes in which the binder is introduced as a solution, the plasticizer must be soluble in the same liquid used to dissolve the binder. In the dry state, the binder and plasticizer are homogeneously mixed as a single substance. The plasticizer molecules get between the polymer chains of the binder, thereby disrupting the chain alignment and reducing the van der Waals bonding between adjacent chains. This leads to softening of the binder but also reduces the strength. Some commonly used plasticizers are listed in Table 6.8.

TABLE 6.8 Common Plasticizers Used in Ceramic Processing

Plasticizer	Melting point (°C)	Boiling point (°C)	Molecular weight
Water	0	100	18
Ethylene glycol	−13	197	62
Diethylene glycol	−8	245	106
Triethylene glycol	−7	288	150
Tetraethylene glycol	−5	327	194
Poly(ethylene glycol)	−10	>330	300
Glycerol	18	290	92
Dibutyl phthalate	−35	340	278
Dimethyl phthalate	1	284	194

6.4 FORMING OF CERAMICS

The common ceramic forming methods were summarized in Table 6.1. We will now describe the key factors in each method and how they can be manipulated to optimize the microstructure of the green body.

6.4.1 Dry and Semidry Pressing

Uniaxial pressing in a die and isostatic pressing are commonly used for the compaction of dry powders, which typically contain <2 wt% water, and semidry powders, which contain ~5–20 wt% water (23,24). Die compaction is one of the most widely used operations in the ceramics industry. It allows the formation of relatively simple shapes rapidly and with accurate dimensions. The agglomeration of dry powders combined with the nonuniform transmission of the applied pressure during compaction leads to significant variations in the packing density of the green body. To minimize the density variations, die pressing is used for the production of relatively simple shapes (e.g., disks) with a height-to-diameter ratio of <0.5–1.0. Isostatic pressing produces better uniformity in the packing density and can be used for the production of green bodies with complex shapes and with much higher height-to-diameter ratios. The green body has irregularities in both shape and surface quality and often requires considerable machining.

6.4.1.1 Die Compaction

In die compaction, the powder or a granular material undergoes simultaneous uniaxial compaction and shaping in a rigid die. The overall process consists of three steps: filling of the die, powder compaction, and ejection of the compacted powder.

Feed Material: Powders and Granules

Powders, often mixed with a small amount of binder (less than 5 vol%), are commonly used as the feed material in laboratory experiments. In industrial practice, the flow properties of the feed material become an important factor when efficient die filling, fast pressing rates, and reproducible green body properties are required. Fine powders do not flow very well and are difficult to compact homogeneously, so it is often necessary to granulate them, commonly by spray drying of a slurry (see Chapter 2). The formulation of the slurry for spray drying typically involves the use of a dispersant (e.g., ammonium polyacrylate), a *binder* [e.g., poly(vinyl alcohol)], a *plasticizer* [e.g., poly(ethylene glycol)], and a lubricant [e.g., ammonium stearate). Figure 6.22 shows a commercial spray-dried Al_2O_3 powder.

Several factors control the granule characteristics. They include the particle size distribution of the initial powder, the degree of flocculation of the slurry, the type of additives, and the spray-drying conditions. The key granule characteristics are

1. *Size, size distribution, and shape*: Granules prepared by spray drying in commercial equipment have nearly spherical shape and sizes in the range of ~50–400 µm, with the average size in the range of ~100–200µm.

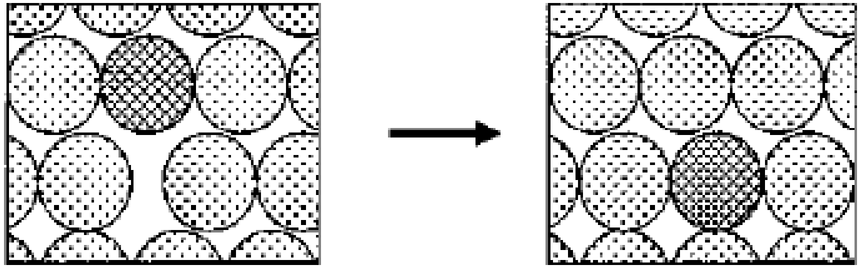
2. *Particle packing*: The particle packing density in the granule is controlled by the particle size distribution of the powder as well as on the particle concentration and colloidal stability of the slurry prior to spray drying (25). Particle packing densities of ~45–55% are common for granules.
3. *Particle packing homogeneity*: The particle packing homogeneity in the granule depends on the colloidal stability of the suspension and on the drying step during spray drying. Granules are commonly prepared from a partially flocculated slurry so the particle packing is not very homogeneous. In addition, if the binder segregates to the granule surface during spray drying, the outer region of the granule will have a low packing density (26).
4. *Hardness*: The hardness of the granule is controlled by the particle packing density and by the nature of the binder used in the slurry formulation. A high particle packing density or a hard binder (e.g., with a high glass transition temperature) leads to the formation of hard granules. On the other hand, soft granules have a lower packing density or contain a soft binder.
5. *Surface friction*: Smooth granule surfaces reduce the friction between the granules themselves and between the granules and the die walls.

Die Filling

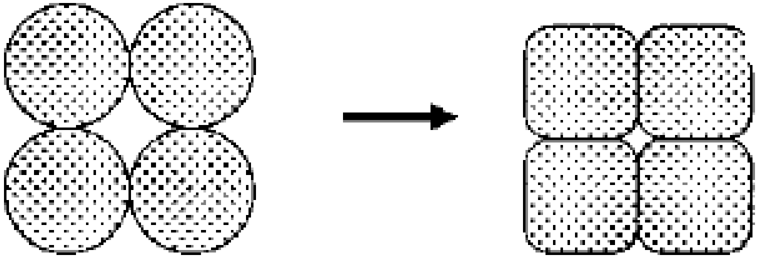
The flow of the granules during die filling is improved by a wide distribution of sizes, a spherical shape, and a smooth surface (14). The uniformity of the die filling must also be considered because it will affect the packing homogeneity of the green body. In addition to the filling method and the geometry of the die, the die filling uniformity depends on the ratio of the granule size to the die diameter. Narrower dies lead to a lower overall packing density in the compact because the packing density near the die walls is lower. Simulations indicate that the effect of the die walls becomes insignificant when the die diameter is greater than ∼250 times the granule diameter (23). For particle packing densities of 45–55% in the granules and assuming loose random packing of the granules (∼60%), the actual particle packing density during die filling is ∼25–35%.

