

Materials Processing

A Unified Approach to Processing of Metals,
Ceramics and Polymers

Materials Processing

A Unified Approach to Processing of Metals,
Ceramics and Polymers

Lorraine F. Francis

University of Minnesota

With contributions from

Bethanie J. H. Stadler

University of Minnesota

Christine C. Roberts

Sandia National Labs



AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO
Academic Press is an imprint of Elsevier



Academic Press is an imprint of Elsevier
125, London Wall, EC2Y 5AS, United Kingdom
525 B Street, Suite 1650, San Diego, CA 92101, United States
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

Copyright © 2016 Elsevier Inc. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

Chapter 6: Copyright © 2016 Elsevier Inc. All rights reserved. The contributions made by Ms. Christine Cardinal Roberts is under Sandia Corporation, Contract No. DE-AC04-94AL85000

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

ISBN: 978-0-12-385132-1

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress.

For Information on all Academic Press publications
visit our website at <http://store.elsevier.com/>



Working together
to grow libraries in
developing countries

www.elsevier.com • www.bookaid.org

Chapter 6

Dispersion and Solution Processes

By Lorraine F. Francis and Christine C. Roberts

6.1 INTRODUCTION

Dispersions and solutions are liquids that contain the building blocks of solid engineering materials. As described in Chapter 3, liquids have advantages for creating detailed 3D shapes, but it is not always possible or convenient to make a melt. A dispersion is a suspension of fine ceramic, metal, or polymer particles in a liquid medium, such as water. A solution, on the other hand, consists of molecules dissolved into a solvent. While there are a variety of solution precursor methods used to process materials, “solution” in this chapter refers to a solution of the final desired material in a solvent. This definition naturally restricts this category to polymer processing. Dispersions and solutions are similar in that they both involve a transient liquid. That is, the liquid medium is used to make the particles or molecules flow, but then eventually that liquid is removed, usually by evaporation, to leave behind a solid. The solid shape or coating may require additional post-processing steps, such as sintering, to develop structure and properties.

Though not a dispersion or a solution, liquid monomers and oligomers are also useful in materials processing and share the strategy of employing a liquid precursor to the final solid. In this regard, liquid monomers and oligomers (i.e., low molecular weight polymers) are easily made into coatings and polymerized by heating or exposure to ultraviolet (UV) radiation. Likewise, monomers are formed into 3D shapes, by virtue of additive manufacturing processes that also involve photopolymerization.

Figure 6.1 shows some examples of processes that employ dispersions, solutions, and liquid monomers. Complex 3D shapes are created using casting processes, such as slip casting (Figure 6.1a). These processes make use of the ability of the liquid precursors to flow into complex shapes defined by molds. After removal from the mold, drying, and sintering are needed. Coating processes (such as slot coating, Figure 6.1b) involve distributing

Materials Processing, DOI: <http://dx.doi.org/10.1016/B978-0-12-385132-1.00006-9>

© 2016 Elsevier Inc. All rights are reserved, including those for text and data mining, AI training, and similar technologies.
The contributions made by Ms. Christine Cardinal Roberts is under Sandia Corporation, Contract No. DE-C04-L85000

415

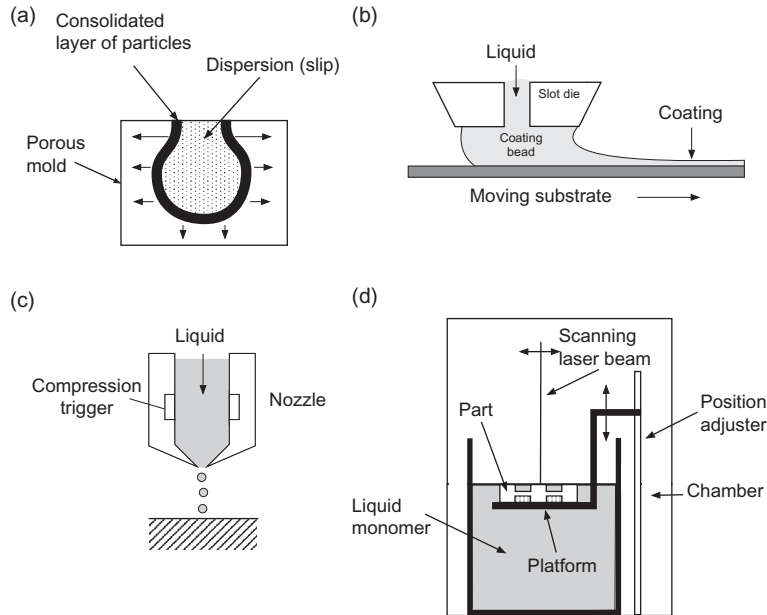


FIGURE 6.1 Schematics for processes that use dispersions, solutions and liquid monomers. (a) Slip casting—an aqueous dispersion is poured into a porous mold; water is extracted into the mold to create a layer of particles, which is the basis of the part. (b) Slot die coating—a dispersion, solution or monomer is forced under pressure through a die onto a moving substrate to create a coating. (c) Inkjet printing—the liquid flows into a nozzle where a compression trigger creates a pressure pulse in the liquid that results in droplets and printed structure. (d) Stereolithography—monomer is distributed on a build platform and converted to solid, layer-by-layer, using a scanning laser beam. [adapted from Venuvinod and Ma (2004)].

liquid uniformly onto a substrate and then solidifying by drying or curing. Printing operations, such as inkjet printing (Figure 6.1c), create 2D patterns on substrates. Such printing can be extended out of the plane of the substrate to make 3D parts, frequently with the use of photopolymerization. Another additive process is stereolithography (Figure 6.1d). Stereolithography, which is given the acronym SLA, uses a scanning laser to convert liquid monomer to a solid 3D part.

The fundamental steps of flow, shape definition, and shape retention are central to the processes in this chapter. Dispersions, solutions, and liquid monomers *flow* by gravity or under pressure into molds and onto substrate surfaces. In additive processes liquid flow is also required; for example, the monomer liquid must flow over the previous layer of the 3D part when the build platform is lowered. *Shape definition* in casting processes is clearly the function of the mold, while in coating processes the shape is essentially the thickness, which is defined by conditions of the process. For example, in slot coating the flow rate of liquid into the slot determines the

thickness of the deposited liquid layer. As in other additive manufacturing techniques, shape is defined by the CAD file, which provides the part size and features. The CAD file is converted into the instructions that drive the position of the inkjet nozzle or laser, for example. *Shape retention* is accomplished in a variety of ways due to the diversity that spans dispersions, solutions and monomers. In some cases, shapes, including coating thicknesses, are stable after drying. In dispersion processes, particles form bonds during drying, sometimes with the aid of a binder, and in polymer solution processes drying leads to solidification by glass transition or a process of fusing latex particles called film formation. Shape retention in monomer processes is due to chemical reactions that increase the molecular weight and form cross-links (i.e., curing). Likewise, a variety of post-processing operations, including continued drying and curing, binder removal, and sintering, are used.

Ceramic and metallic parts are made by a variety of processes that begin with a dispersion. The same sort of metal and ceramic particles that are discussed in Chapter 5 are used in dispersions. Particle sizes, however, are frequently tailored differently than they are for compaction of a dry powder. Ceramic and metal coatings are prepared by depositing dispersions onto substrates, followed by drying and sintering. Since these dispersions are made in simple liquids, such as water and organic solvents, fine particles are needed to prevent gravitational settling from dominating the dispersion characteristics. The particle size is frequently small enough that they are referred to as colloidal dispersions. However, in processes that involve the particles dispersed in polymer melts, which have a high viscosity, the sizes are tailored more to maximize the particle content as well as encourage subsequent sintering. Dispersions of metal and ceramic powders in polymer melts are injection molded into complex shapes. These shapes contain fairly high polymer content and require careful pyrolysis or “burnout” of the polymer before densification by sintering. For ceramics injection molding and slip casting, another dispersion-based process, are two common methods for creating complex shapes.

Polymeric parts and coatings are prepared from dispersions, solutions, or monomers. The polymer dispersion of most importance is latex. Latex is a generic term for submicron polymer particles created by emulsion polymerization in water. It is the starting material for making coatings, including adhesives and when combined with ceramic particles and additives, paints. Polymer solutions are frequently polymers dissolved in organic solvents that are deposited onto substrates and dried into solid polymer coatings. Lastly, monomers and oligomers are converted to polymer coatings or 3D shapes using thermal or more frequently energetic polymerization, such as UV curing.

The engineering of processes based on dispersions, solutions, and liquid monomers involves considerable attention to *formulation* in addition to the process steps themselves. In processes based on dispersions and solutions, the choice of the transient liquid and the formulation (i.e., the relative

amounts of all the components) are critical. The rheology of the liquid or the microstructure of the solids within the liquid can impact final product qualities and process costs in positive or negative ways. For example, for a liquid to properly fill a mold or spread onto a substrate requires it to flow easily, yet diluting the liquid can be expensive in terms of initial starting materials and create extensive drying process steps. Choice of the transient liquid, aqueous or organic, impacts the stability of the dispersion or solution as well as the drying process. Consequently, understanding and optimizing the liquid formulation so that its behavior is acceptable throughout all of the process steps is a main challenge. For liquid monomers, the engineering involves formulating monomers with initiators and selecting the conditions, such as the wavelength and intensity of the UV source, for rapid curing.

In this chapter, there is a section on fundamentals followed by examples of processes. The fundamentals section begins with an introduction to the colloidal dispersions, with an emphasis on understanding how to create a stable dispersion that does not sediment or aggregate appreciably with time, followed by an introduction to polymer solutions. The rheology of dispersions and solutions is then discussed, building on the rheological principles presented in Chapter 3. The fundamentals section rounds out with introductions to drying and curing. Four types of processes are then explored: shape casting, coating and tape casting, extrusion and injection molding, and liquid monomer-based additive processes.

6.2 FUNDAMENTALS

6.2.1 Colloidal Dispersions

Solid particles are often suspended or dispersed in a liquid medium as a means of preparing them for shape casting or coating. Dispersions are also called “suspensions,” and “slips” (i.e., ceramic dispersions that are used in the slip casting process). The phenomena that govern the interactions between particles and the behaviors of suspensions are independent of whether the particles are ceramic, polymer, or metal. However, there are substantial differences in behavior based on particle characteristics, such as density, electronic structure, and surface properties.

Dispersions are not thermodynamically stable, but dispersions of small particles can be made kinetically stable (i.e., the particles remain uniformly dispersed in the liquid medium without settling appreciably over time). In most cases, the particles are denser than the liquid that surrounds them and hence gravity opposes stability, especially for large particles or aggregates. Therefore, a stable suspension requires that the particles are small enough and that they do not aggregate. How small is small enough? The answer to this question depends on several factors, as described below. In general, the particles should be in the *colloidal* size range. Roughly speaking, a colloid is

a particle with a diameter less than $\sim 1\ \mu\text{m}$, small enough for Brownian motion to dominate over gravity (see below). Colloidal dispersions consist of colloids suspended in a liquid medium, usually, but not always, water.

This section provides background on the behavior of dispersions, focusing on the forces acting on particles and between particles. The simple forces acting on a single particle in a liquid are described first, followed by the attractive interactions between particles and the more complex repulsive interactions that are needed to make a suspension stable. The topic is presented as an introduction; the books on colloid science, listed at the end of the chapter, provide more details.

Forces Acting on a Single Particle in a Liquid. Consider the simplest suspension: a single, spherical particle in a liquid. This particle has a density of ρ_P , radius of R , and volume of V . The particle is suspended in a liquid of density ρ_L . The force of gravity, F_g , pulls the particle down and a buoyancy force, F_b , pulls the particle up. As shown in Figure 6.2, the net force depends on the densities and volume of the particle. In the most typical case, the density of the particle is greater than that of the liquid and the net force causes the particle to accelerate downward. As the particle velocity increases, the viscous force of resistance, F_v , opposing its movement also increases. In 1851, Stokes found that this viscous resistance is given by:

$$F_v = 6\pi\eta_L Rv \quad (6.1)$$

where η_L is the viscosity of the liquid surrounding the sphere and v is the velocity. Equation (6.1) holds true only when the flow of the liquid around the particle is laminar, a condition conveniently expressed as a limit on the single particle Reynolds number, Re_p :

$$Re_p = \frac{2Rv\rho_L}{\eta_L} \quad (6.2)$$

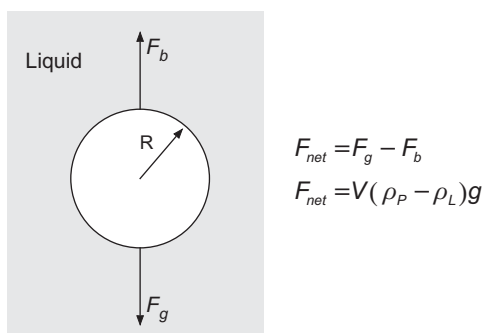


FIGURE 6.2 Forces acting on a spherical particle (density = ρ_P , radius = R , volume = V) suspended in a liquid (density = ρ_L , viscosity = η_L). The downward direction is taken as positive. When sphere begins to move, a viscous force is added in the direction opposite to the particle movement.

The Reynolds number is a ratio of the inertial force to the viscous force. For laminar flow, Re_p should be approximately less than one.

So, the velocity of the sphere in Figure 6.2 increases due to acceleration from gravity, but as its velocity increases so does the viscous drag force, which slows the particle. Eventually, the gravitation and viscous forces balance and a steady state or terminal velocity is reached:

$$v = \frac{2R^2(\rho_p - \rho_L)g}{9\eta_L} \quad (6.3)$$

In Equation (6.3), g is the gravitational constant and ρ_p is the density of the particle. Note that this equation predicts the rate of downward motion of particles denser than the liquid (sedimentation) as well as the rate of upward motion of particles (or bubbles) that are less dense than the liquid. The rate of sedimentation of particles (denser than the liquid) increases with particle size and density. The influence of liquid viscosity is also apparent.