The Compaction Step

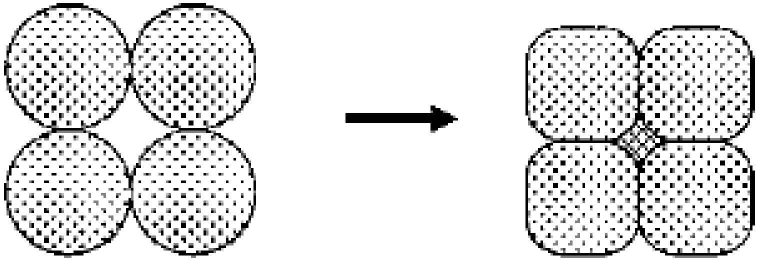
After die filling, the structure of a system of granules contains large voids on the order of the granule size and voids that are smaller than the granule size (Fig. 6.23). The compaction of this system can be divided into two stages. The first stage of compaction involves reduction of the large voids by *rearrangement* of the granules, while in the second stage, the small voids are reduced by *deformation* of the granules.



Rearrangement: filling of large voids



Deformation: filling of small voids



Fragmentation: filling of voids with fine particles

FIGURE 6.23 Schematic diagram showing the stages of compaction for granules.

Factors Influencing the Compaction of Particles HW: READ

Factors Influencing the Compaction of Granules HW: READ

Ejection of the Powder Compact

As outlined earlier, the powder undergoes elastic compression during the compaction process. The stored elastic energy leads to an expansion of the compact when the applied pressure is released. This expansion is referred to as *springback*, *strain recovery*, or *strain relaxation*. Springback is almost instantaneous on release of the pressure. The amount of springback depends on several factors, including the powder, the organic additives, the applied pressure, the rate of pressing, and the gas permeability of the powder compact. Generally, it is higher for higher amounts of organic additives and for higher applied pressure. While a small amount of strain recovery is desirable to cause the compact to separate from the punch, an excessive amount can lead to flaws. Ejection of the powder compact from the die is resisted by friction between the compact and the die wall. Lubricants added to reduce die-wall friction during the compaction process have an additional benefit in that they reduce the pressure required for ejection.

Compaction Defects

After the completion of the die compaction process, we require that the green body be free of macroscopic defects and that density gradients be as low as possible. Density gradients lead to the development of cracklike voids in the sintered body and can also lead to cracking and warping of the body during sintering. They also enhance the formation of defects in the compact on ejection from the die. Several factors can be controlled to reduce the extent of density gradients in the powder compact. Uniform die filling reduces the amount of internal movement of the powder during the compaction process. The use of lubricants to reduce the internal friction between the particles and die-wall friction can lead to significant improvements. Stress gradients (and hence, density gradients) due to die-wall friction are enhanced with increasing ratio of the length to diameter (*L/D*) of the compact. For the single-action mode of die compaction, *L/D* should be less than 0.5, while for the double-action mode, it should be less than 1.

The common defects in compacts formed by die pressing are illustrated in Fig. 6.31. They are caused by springback and by friction at the die walls. The use of a binder to increase the compact strength, reduction of the applied pressure to reduce the extent of the springback, and the use of a lubricant to reduce die wall friction can significantly reduce the tendency for defect formation.

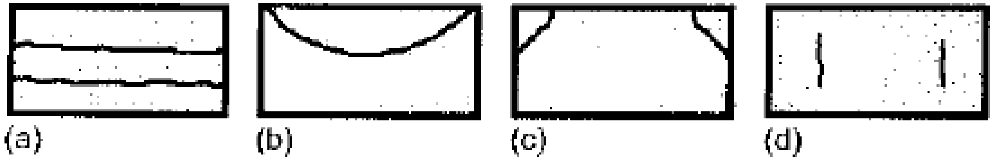


FIGURE 6.31 Illustrations of typical defects in die compaction of dry or semidry powders: (a) delamination, (b) end capping, (c) ring capping, and (d) vertical cracks.

6.4.1.2 Isostatic Compaction

Isostatic pressing involves the application of a uniform hydrostatic pressure to the powder contained in a flexible rubber container. There are two modes of isostatic pressing: wet-bag pressing and dry-bag pressing (Fig. 6.32). In wet-bag pressing, a flexible rubber mold is filled with the powder, which is then submerged into a pressure vessel filled with oil and pressed. After pressing, the mold is removed from the pressure vessel and the green body is retrieved. Wet-bag pressing is used for the formation of complex shapes and for large sizes. In dry-bag pressing, the mold is fixed in the pressure vessel and need not be removed. The pressure is applied to the powder situated between a fairly thick rubber mold and a rigid core. After release of the pressure, the powder compact is removed from the mold. Dry-bag pressing is easier to automate than wet-bag pressing. It has been used for the formation of spark plug insulators by compressing a porcelain powder mixture around a metal core as well as for plates and hollow tubes. Compared to die compaction, the formation of defects in isostatically pressed compacts is much less severe, but delamination and fracture (caused by springback) can still occur if the pressure is released too rapidly after compaction.