The particle size dependence of sedimentation rates is exploited in particle size measurement instruments such as an optical or X-ray sedigraph. In these techniques, the sedimentation of a dispersion is tracked, not a single particle. The dispersion is dilute enough to ensure that the presence of neighboring particles does not influence the liquid flow. Hydrodynamic and thermodynamic interactions become important at high particle concentrations, causing deviations from Stokes' law (Eq. (6.1)). The method has other limitations. The upper size limit is set by the restriction that Stokes' law is obeyed, which requires Re_p to be below 1. Large particles accelerate to velocities high enough that the inertia of the liquid surrounding the particle becomes important and the condition of laminar flow is not met. See Example 6.1. For these particles, Eq. (6.1) cannot be used. The lower size limit is based on the time that it takes for very small particles to settle. This size limit can be adjusted by using a centrifuge, which adds a force to accelerate the particles.

In addition to the effects of gravity and buoyancy, another force can affect particle position. Molecules in the liquid are under constant thermal motion. Therefore, the local molecular density in the liquid fluctuates, leading to unbalanced forces on the particle surface and random motion of the particle. This random motion is known as Brownian motion, after R. Brown, the scientist who first observed the phenomena. Einstein treated Brownian motion as a random walk problem. The root mean square displacement of the particle over time t is given by:

$$\begin{aligned} \bar{x} &= \langle x^2 \rangle^{1/2} = \sqrt{2Dt} \quad (\text{one dimensional}) \\ \bar{x} &= \langle x^2 \rangle^{1/2} = \sqrt{6Dt} \quad (\text{three dimensional}) \end{aligned} \quad (6.4)$$

EXAMPLE 6.1 Calculate upper particle size limit for the use of sedimentation velocity for particle size measurement of the following particles suspended in water (20°C): (a) tungsten, (b) alumina, and (c) polystyrene. Assume spherical particles.

The use of sedimentation velocity (Eq. (6.3)) requires that Re_p is less than ~ 1 . So, at the upper size limit Re_p is equal to 1.

$$Re_p = \frac{2Rv\rho_L}{\eta_L} = 1.0$$

The velocity is given by Eq. (6.3).

$$v = \frac{2}{9} \frac{R^2(\rho_p - \rho_L)g}{\eta_L}$$

Therefore,

$$1.0 = \frac{4}{9} \frac{R^3 \rho_L (\rho_p - \rho_L) g}{\eta_L^2}$$

At 20°C, the viscosity and density of water are 1.005×10^{-3} Pa•s and 998 kg/m³, respectively. The expression above can be solved for R , which in this case is the maximum size. The magnitude of R depends on the density of the particle. Density data and the calculated $R_{\max}$ are given in the following table.

Material	Density (kg/m ³)	$R_{\max}$ (μm)	Max particle diameter (μm)
Tungsten (W)	19,300	23	46
Alumina (Al ₂ O ₃)	3,980	43	86
Polystyrene (PS)	1,050	164	328

where t is time and D is the diffusion coefficient of the particle. Here, $\bar{x}$ is used for the average distance a particle will travel from its starting point by Brownian motion. The particle diffusion coefficient takes into account the viscous resistance discussed above and is given by the Stokes-Einstein relationship:

$$D = \frac{kT}{6\pi R\eta_L} \quad (6.5)$$

where k is Boltzmann's constant, R is the sphere radius, and T is temperature in Kelvin. See Example 6.2. In combination with Fick's laws, this diffusion coefficient can be used to predict how the concentration of particles varies in space and time. For example, when a drop of a concentrated dispersion of small particles is added to water, the particles diffuse from high concentration to low concentration, eventually erasing the concentration gradient.

Since the rate of Brownian motion depends on the particle diameter, it is also exploited in particle size measurement techniques. Light scattering, also called photon correlation spectroscopy, is one of the most common techniques for measuring particle size. As particles diffuse in and out of the path of a laser

EXAMPLE 6.2 Consider an alumina particle with a diameter of 0.1 μm suspended in water at 20°C for one minute. Calculate the mean distance the particle travels by Brownian motion in three dimensions. Repeat for a 1 μm particle and a 10 μm particle.

The diffusion coefficient of the 0.1 μm alumina particle is:

$$D = \frac{kT}{6\pi R\eta_L} = \frac{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{6\pi(5 \times 10^{-8} \text{ m})(1.005 \times 10^{-3} \text{ Pa} \cdot \text{s})} = 4.27 \times 10^{-12} \text{ m}^2/\text{s}$$

Therefore the mean distance traveled in 1 min is:

$$\bar{x} = \sqrt{6Dt} = \sqrt{(6)(4.27 \times 10^{-12} \text{ m}^2/\text{s})(60 \text{ s})} = 3.9 \times 10^{-5} \text{ m} = 39 \mu\text{m}$$

Repeating these calculations for 1 μm and 10 μm size particles reveals diffusion coefficients of $4.27 \times 10^{-13} \text{ m}^2/\text{s}$ and $4.27 \times 10^{-14} \text{ m}^2/\text{s}$, respectively, and mean displacements of 12.3 μm and 3.9 μm , respectively.

beam, they create light intensity fluctuations that can be correlated to the diffusion rate. The inferred diffusion coefficient can then be used to calculate the particle size assuming the particles are only experiencing Brownian motion. Particle tracking is another common technique, whereby an optical microscope and a high-speed video camera are used to directly image diffusing particles. Particle tracking algorithms have been developed to identify the particles in the images and link their positions into tracks. Since the images are only two-dimensional projections of a three-dimensional diffusion process, a modified form of Eq. (6.4) is used to relate the distance traveled by the particle and the diffusion coefficient ($\bar{x} = \sqrt{4Dt}$). From the Brownian diffusion coefficient, the particle size can be calculated using Eq. (6.5). However, particle tracking is more commonly used to find the fluid viscosity when the particle size is known and the fluid viscosity is unknown. As with sedimentation, if Eq. (6.5) is to be used, it must be valid; particles must be dilute in the suspension and of colloidal size. Furthermore, the fluid must be optically clear for both techniques.

Unlike this simple starting point of a single sphere in a liquid, dispersions are composed of many, many particles in a liquid medium. Each particle is simultaneously moving due to gravity, Brownian motion, and perhaps other forces. As a consequence, particles periodically approach one another, where they are subjected to particle-particle interaction forces. For example, van der Waals attractive forces act to draw particles nearer and nearer to each other so that agglomerates are formed. However, repulsive forces that come about due to particle surface charge or steric effects from adsorbed polymers or surfactants on the particle surfaces can counter this attraction.

Van der Waals Attraction. The origin of van der Waals attractive forces between particles is the interaction between atomic and molecular dipoles on the particle surfaces. There are different types of van der Waals forces, the most

common of which are called the “London forces.” London forces arise when an atomic dipole, created by a momentary fluctuation of the atom’s electron cloud, induces a dipole in a nearby atom or molecule. The negative side of one dipole is attracted to the positive side of the other. Additional van der Waals forces arise if a molecule has a permanent dipole (e.g., HCl); neighboring permanent dipoles may attract each other (Keesom forces) and the permanent dipole can induce dipoles in neighboring atoms or molecules (Debye forces).

Van der Waals forces are considered weak in the context of interatomic bonding. However, the forces are additive, which means that the strength of the van der Waals attraction between surfaces is obtained by summing over the attractive interactions between many, many atoms or molecules on the neighboring surfaces. For interactions between colloidal particles, therefore, van der Waals forces are significant.