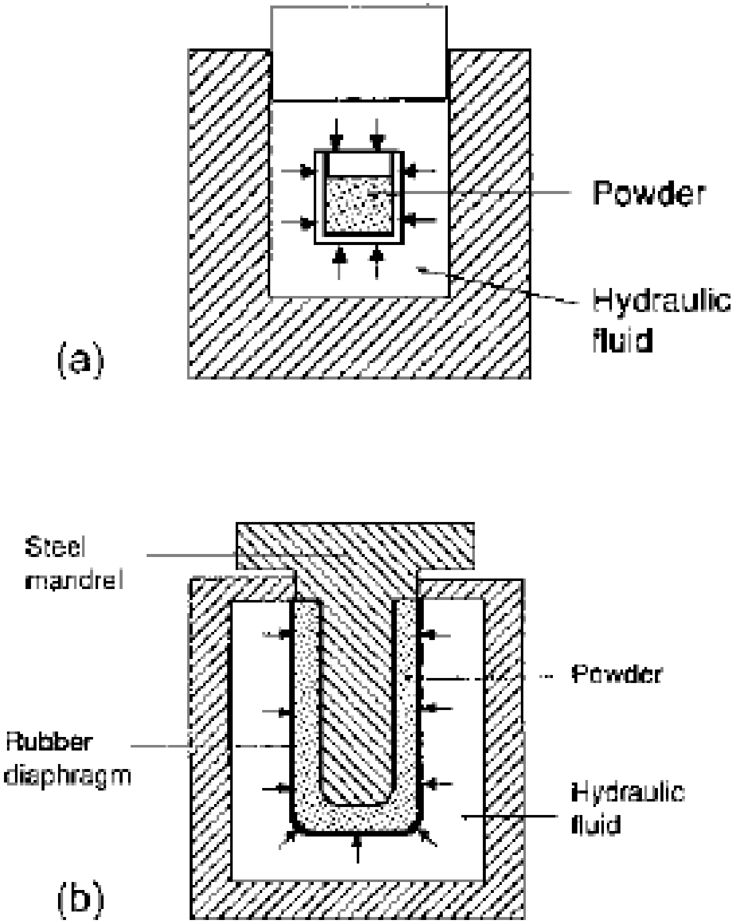


FIGURE 6.32 Two modes of isostatic pressing: (a) wet bag and (b) dry bag.

6.4.2 Casting Methods

The common casting methods are *slip casting*, *pressure casting*, and *tape casting*. They are based on colloidal systems in which removal of the liquid is used to consolidate particles suspended in a slurry. In slip casting and pressure casting, consolidation of the particles is accomplished as the liquid flows through a porous medium under a pressure gradient. In tape casting, consolidation is accomplished by evaporation of the liquid. *Gel casting* is a recently introduced method in which the particles in a slurry are immobilized by polymerization and cross-linking of a monomer solution to form a gel prior to evaporation of the liquid. *Electrophoretic deposition* is a process in which ceramic bodies are deposited on an electrode by applying a direct current (dc) electric field to a colloidal suspension.

6.4.2.1 Slip Casting

A recent review of slip casting is given by Fries and Rand (35) and much practical details of the process can be found in a set of earlier articles (36). In the process, a slurry is poured into a microporous plaster of Paris mold. The porous nature of the mold provides a capillary suction pressure, estimated to be of the order of ~0.1–0.2 MPa, which draws the liquid from the slurry into the mold. A consolidated layer of solids, referred to as a *cast* (or *cake*), forms on the walls of the mold (Fig. 6.33). After a sufficient thickness of the cast is formed, the surplus slip is poured out and the mold and cast are allowed to dry. Normally, the cast shrinks away from the mold during drying and can be easily removed. Once fully dried, the cast is heated to burn out the binder and sintered to produce the final article. Examples of slip casting compositions are given in Table 6.9.

Slip Casting Mechanics

Some of the early analyses incorrectly treated the mechanics of slip casting in terms of a *diffusion* process. The slip casting process involves the *flow* of liquid through a porous medium, which is described by Darcy's law. In one dimension, Darcy's law can be written as

$$J = \frac{K\left(dp/dx\right)}{\eta_L} \tag{6.8}$$

where J is the flux of liquid, K is the permeability of the porous medium, dp/dx is the pressure gradient in the liquid, and η_L is the viscosity of the liquid.

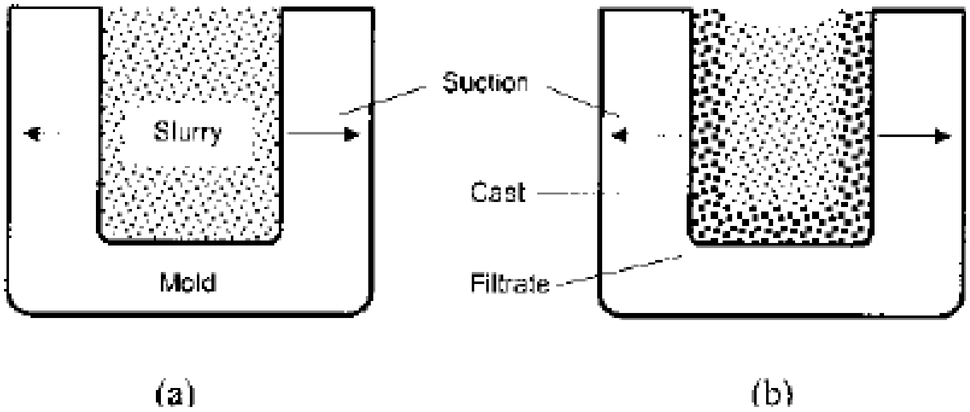


FIGURE 6.33 Schematic diagram of the slip-casting system: and (a) initial system (b) after the formation of a thin cast.

TABLE 6.9 Examples of Slip Casting Compositions

Whiteware		Alumina	
Material	Concentration (vol %)	Material	Concentration (vol %)
Clay, silica, feldspar	45–50	Alumina	40–50
Water	50	Water	50–60
Sodium silicate, polyacrylate, or lignosulfate (dispersant)	<0.5	Ammoniul polyacrylate (dispersant)	0.5–2
Calcium carbonate (flocculant, if required)	<0.1	Ammonium alginate or methyl cellulose (binder)	0–0.5

Effect of Slurry Parameters

The colloidal stability of the slurry has the strongest influence on the microstructure of the cast. A flocculated slurry leads to a cast with a fairly high porosity. Moreover, in this case, the effective pressure in the cast (p_s in Fig. 6.34) decreases rapidly and nonlinearly from the mold–cast interface. The compressible nature of the highly porous cast coupled with the variation in p_s leads to a rapid reduction in the density of the cast as it builds up and to an almost constant high porosity region in the bulk of the cast (37). Heterogeneities in the green body microstructure, as we will recall, hinder microstructural control during the firing process. A well dispersed slip containing no agglomerates and stabilized by electrostatic or steric repulsion leads to the formation of a fairly dense cast with better microstructural uniformity. In practice, the fairly dense cast formed from a well-dispersed slip has a low permeability, and the rate of casting is therefore low. For industrial operations where such low casting rates are uneconomical, the slip is only partially deflocculated.

Other parameters such as the size, size distribution, and shape of the particles can also influence the compressibility and, hence, the packing density of the cast. Figure 6.35 summarizes the effects of particle size, particle shape, and the degree of flocculation of the slurry on the packing density of the cast. For fairly coarse particles (greater than ~10–20 μm), colloidal effects are insignificant and the degree of dispersion of the particles has no effect on the packing density. Large spheres of the same size produce casts with a packing density of ~0.60–0.65, close to that for dense random packing whereas irregular particles produce casts with a lower packing density. As the particle size decreases below ~10 μm, colloidal effects control the packing density. At one extreme, well-dispersed slips produce casts with high packing density while at the other extreme, flocculated slips yield a low packing density. As outlined above, particles with

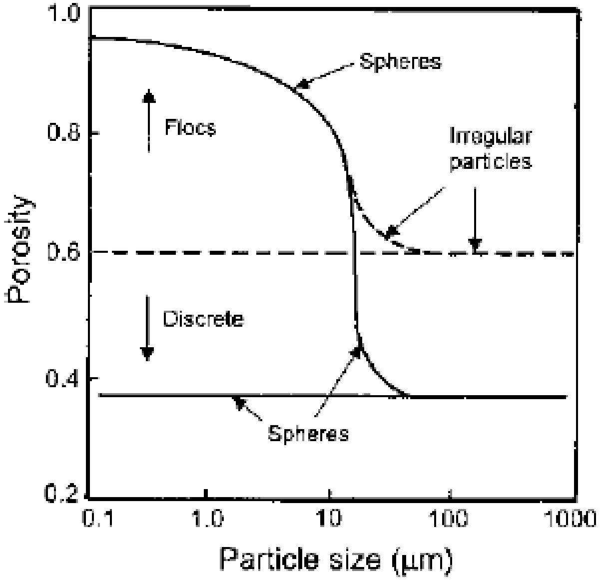


FIGURE 6.35 Schematic diagram showing the effects of particle size, shape, and degree of flocculation on the porosity of the cast produced in slip casting. (From Ref. 39.)

Microstructural Defects in Slip-Cast Green Bodies

Several types of microstructural defects can be present in green articles formed by slip casting. They arise during the casting operation and are generally related to the properties of the slurry. *Large voids* due to air bubbles in the slurry are a common occurrence. They can be avoided by improving the wetting characteristics of the particles by the liquid, proper de-airing of the slurry, and the avoidance of turbulent flow of the slurry during the casting operation. Elongated (anisometric) particles can be *preferentially aligned* along certain directions, usually parallel to the mold surface. *Segregation*, in which the larger particles settle faster than the smaller, can be alleviated by improving the colloidal stability of the slurry.

6.4.2.3 Tape Casting

The principles and practice of tape casting are covered in a recent text (42) and the process also forms the subject of several review articles (43–46). In tape casting, sometimes referred to as the *doctor-blade process*, the slurry is spread over a surface covered with a removable sheet of paper or plastic using a carefully controlled blade referred to as a doctor blade. For the production of long tapes, the blade is stationary and the surface moves (Fig. 6.38), whereas for the production of short tapes in the laboratory, the blade is pulled over a stationary surface. Drying occurs by evaporation of the solvent to produce a tape, which adheres to the carrier surface, consisting of particles bonded by the polymeric additives. The flexible green tape can be stored on take-up reels or stripped from the carrier surface and cut into the desired lengths for subsequent operations. Sheets with thicknesses from as low as 10 μm to as thick as 1 mm are prepared by tape casting. The steps in the production of an MgO-doped Al_2O_3 component by tape casting are summarized in Fig. 6.39.

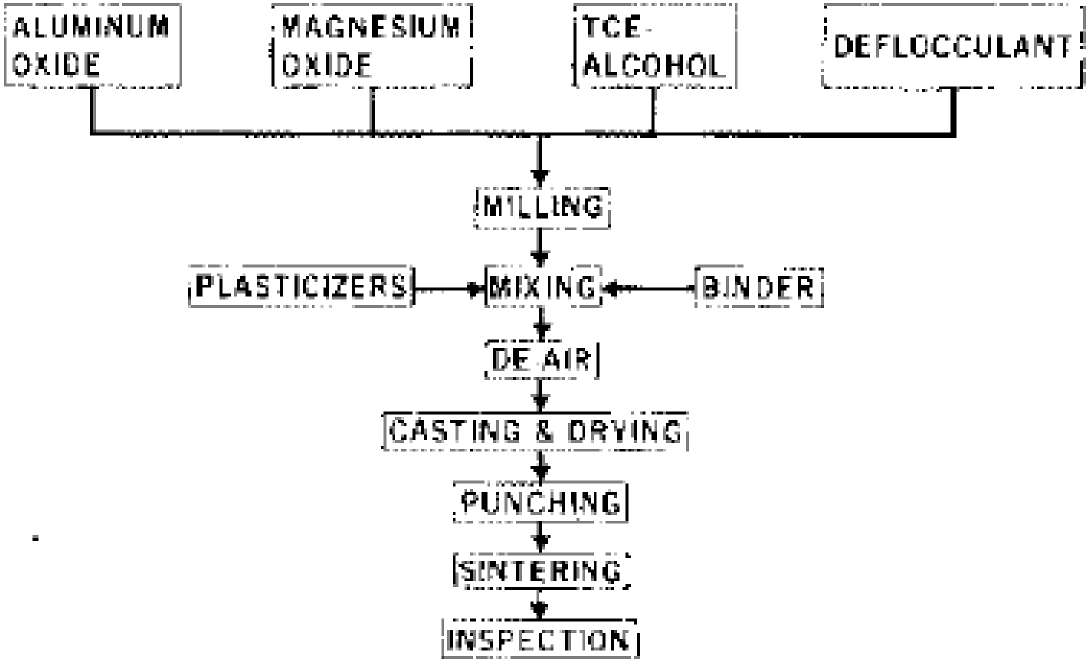


Figure 6.39 Schematic flow diagram for the tape casting of an alumina substrate material.