To find an expression for the van der Waals attractive force, the geometry of the surfaces must be specified. For two identical spherical particles of radius R , the van der Waals force of attraction, F_A , is given by:

$$F_A = \frac{AR}{12h^2} \quad (6.6)$$

where A is the Hamaker constant (see below) and h is the separation distance between the particles. This expression holds when the separation distance is small compared to the particle size ($h \ll R$). Equation (6.6) shows that the force of attraction becomes stronger as the separation distance between the particles becomes smaller.

The Hamaker constant depends not only on the material that makes up the colloid, but also on the liquid (or gas) that intervenes between the particles. The Hamaker constant required to predict the van der Waals force of attraction between two identical particles of material 1 with material 3 intervening is approximately:

$$A_{131} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right)^2 \quad (6.7)$$

where A_{11} and A_{33} represent the constant for the material interacting with itself across a vacuum. Different equations are needed to find the attractive interactions between dissimilar particles. Hamaker constants for several materials with vacuum or water as the intervening material are given in Table 6.1.

The potential energy of attraction, U_A , is found by integrating Eq. (6.6) with respect to separation distance:

$$U_A = \frac{-AR}{12h} \quad (6.8)$$

This equation, like the force equation, is valid only for the condition that the separation distance is much less than the size of the particle ($h \ll R$).

TABLE 6.1 Hamaker Constants for Metals, Ceramics and Polymers
(in units of 10^{-20} J)^a

Material	With Vacuum Intervening	With Water Intervening
Silver	50	40
Copper	40	30
Fused Silica (SiO ₂)	6.5	0.83
Sapphire (Al ₂ O ₃)	15.6	5.32
Polystyrene (PS)	7.9	1.3
Polytetrafluoroethylene (PTFE)	3.8	0.33

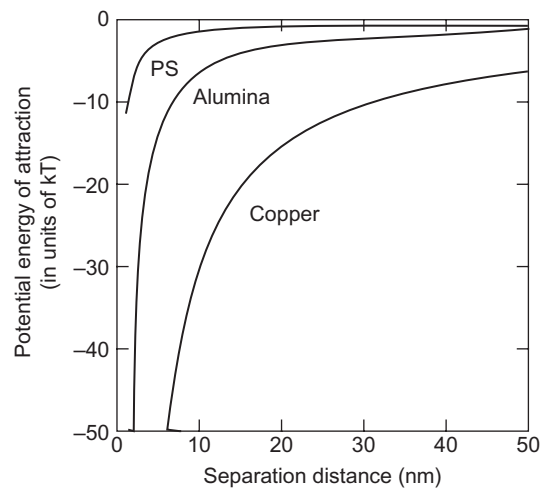
^aData tabulated in *Russel et al. (1989)***FIGURE 6.3** The effect of separation distance on the van der Waals attraction between $0.1\ \mu\text{m}$ diameter particles of polystyrene (PS), alumina and copper at 25°C . Note at 25°C , $kT = 4.11 \times 10^{-21}$ J.

Figure 6.3 shows the effect of separation distance on the potential energy of attraction for $0.1\ \mu\text{m}$ diameter colloids of different materials in water. As particles approach, attraction becomes stronger and stronger. The strength of the attraction also depends on the type of material; materials with higher Hamaker constant are more strongly attracted to each other than those with lower Hamaker constants.

While van der Waals attraction pulls particles close together, repulsive interactions between the particles prevent the separation distance from reaching zero. For bare, neutral particles, this repulsion arises from the overlap of core shell electrons of the atoms on the surface of the particles (i.e., the same repulsion that is considered in interatomic bonding). This repulsion is very short range (i.e., less than 1 nm) and the resulting total interaction energy attained by summing the attractive and repulsive components has a very deep, primary minimum. This minimum means that it is energetically favorable for particles to approach each other and remain at the separation distance defined by the position of this deep potential energy minimum. The depth of this minimum is many times the thermal energy (kT). Intense mechanical agitation is needed to break apart particles drawn together in such a primary minimum.

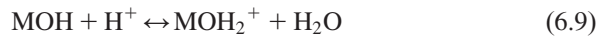
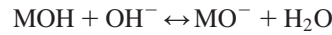
Repulsive forces, beyond those provided by inner shell electrons, are needed to prepare a stable suspension. When van der Waals attraction dominates, particles that approach one another are drawn together, forming agglomerates. Over time, more particles join the agglomerates and eventually, the size of the agglomerates makes them susceptible to sedimentation. Or if the particle concentration is high then the particles can actually interconnect into a gelled network. To prevent this spiraling process, repulsive interactions must be deliberately built into the system. One approach is to design the suspension so that the particles gain a surface charge and electrostatic repulsion goes into effect. Another route is to adsorb a polymer or surfactant on the particle surfaces, creating a steric layer that presents a repulsive interaction.

Electrostatic Repulsion. Particles that have the same type of surface charge (positive or negative) repel each other. The effectiveness of this electrostatic repulsion depends on the magnitude of the surface charge and also the characteristics of the liquid in which the particles are dispersed. Below, mechanisms for gaining surface charge are outlined, followed by a description of the response of the liquid medium to the charged surface (the electrical double layer) and, lastly, expressions for the potential energy of electrostatic repulsion.

There are several ways in which solid particles acquire a charge in a liquid medium. The most common are adsorption of potential determining ions, ionization of surface groups, and ion dissolution. The tendency of a material to acquire charge by any of these mechanisms depends on the material's chemistry and structure, and the nature of the liquid. Water, as a polar liquid, is an effective medium for developing a surface charge on a particle. The modes of surface charge development are discussed by way of examples, below.

A common mechanism is the adsorption of potential determining ions from the liquid. The term "potential determining ions" comes about because the adsorption of these ions onto the surface of the material sets up a charge on the surface and in turn, the charge determines the electric potential at

the surface. For example, hydrogen and hydroxyl ions are potential determining ions for ceramic metal oxide particles dispersed in water. In water, the surfaces of metal oxides tend to be hydrated (i.e., covered with hydroxyl groups). Lowering the pH of the water results in adsorption of hydrogen ions and an increase in the number of positive surface sites (OH_2^+), while raising the pH leads to adsorption of hydroxyl ions and an increase in the number of negative surface sites (O^-). For a generic metal oxide (MO) with surface hydroxyls (MOH), these adsorption reactions are given as:



Each reaction has an equilibrium constant and the tendency for one reaction over the other depends on the metal oxide structure, particularly the nature of the metal-oxygen bond. At a certain pH, there are equal numbers of positive and negative surface charges and hence a neutral surface. This special pH is known as the point of zero charge (PZC). See Figure 6.4. The PZC

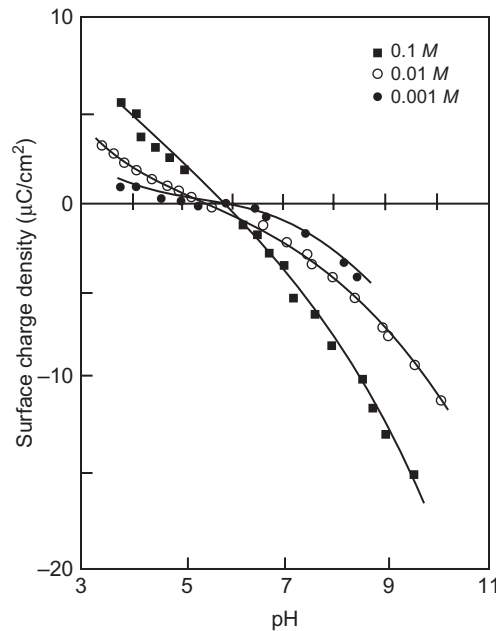


FIGURE 6.4 Change in the surface charge density of titania particles with pH in aqueous KNO_3 solutions. At $\text{pH} < \text{point of zero charge (PZC)}$, the net surface charge is positive and at $\text{pH} > \text{PZC}$ the net surface charge is negative. PZC is pH 5.8. Note that the presence of the K^+ and NO_3^- ions does not change the position of the PZC, but does affect the magnitude of the surface charge density away from the PZC. K^+ and NO_3^- are called indifferent ions. Adapted from Yates and Healy (1980).

depends on the chemistry of the oxide. At pH values well above the PZC or well below the PZC, surface charge density is greatest.