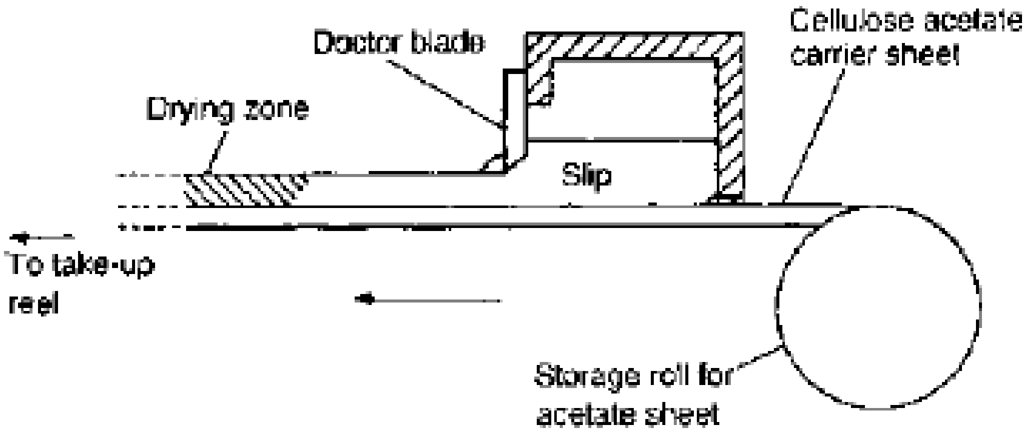


FIGURE 6.38 Schematic diagram of the tape casting process.

Slurry (Slip) Preparation

The preparation of the slurry is a critical step in the tape casting process. The factors that govern the selection of solvent, dispersant, binder, plasticizer, and other additives were described earlier in this chapter. Most tape casting operations currently use organic solvents, but the trend is towards aqueous-based systems. Other considerations in the selection of a solvent are the thickness of the tape to be cast and the surface on which the cast is to be made. Thin tapes are cast from highly volatile solvent systems (e.g., acetone or methyl ethyl ketone), whereas thicker tapes ($\geq$0.25 mm) have to be cast from slower drying solvents (e.g., toluene).

The dispersant may be the most important organic additive in that it serves to lower the viscosity of the slurry, thereby allowing the use of a high particle concentration. Another important selection to be made is that of the binder–plasticizer combination because the concentration used in tape casting slurries is high. It must provide the required strength and flexibility of the green tape and must also be easily burnt out prior to sintering of the tape. Many organic systems can easily satisfy this criterion if the binder burnout process is carried out in an oxidizing atmosphere at reasonably high temperatures. However, several ceramic systems require the use of a binder–plasticizer system that can be removed in a nonoxidizing atmosphere. Typical slurry formulations for tape casting are given in Table 6.10.

Table 6.10 Examples of Tape-Casting Compositions (Concentration in wt%)

Powder	Solvent	Binder	Plasticizer	Dispersant	Other additives
Nonaqueous formulation for use in oxidizing atmospheres					
Al_2O_3 (59.5)	Ethanol (8.9)	PVB (2.4)	Octylphthalate (2.2)	Fish oil (1.0)	
MgO (0.1)	TCE (23.2)		PEG (2.6)		
Nonaqueous formulation for use in nonoxidizing atmospheres					
$BaTiO_3$ (69.9)	MEK (7.0) Ethanol (7.0)	30 wt% solution of acrylic in MEK (9.3)	PEG (2.8) Butyl benzyl phthalate (2.8)	Fish oil (0.7)	Cyclohexanone (homogenizer) (0.5)
Aqueous formulation					
Al_2O_3 (69.0)	Deionized water (14.4)	Acrylic emulsion (cross-linkable) (6.9)	Acrylic emulsion (low T_g) (9.0)	Ammonium polyacrylate (0.6)	Poly (oxyalkylene-diamine) (0.1)

Source: Refs. 42, 44, and 45.

The Tape Casting Process

As illustrated in Fig. 6.38, the key component of the tape casting equipment is the doctor blade assembly. It consists of an adjustable doctor blade mounted in a frame with a reservoir to hold the slurry (or slip) before it is metered out under the blade to form the thin layer of slurry on the carrier surface. The flow behavior of the slurry during the casting of the tape has been analyzed theoretically to estimate the influence of the casting parameters on the thickness of the tape (47).

Assuming a Newtonian viscous slurry and laminar flow in a simple casting unit (Fig. 6.40), the thickness of the dry tape, h_d is given by

$$h_d = \frac{\alpha\beta}{2}\frac{\rho_w}{\rho_d}h_0\left(1+\frac{h_0^2\Delta p}{6\eta UL}\right) \qquad (6.18)$$

where α (<1) and β (<1) are correction factors, ρ_w and ρ_d are the densities of the slurry and the dry tape, respectively, h_0 and L are the height and thickness of the doctor blade, respectively, Δp is the pressure difference (determined by the height of the slurry in the reservoir), η is the viscosity of the slurry, and U is the velocity of the doctor blade relative to the casting surface.

According to Eq. (6.18), the thickness of the dried tape would simply be proportional to the height h_o of the doctor blade if the second term in the brackets is much smaller than unity. For values of h_o smaller than ~200 μm, this can be achieved if the parameters η, U, L, and Δp are kept within certain ranges. Large values of h_o can lead to significant deviations from this simple relationship. The effect is more pronounced for small values of η, U, and L. A knife-edged doctor blade (very small value of L) appears to be unsuitable for tape-casting. While a variety of blade designs and shapes are used in the tape casting sector, a flat-bottomed doctor blade is effective practically and has some theoretical support based on Eq. (6.18). A double doctor blade is often found to be useful when a uniform thickness must be maintained over a long length of tape.

In practice, the casting speed is largely determined by the type of casting process: continuous or batch. For a continuous process, the speed is determined by the length of the casting machine, the thickness of the tape, and the volatility of the solvent.