Non-oxide ceramics, such as silicon nitride, and some metals develop a thin layer of metal oxide on their surfaces when placed in water and therefore develop surface charge in a similar way as their the complementary metal oxide.

Dissociation or ionization of surface groups is a common means by which polymer latex particles acquire charge. The emulsion polymerization technique that generates the latex often leaves behind initiators that bear charge or stabilizers (e.g., surfactants) that are ionic or contain ionizable groups (e.g., carboxylic acid groups, COOH). Carboxylic acid groups, for example, ionize as the pH increases, forming COO^- groups, leading to a negative surface charge. Likewise, polyelectrolytes (polymers that have ionizable groups) behave in a similar way when they are adsorbed onto particle surfaces.

Ion dissolution is a means of developing surface charges on clay particles. Clays have a layered crystal structure with positive cations between the layers. These cations dissolve into water when the particles are dispersed, leaving the particles deficient in positive charge. This interaction results in a net negative charge on clay platelet faces, while the charge on the edges of the platelets responds to the pH-dependent ion adsorption.

Surface charge density can be quantified using titration methods; the data in Figure 6.4 is an example. However, expressions for the repulsive force between charged particle surfaces require knowledge of the electric potential, which is the consequence of the charged surface. There is a distribution in electric potential away from the charged surface into the electrolyte liquid. The sign of the surface potential is the same as that of the surface charge, but uncovering the relationship between the two requires first an understanding of the electric potential distribution.

The Electrical Double Layer. Charged particle surfaces influence the distribution of ions in the adjacent liquid. Oppositely charged ions (counter-ions) are attracted to the surface and those of the same charge (co-ions) are repelled. Electrical neutrality is achieved by the accumulation counterions near the surface, but thermal motion results in a diffuse region of varying ion concentration rather than a discrete layer of ions. (See Figure 6.5.) Hence, the electric potential varies continuously as a function of the distance away from the surface. As might be imagined, the nature of this variation depends on properties of the liquid, namely its dielectric constant and its ionic composition. The combination of the charged surface and the diffuse charged layer in the liquid is commonly referred as a *double layer*.

In the early 1900's, Gouy and Chapman derived an expression for the variation in potential away from the charged surface. The starting point for the derivation is Poisson's equation, which is given here for the

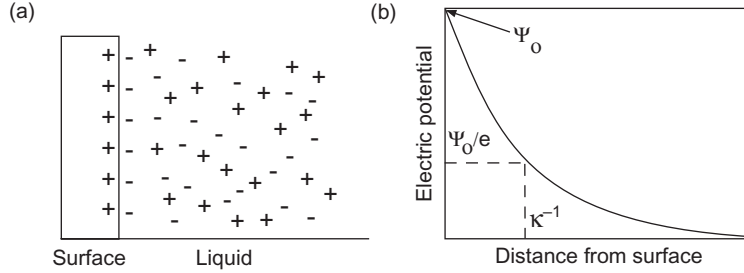


FIGURE 6.5 Schematic diagrams showing (a) a charged surface and the distribution of ions in the adjacent liquid and (b) the variation in electric potential with distance from the surface, based on a functional form derived in the text.

one-dimensional variation in electric potential Ψ as a function of distance (x) away from the charged surface:

$$\frac{d^2\Psi}{dx^2} = -\frac{\rho}{\varepsilon_o\varepsilon_r} \quad (6.10)$$

where ε_r is the relative permittivity or dielectric constant of the liquid, ε_o is the permittivity of free space (8.85×10^{-12} F/m), and ρ is the charge density of the liquid. A solution to this equation provides the functional form of the potential distribution away from the surface, but it does not give the magnitude of the potential at the surface (Ψ_0). Relating this value to the surface charge density is the second step.

The charge density of the liquid is found by summing the contributions of all free ions in the liquid.

$$\rho = \sum_i Z_i e N_i \quad (6.11)$$

where Z_i is the sign and valence of the i th ion (e.g., for Na^+ , $Z = +1$ and for Cl^- , $Z = -1$), e is the electron charge (1.602×10^{-19} C), and N_i is the concentration of the i th ion in number per unit volume. It is instructive to consider the charge density of an aqueous NaCl solution in the absence of any charged particles. The charge density of this solution is 0, because there are equal numbers of positive and negative ions (electrical neutrality). Due to the presence of ions, the solution is called an electrolyte. The electrical neutrality condition holds for all electrolytes, even pure water. The charge density of an electrolyte, however, changes locally near a charged particle surface and this variation gives rise to the variation in potential.

The concentration of ions in the electrolyte at some position near a charged surface depends on the value of Ψ at that position and the effects of

thermal disorder. The Boltzmann equation provides a distribution based on these two effects:

$$N_i = N_{io} \exp\left(\frac{-Z_i e \Psi}{kT}\right) \quad (6.12)$$

where k is Boltzmann's constant (1.38×10^{-23} J/K) and T is absolute temperature. N_{io} is the bulk concentration of ion i , the concentration at some distance away from the charged surface where Ψ drops to zero.

With this information, Poisson's equation becomes:

$$\frac{d^2 \Psi}{dx^2} = -\frac{1}{\varepsilon_o \varepsilon_r} \sum_i Z_i e N_{io} \exp\left(\frac{-Z_i e \Psi}{kT}\right) \quad (6.13)$$

The solution to this equation is the electric potential as a function of position away from the charged surface. To get to a solution easily, a simplifying assumption is helpful. If $Z_i e \Psi$ is much less than kT (which amounts to assuming that the electrostatic energy of the ions is much less than their thermal energy), then the higher order terms in the expansion of the exponential in Eq. (6.13) can be ignored (i.e., $\exp(y) = 1 + y$). This assumption is called the Debye-Huckel approximation and results in:

$$\frac{d^2 \Psi}{dx^2} = -\frac{1}{\varepsilon_o \varepsilon_r} \sum_i Z_i e N_{io} \left(1 - \frac{Z_i e \Psi}{kT}\right) = -\frac{1}{\varepsilon_o \varepsilon_r} \left[\sum_i Z_i e N_{io} - \sum_i \frac{(Z_i e)^2 N_{io} \Psi}{kT} \right] \quad (6.14)$$

Electrical neutrality requires the bulk solution to have no net charge (i.e., $\sum_i Z_i e N_{io} = 0$); therefore:

$$\frac{d^2 \Psi}{dx^2} = \frac{\sum_i (Z_i e)^2 N_{io}}{\varepsilon_o \varepsilon_r kT} \Psi = \kappa^2 \Psi \quad (6.15)$$

The term κ lumps together a number of parameters that are constant for a given electrolyte liquid. The solution to Eq. (6.15) then can be found, using the boundary conditions of $\Psi = \Psi_o$ at $x = 0$ (the position of the charged surface) and $\Psi = 0$ at a distance far from the surface ($x = \infty$).

$$\Psi = \Psi_o \exp(-\kappa x)$$

or

$$\Psi = \Psi_o \exp\left(-\frac{x}{\kappa^{-1}}\right) \quad (6.16)$$

The term κ^{-1} is a benchmark distance known as the double layer thickness or Debye length. Numerically, κ^{-1} is the distance at which the potential drops to $1/e$ of its value at the surface, Ψ_o (the surface potential).

Based on Eqs. (6.15) and (6.16) the double layer thickness is given by:

$$\kappa^{-1} = \left(\frac{\varepsilon_o \varepsilon_r kT}{\sum_i (Z_i e)^2 N_{io}} \right)^{1/2} \quad (6.17)$$

The double layer thickness decreases as the concentration of ions in the liquid increases. This trend is intuitive as the presence of more ions allows the surface charge to be screened more effectively. Likewise, ions of higher valence (Z_i) compress the double layer more than those of lower valence. The dielectric constant of the liquid also plays an important role in the potential variation: liquids with higher dielectric constants create larger electrical double layers if all other parameters are equal. Note that the double layer thickness characterizes the potential distribution; it is not affected by the magnitude of the surface charge. [Example 6.3](#) shows how the double layer thickness is calculated.

EXAMPLE 6.3 (a) Calculate the double layer thickness for a 0.1 M aqueous solution of potassium nitrate (KNO_3) with a pH 4. (b) Repeat for a 0.01 M KNO_3 solution also with pH 4. (c) Plot the variation in potential as a function of distance away from a charged surface for the two electrolytes in (a) and (b). Assume $T = 25^\circ\text{C}$ for all calculations.

- a. The concentrations of K^+ and NO_3^- are given in moles per liter and therefore must first be converted to number per m^3 .

$$[\text{K}^+] = [\text{NO}_3^-] = 0.1 \text{ mol/L}$$

$$\frac{0.1 \text{ mol}}{\text{L}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{6.023 \times 10^{23} \text{ ions}}{\text{mole}} = 6.023 \times 10^{25} \text{ ions/m}^3$$

$$N_{K,o} = N_{\text{NO}_3,o} = 6.023 \times 10^{25} \text{ ions/m}^3$$

The pH of the solution is given and so the concentrations of H^+ and OH^- can also be found.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4} \text{ mol/L} \text{ and } [\text{OH}^-] = 10^{-(14-\text{pH})} = 10^{-10} \text{ mol/L}$$

The concentrations of these ions are negligible compared with those of K^+ and NO_3^- .

Given or known: ε of water is 80, $\varepsilon_o = 8.85 \times 10^{-12} \text{ F/m}$, $k = 1.38 \times 10^{-23} \text{ J/K}$, $T = 298\text{K}$, $e = 1.602 \times 10^{-19} \text{ C}$. [Note that $\text{F/m} = \text{C}/(\text{V} \cdot \text{m})$ and $\text{J} = \text{V} \cdot \text{C}$.]

$$\begin{aligned} \kappa^{-1} &= \left(\frac{\varepsilon_o \varepsilon_r kT}{\sum_i (Z_i e)^2 N_{io}} \right)^{1/2} \\ &= \left(\frac{(8.85 \times 10^{-12} \text{ F/m})(80)(1.38 \times 10^{-23} \text{ J/K})(298\text{K})}{(1.602 \times 10^{-19} \text{ C})^2 [(+1)^2 (6.023 \times 10^{25} \text{ ions/m}^3) + (-1)^2 (6.023 \times 10^{25} \text{ ions/m}^3)]} \right)^{1/2} \\ &= 9.7 \times 10^{-10} \text{ m} = 0.97 \text{ nm} \end{aligned}$$

- b. For the electrolyte with lower salt concentration, the calculation is repeated using the same methods as in (a). The result is $\kappa^{-1} = 3.07 \times 10^{-9} \text{ m} = 3.07 \text{ nm}$.
- c. The potential distribution is found by plotted Ψ/Ψ_o as a function of x from Eq. (6.16). Note that the thin horizontal line represents the condition of $\Psi = \Psi_o/e$ and therefore the intersection of the horizontal line with the data gives the double layer thickness.

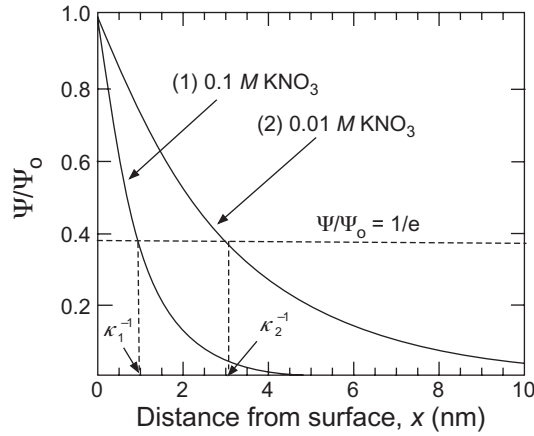


FIGURE E6.3

Equation (6.16) shows how the potential varies as a function of distance away from the surface, but it does not give any information on the value of surface potential, Ψ_o . The surface potential depends on the surface charge density, σ_o , which is established by one of the mechanisms described above, and the properties of the liquid medium. For electrical neutrality, the surface charge density is balanced by an equal and opposite number of charges per unit area in the electrolyte as it extends from the surface.

$$\sigma_o = - \int_0^{\infty} \rho dx \quad (6.18)$$

Again, x is the position coordinate with $x = 0$ at the charged surface and the electrolyte at $x > 0$. Using Poisson's equation (Eq. (6.10)), the surface charge density can be shown to be directly proportional to the gradient in potential at the surface.

$$\sigma_o = \epsilon_r \epsilon_o \int_0^{\infty} \frac{d^2 \Psi}{dx^2} dx = \epsilon_r \epsilon_o \left. \frac{d\Psi}{dx} \right|_0^{\infty} = - \epsilon_r \epsilon_o \left. \frac{d\Psi}{dx} \right|_0 \quad (6.19)$$

Then, using the approximate solution for $\Psi(x)$ in Eq. (6.16), the surface charge density is found to be proportional to the surface potential.

$$\sigma_o = \frac{\varepsilon_r \varepsilon_o}{\kappa^{-1}} \Psi_o \quad \text{or} \quad \Psi_o = \frac{\kappa^{-1}}{\varepsilon_r \varepsilon_o} \sigma_o \quad (6.20)$$

Equation (6.20) shows that surface potential has the same sign as the surface charge density and is proportional to it, but the characteristics of the electrolyte are also important. For example, consider the data in Figure 6.4, which shows surface charge density of titania particles in water at a pH less than the PZC increases with an increase in salt concentration (decrease in κ^{-1}). For titania (and most other metal oxides), H^+ and OH^- are the potential determining ions and their concentration determines the surface potential; the salt ions are indifferent (located in the diffuse layer only). At a given pH, the surface potential remains constant as the salt is added; to maintain electrical neutrality, the surface charge density increases. That is, more H^+ ions are adsorbed onto the surface as salt is added. Example 6.4 explores local ionic concentrations. On the other hand, if the charge on the particles is determined by ion dissolution (e.g., clays), then that surface charge density remains constant as salt is added and the surface potential adjusts.