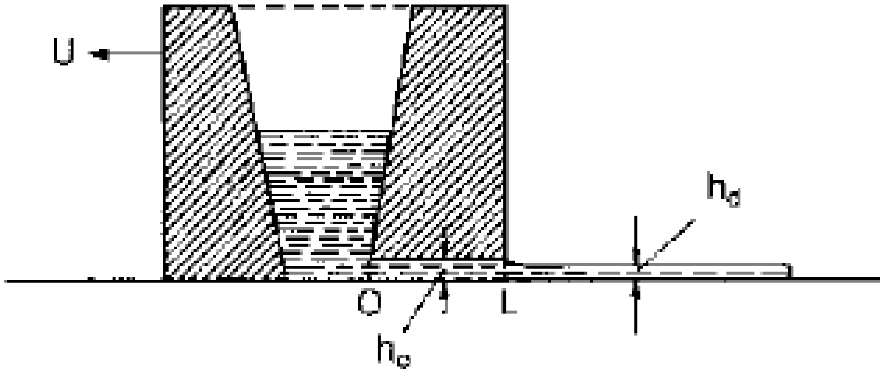


FIGURE 6.40 Section of a tape casting unit.

Drying occurs by evaporation of the solvent from the surface and the tape adheres to the carrier surface, so the shrinkage during drying occurs in the thickness of the tape. Typically, the dried tape has a thickness equal to approximately half the doctor blade height and consists of approximately 50 vol% ceramic particles, 30 vol% organic additives, and 20 vol% porosity. Despite the relatively low density of the tape after binder burnout, the fired tape can reach nearly full density. However, the binder burnout step can provide significant difficulties due to the large amount of organic additives that must be removed. Drying of granular ceramics and binder burnout are considered later in this chapter.

Microstructural Defects in Green Tapes

The main types of microstructural defects in green tapes are similar to those outlined earlier for slip-cast bodies. *Large voids* are caused by air bubbles in the slurry or by rapid evaporation of the liquid during drying and can be avoided by proper de-airing of the slurry or controlling the drying rate. *Segregation* due to differential settling of particles with different sizes is not a severe problem unless the tape is thick, the rate of drying is slow, or the colloidal stability of the slurry is poor. Because of the high concentration of binder in the slurry, binder segregation to the surface of the tape during drying can lead to a gradient in the packing density. The effect of particle or binder segregation is to produce warping (or even cracking) of the tape during sintering. If the particles in the slurry are elongated (anisometric), flow under the doctor blade produces *preferential alignment* of the particles along the direction of flow.

6.4.2.5 Electrophoretic Deposition

The method of electrophoretic deposition (EPD) is shown schematically in Fig. 6.42. A dc electric field causes the charged particles in a colloidal suspension to move toward and deposit on the oppositely charged electrode. EPD involves a combination of electrophoresis (described in Chapter 4) and particle deposition on the electrode. Successful EPD to form a deposit with high packing density requires a stable suspension. Agglomerated particles in an unstable suspension move toward the oppositely charged electrode and form a low-density deposit. Therefore, an understanding of colloidal interactions in a suspension (Chapter 4) is important to EPD.

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A recent review of EPD discusses the mechanisms and kinetics of the deposition process and includes a detailed list of references to the application of EPD to ceramics (52). EPD is a facile forming technique that has the additional benefit of controllability because the rate and extent of deposition are manipulated electrically. It is best used for depositing coatings and thin objects.

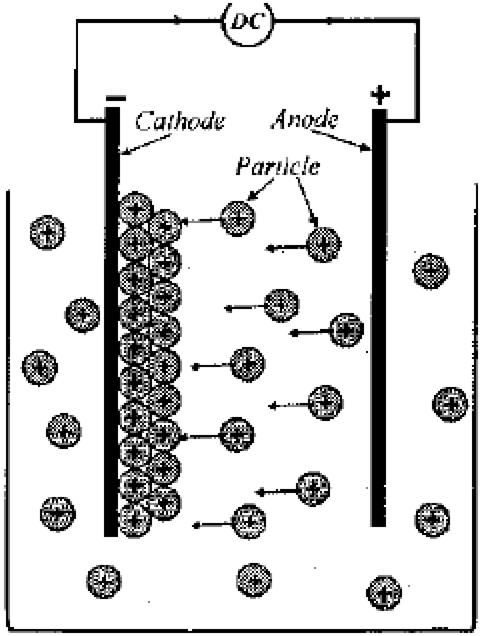

FIGURE 6.42 Schematic drawing of an electrophoretic deposition cell showing the process.

6.4.3 Plastic Forming Methods

Plastic deformation of a moldable powder–additive mixture is employed in several forming methods for ceramics. *Extrusion* of a moist clay-water mixture is used extensively in the traditional ceramics sector for forming components with a regular cross section (e.g., solid and hollow cylinders, tiles, and bricks). The method is also used to form some oxide ceramics for advanced applications (e.g., catalyst supports, capacitor tubes and electrical insulators). A recent development is the repeated *co-extrusion* of a particle-filled thermoplastic polymer to produce textured microstructures or fine-scale structures. *Injection molding* of a ceramic–polymer mixture is a potentially useful method for the mass production of small ceramic articles with complex shapes. However, the method has not yet materialized into a significant forming process for ceramics mainly because of two factors:

1. High tooling costs relative to other common forming methods.
2. Removal of the high concentration of binder prior to sintering remains a limiting step for thicknesses greater than ~1 cm.

The application of extrusion and injection molding to the forming of ceramic powders has benefited considerably from the principles and technology developed in the plastics industry. Extruders and molding machines used in the plastics industry are employed but some modification of the machines is required for ceramic systems (e.g., hardening of the contact surfaces).

Two basic requirements must be satisfied for plastic forming to be successful:

1. The mixture must flow plastically (above a certain yield stress) for the formation of the desired shape.
2. The shaped article must be strong enough to resist deformation under the force of gravity or under stresses associated with handling.

6.4.3.1 Extrusion

In extrusion, a powder mixture in the form of a stiff paste is compacted and shaped by forcing it through a nozzle in a piston extruder or a screw-fed extruder (53). The piston extruder is simple in design, consisting of a barrel, a piston, and a die. In contrast, as illustrated by Fig. 6.44, the screw extruder is complex, and considerable attention goes into the design of the extruder barrel and screw (54). The screw has to mix the powder and other additives into a homogeneous mass and generate enough pressure to transport the mixture against the resistance of the die. Shaping of the extruded body is achieved with the head of the extruder screw and the die. The extruder screw head changes the rotational flow of the mixture produced by the screw into an axial flow for extrusion and to produce uniform flow in the die. In the release of the body from the extruder, the die must generate the required cross section, allow uniform flow across the entire cross section, and ensure a smooth surface.

The main approaches for imparting the required plastic properties to the feed material are (1) manipulating the characteristics of the powder–water system, commonly used for clays and (2) adding a binder solution to the powder, commonly used for advanced ceramics. Clay particles develop desirable plastic characteristics when mixed with a controlled amount of water (15–30 wt% depending on the type of clay). The plasticity arises from two main factors: (1) particle to particle bonding due to the charged particle surfaces and intervening charges (''house of cards'' structure described in Chapter 4) and (2) surface tension effects due to the presence of water.

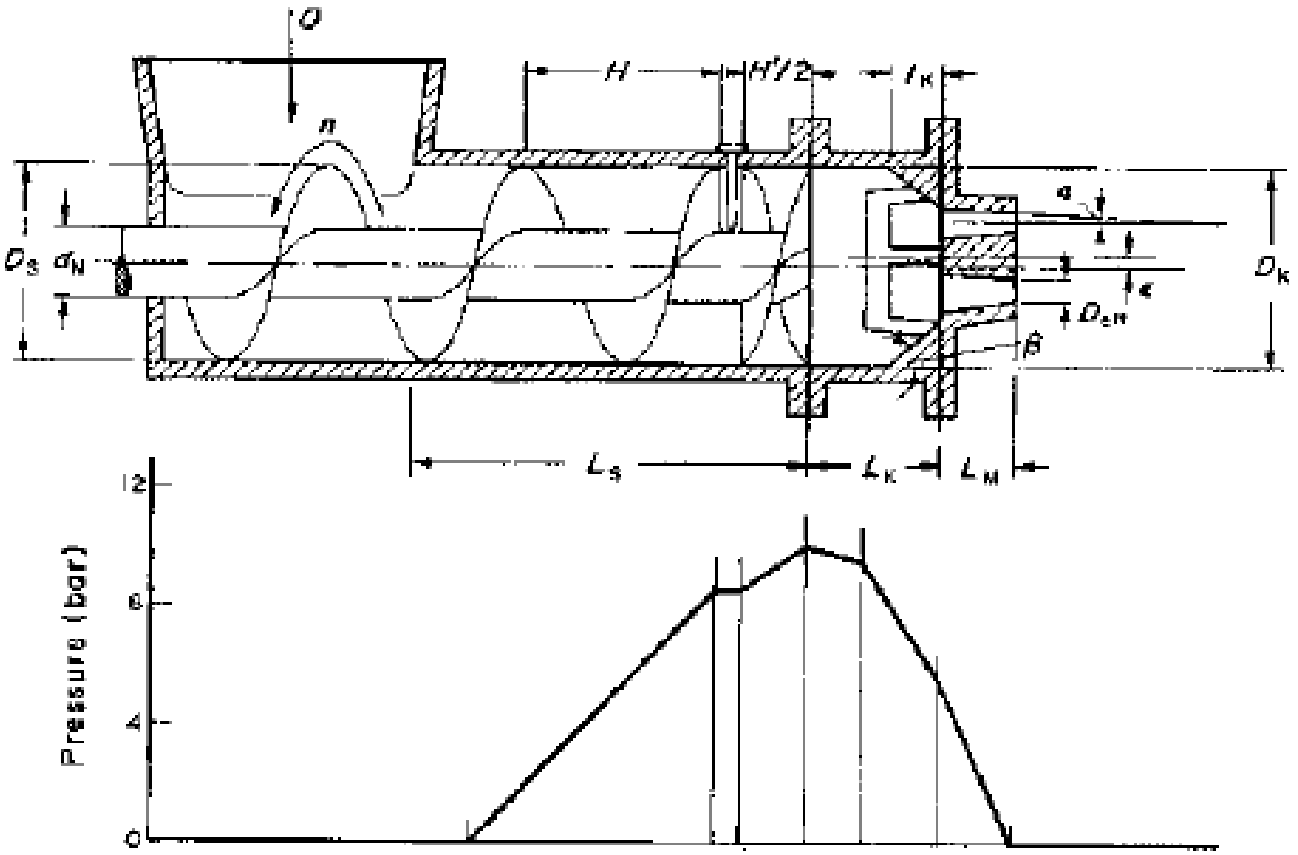

FIGURE 6.44 Pressure variation along a screw extrusion press. (From Ref. 54.)

The powders of advanced ceramics, when mixed with water, do not possess the desirable plastic characteristics found in the clay–water system. For this reason, they are mixed with a viscous solution containing a few weight percent of an organic binder to provide the desired plastic characteristics. The solvent is commonly water, but nonaqueous solvents (e.g., alcohols; mineral spirits) can also be used. Since the extruded body must also have sufficient green strength, the binder is generally selected from the medium to high viscosity grades, e.g., methylcellulose, hydroxyethyl cellulose, poly(acrylimides), or poly(vinyl alcohol). Methylcellulose undergoes *thermal gelation*, a property that offers considerable benefits for extrusion of ceramics (55).

Examples of compositions used in extrusion are given in Table 6.12. Aqueous systems are often flocculated using a small concentration of an additive (such as $MgCl_2$, $AlCl_3$, or $MgSO_4$). In addition, lubricants (e.g., stearates, silicones, or petroleum oils) are commonly used to reduce die-wall friction.