The repulsion that develops between the charged surfaces depends on the magnitude of the surface potential and the nature of the potential distribution away from the surface (i.e., the double layer thickness). The effect of the surface potential is easy to understand—the higher the surface potential, the higher is the repulsive force and the potential energy of repulsive interaction. The effect of the double layer thickness takes some thought. If we imagine two charged surfaces approaching one another, they begin to “feel” repulsion when the outermost portions of their diffuse layers overlap. Therefore, if the surface potential is constant, a larger electrical double thickness results in repulsion appearing at a point further from the charged surface. Having this sort of far-reaching repulsive effect is important for stability, which is essentially combating the van der Waals attraction as discussed more below.

Deriving an expression for the potential energy of repulsion between particles requires assumptions about the particle size, distance over which the expression is accurate, and the double layer thickness relative to the particle size. Here, two expressions for the potential energy of repulsion between spherical particles that have constant surface potential are presented. When the particles are large relative to the double layer thickness ($\kappa R > 10$), the potential energy of repulsion, U_R , as a function of separation distance, h , is:

$$U_R = 2\pi\varepsilon_r\varepsilon_o\Psi_o^2R \ln[1 + \exp(-\kappa h)] \quad (6.21)$$

EXAMPLE 6.4 Consider a suspension of titania particles in an aqueous KNO_3 solution at pH 4. (a) Estimate the surface potential of the titania particles in a suspension 0.1 M KNO_3 . Use data in Figure 6.4 and Example 6.3. (b) Plot the potential as a function. (c) Plot the variation in ion concentrations (K^+ and NO_3^-) as a function of distance from the titania surface. Assume $T = 25^\circ C$ for all calculations. Assume that the Debye-Huckel approximation holds.

- a. The surface potential can be calculated using Eq. (6.20) and data from Figure 6.4 and Example 6.3.

From Figure 6.4, the surface charge density of titania at pH 4 and 0.1 M KNO_3 is $\sim 5 \mu C/cm^2$. From Example 6.3, κ^{-1} for this electrolyte is $9.7 \times 10^{-10} m$.

$$\Psi_o = \frac{\kappa^{-1}}{\epsilon_r \epsilon_o} \sigma_o = \frac{9.7 \times 10^{-10} m}{(80) \left(8.85 \times 10^{-12} \frac{C}{Vm} \right)} (5 \times 10^{-2} C/m^2) = 6.85 \times 10^{-2} V$$

- b. The potential distribution is plotted using the answer to (a) and Eq. (6.16).

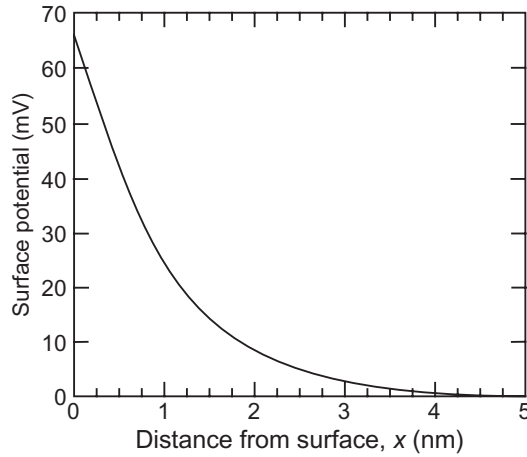


FIGURE E6.4A

- c. The ion concentrations are found using the answers above and Eq. (6.12). The bulk ion concentrations are given in Example 6.3.

$$N_{K,o} = N_{NO_3,o} = 6.02 \times 10^{25} \text{ ions}/m^3$$

$$N_K = N_{K,o} \exp\left(\frac{-(1)e\Psi}{kT}\right) \text{ and } N_{NO_3} = N_{NO_3,o} \exp\left(\frac{-(-1)e\Psi}{kT}\right)$$

$$\frac{N_K}{N_{K,o}} = \exp\left(\frac{-e\Psi}{kT}\right) \text{ and } \frac{N_{NO_3}}{N_{NO_3,o}} = \exp\left(\frac{e\Psi}{kT}\right)$$

The ion concentrations as a function of position are calculated using the potential distribution found in part (b), being careful of units (recall that $J = V \cdot C$).

The plots above show the higher concentration of anions near the positively charged surface. The concentrations plotted are relative to the bulk concentration.

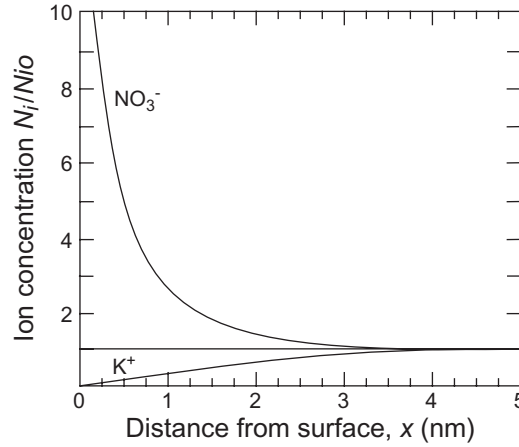


FIGURE E6.4B

When the particles are smaller relative to the double layer thickness ($\kappa R < 5$), the potential energy of repulsion as a function of separation distance is:

$$U_R = 2\pi\epsilon_r\epsilon_o\Psi_o^2 R \exp(-\kappa h) \quad (6.22)$$

These expressions are approximations that are best used with particles having a low surface potential (< 25 mV). In spite of this limitation, they are useful in illustrating the effect of key parameters on repulsive interaction. Both show that regardless of the position h , U_R increases with an increase in the dielectric constant of the liquid as well as with an increase in the size or surface potential of the particles. The spatial variations depend on the double layer thickness: both $\exp(-\kappa h)$ and $[1 + \exp(-\kappa h)]$ decrease with h and that decrease is steeper when κ is large (κ^{-1} small). For more information on the origin of these expressions and for additional information, see [Hunter \(1989\)](#).

Clearly, the surface potential is an important characteristic; however, it is difficult to quantify exactly. The most practical way to estimate the surface potential is to set the particle into motion by applying an electric field and determine the potential at the shear plane between the moving particle and the liquid. This shear plane is close to the particle surface and so the potential there, a quantity known as the zeta potential, can be considered as an approximation for the surface potential. Consider a nonconducting particle of radius R in a liquid with a viscosity of η_L and dielectric constant

of ε_r . Applying an electric field of strength E causes the particle to move with a velocity v_E , which can be measured and the zeta potential is computed by the following expression:

$$\zeta = \frac{C\eta_L v_E}{\varepsilon_o \varepsilon_r E} \quad (6.23)$$

where C is a constant that depends on κR . The value of C ranges from $C = 2/3$ at $\kappa R < 1$ to $C = 1$ at $\kappa R > 100$.