TABLE 6.12 Examples of Compositions Used in Extrusion

Whiteware		Alumina	
Material	Concentration (vol %)	Material	Concentration (vol %)
Kaolin	16	Alumina	45–50
Ball clay	16	Water	40–45
Quartz	16	Ammoniul polyacrylate (dispersant)	1–2
Feldspar	16	Methyl cellulose (binder)	5
Water	36	Glycerin (plasticizer)	1
$CaCl_2$ (flocculant)	<1	Ammonium stearate (lubricant)	1

6.4.3.3 Injection Molding

Two recent texts cover the principles and practice of injection molding of metals and ceramics (61,62). The subject is also considered in several review articles (63–65). The production of a ceramic article by injection molding involves the following steps: selection of the powder and the binder; mixing the powder with the binder, production of a homogeneous feed material in the form of granules, injection molding of the green body, removal of the binder (debinding) at lower temperatures and, finally, sintering at higher temperatures to produce a dense, final article. The debinding step involves features that are common to other forming methods (e.g., tape casting) and is considered later in this chapter. Here, we shall consider the key factors in powder and binder selection, preparation of the feed material, and injection molding of the green body.

Powder Characteristics

When the forming step is considered in combination with other processing steps such as debinding and sintering, the desirable powder characteristics for injection molding are generally no different from those described in Chapter 2 for powder processing. A small *particle size* is beneficial for shape retention during debinding and for ease of sintering, but the viscosity of the powder/binder mixture is higher and binder removal from the molded article is slower. A wide *distribution of particle sizes* gives a higher packing density, higher green strength, and lower shrinkage during sintering. On the other hand, the rate of binder removal is slower, the system is prone to segregation, and microstructural evolution during sintering is inhomogeneous. A spherical (or equiaxial) *shape* leads to higher packing density, lower viscosity of the powder–binder mixture, and improved flow during forming but also produces a lower green strength and leads to slumping during binder removal. Generally, an equiaxial powder, free from agglomeration and having an average particle size smaller than 10 μm, a narrow or wide particle size distribution, and a packing density greater than ~60%, is often suitable for most ceramic injection molding operations.

Binder System

Although the binder plays a transient role in the overall fabrication route, careful selection of a binder is vital to the success of the injection molding operation. The binder must provide the desired rheological properties to the feed material so that the powder can be formed into the desired shape and then must be removed completely from the shaped article prior to firing, without the disruption of the particle packing or any chemical reaction with the powder. A good binder must therefore have desirable rheological, chemical, and debinding characteristics. In addition, it must possess many qualities suitable for manufacturing such as environmental safety and low cost.

A single binder cannot provide all the desirable characteristics and, in practice, the binder system is generally a blend of at least three components: a major binder, a minor binder, and a processing aid. The *major binder* controls the rheology of the feed material during injection molding to produce a body free from defects and also controls the strength of the green body and the debinding behavior. The *minor binder* is used to modify the flow properties of the feed material for good filling of the mold. It may also provide benefits in the debinding stage by extending the range of conditions over which the binder is removed. The removal of the minor binder (by dissolution or by pyrolysis) creates a network of porosity through which the decomposition products of the major binder can be removed more easily. The processing aid may include small concentrations of one or all of the following: a plasticizer to reduce the glass transition temperature of thermoplastic binders, a surfactant to improve the wetting between the particle surfaces and the polymer melt, and a lubricant to reduce interparticle and die-wall friction.

Many binder systems are used in ceramic injection molding, and they can be classified into five types, based on the composition of the major binder phase: (1) thermoplastic compounds, (2) thermosetting compounds, (3) water-based systems, (4) gelation systems, and (5) inorganics. Of these, the thermoplastic compounds are the most widely used and understood. They include most of the common commercial polymers, such as polystyrene, polyethylene, polypropylene, poly(vinylacetate), and poly(methyl methacrylate). Examples of materials used for thermoplastic binder systems are given in Table 6.13.

TABLE 6.13 Thermoplastic Binder Systems for Ceramic Injection Molding

Major Binder	Minor binder	Plasticizer	Other additives
Polypropylene	Microcrystalline wax	Dimethyl phthalate	Stearic acid
Polyethylene	Paraffin wax	Diethyl phthalate	Oleic acid
Polystyrene	Carnauba wax	Dibutyl phthalate	Fish oil
Poly(vinyl acetate)		Dioctyl phthalate	Organo silane
Poly(methyl methacrylate)			Organo titanate

Powder–Binder Mixture

The ratio of powder to binder is a key parameter for successful injection molding. Too little binder in the mixture leads to a high viscosity and to the formation of trapped air pockets, both of which make molding difficult. On the other hand, too much binder leads to microstructural heterogeneities in the molded article and to slumping during binder burnout.

If f_m is the maximum packing density of the particles, defined as the volume fraction at which the particles touch so that flow is not possible, then the actual particle volume fraction f used in injection molding is 5–10 vol% lower than f_m. The remainder of the mixture consists of the binder and other additives. This means that for a well-dispersed powder, the particles are separated from their neighbors by a thin layer of polymer (~50 nm thick) during molding, which is required to achieve flow of the mixture. The volume fraction of particles f incorpo-

Two examples of the composition of the feed material are given in Table 6.14.

Table 6.14 Examples of Ceramic Injection Molding Feed Materials

Component	Composition (wt%)	
Powder	1 μm Al_2O_3 (85)	20 μm Si (82)
Major binder	Paraffin wax (14)	Polypropylene (12)
Minor binder	—	Microcrystalline wax (4)
Other additives	Oleic acid (1)	Stearic acid (2)

Molding

When compared to injection molding of plastics, control of the molding process in ceramics is more difficult because of the higher density, viscosity, thermal conductivity, and elastic modulus associated with the particle-filled polymer. The higher modulus and faster cooling rate (due to the higher thermal conductivity) coupled with the lower fracture toughness of the particle-filled polymer means that the molded article is prone to cracking due to the development of residual stress during the solidification process. Attempts have been made to model the residual stress development in ceramic injection molding, but a more practical approach, involving a systematic variation of the process variables, is often used to optimize the molding conditions.

Figure 6.48 illustrates the principle of operation of an injection molding machine and some of the parameters that influence its functioning. The feed material in the form of granules is fed into the machine, transported by a screw or plunger to the injection chamber where it is heated to produce a viscous mass, and then injected under pressure into the mold cavity. When the cavity is filled, the mold is cooled and the green body is ejected. It is obvious from Fig. 6.48b that a given machine variable can influence more than one of the fundamental variables. This, combined with the large number of variables, makes optimization of the process a considerable task. In general, injection molding is best applied selectively to the forming of small articles with complex shapes.