The value of the zeta potential is an important factor determining the extent of the electrostatic repulsive interaction between particles. The zeta potential is used in the calculation of the potential energy of repulsion (Eqs. (6.21) and (6.22)). Like surface potential, the zeta potential of an oxide particle changes with pH. See Figure 6.6. The pH value at which the zeta potential is zero is called the isoelectric point, *IEP*. Suspensions at pH values appreciably higher or lower than the *IEP* have higher zeta potentials and hence higher surface potentials and greater repulsive interactions. Because the magnitude of the zeta potential is close to that of the surface potential,

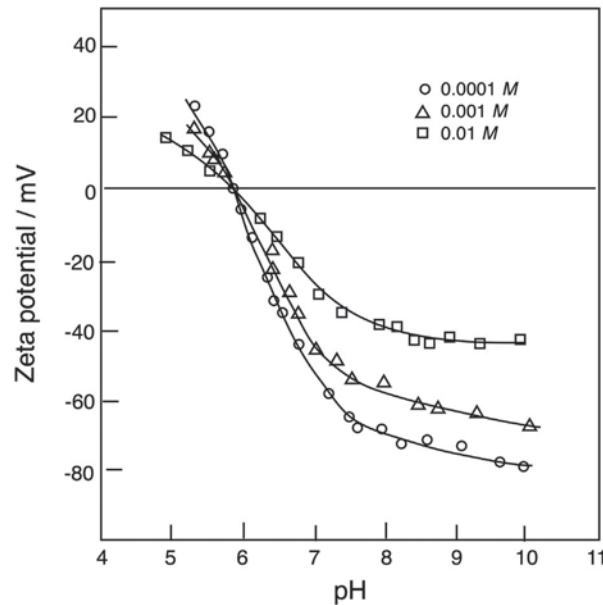


FIGURE 6.6 Change in the zeta potential of titania particles with pH in aqueous KNO_3 solutions (particle loading is 0.05 g/L). At $\text{pH} < \text{isoelectric point (IEP)}$, the zeta potential is positive and at $\text{pH} > \text{IEP}$ the zeta potential is negative. The IEP is 5.9, a value very close to the PZC in Figure 6.4. Note that the presence of the K^+ and NO_3^- ions does not change the position of the IEP, but does affect the magnitude of the zeta potential away from the IEP. Reprinted from *J. Colloid Interface Sci.*, 51, Weise, G. R., & Healy, T. W., *Coagulation and electrokinetic behavior of TiO_2 and Al_2O_3 colloidal dispersions*, 427–442, Copyright (1975), with permission from Elsevier.

the *IEP* is close to the point of zero charge. At constant surface potential, however, the zeta potential changes with the characteristics of the liquid medium (i.e., the electrical double layer thickness). When κ^{-1} is large (e.g., ion concentration low), potential drops more gradually with distance away from the particle surface, and hence the zeta potential is closer to the surface potential. See Figure 6.7. Table 6.2 gives some examples of isoelectric points of common ceramics.

Steric Repulsion. Polymers adsorbed on particle surfaces also cause a repulsive interaction. A complete discussion of the factors that encourage adsorption on surfaces is beyond the scope of this section, but some principles can be simply stated. A polymer adsorbs when it is energetically favorable. Therefore, one does not expect much adsorption when the liquid phase of the dispersion is a very good solvent for the polymer, because the polymer has a lower free energy in the solvent than on the particle surface. Further, adsorption is favored when there is some chemical interaction (i.e., hydrogen bonding) between sites on the polymer chain and the particle surface. Another strategy is to use diblock copolymers, which consist of two dissimilar polymer chains covalently bonded together. For example, a PS-PEO block copolymer consists of a segment of polystyrene (PS) connected to a segment of polyethylene oxide (PEO). One block can be designed to bond with the particle surface and the other to extend into the solvent.

Once the polymer molecules have adsorbed on the particle surfaces, repulsion between particles arises as particles approach and the polymer layers on adjacent particles interact. Mixing of these layers (in most solvents) results in repulsion due to an osmotic pressure effect related to the increase in

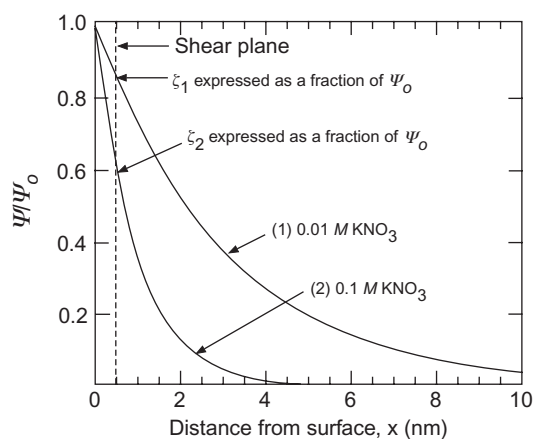
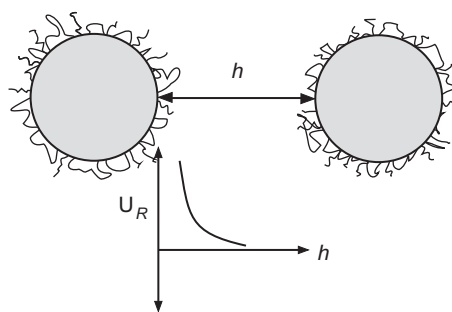


FIGURE 6.7 Data from Example 6.3 plotted to show the position of the shear plane, the definition of zeta potential (in this plot it is expressed as a fraction of the surface potential but ordinarily it is a number expressed in volts), and the variation in zeta potential with ionic concentration of the liquid. The higher concentration electrolyte has a smaller electrical double layer thickness and a lower zeta potential.

TABLE 6.2 Isoelectric Points (IEP) of Ceramic Oxides^a

Material	pH at the IEP
Quartz (SiO ₂)	2
Soda lime glass	2–3
Orthoclase (K ₂ O•Al ₂ O ₃ •6SiO ₂)	3–5
Silica, Amorphous (SiO ₂)	3–4
Zirconia (ZrO ₂)	4–5
Rutile (TiO ₂)	4–5
Tin oxide (SnO ₂)	4–7
Kaolin, edges only (Al ₂ O ₃ •2SiO ₂ •2H ₂ O)	6–7
Mullite (3Al ₂ O ₃ •2SiO ₂)	7–8
Alumina (α-Al ₂ O ₃)	9–9.5
Zinc oxide (ZnO)	9
Yttira (Y ₂ O ₃)	11
Magnesia (MgO)	12–13

^aData tabulated in Reed (1995).**FIGURE 6.8** Schematic diagram of particles with steric layers approaching one another and the increase in potential energy of repulsion with decrease in separation distance, h .

concentration of polymer between the particles. In addition, intermingling of the adsorbed polymers is not favored because it decreases the configurational entropy of the polymer chains and thus results in a higher free energy. These factors lead to a repulsive interaction. Qualitatively, the U_R increases as separation distance approaches the thickness of the steric (polymer) layer itself. See Figure 6.8. The thickness of the layer as well as other factors, such as the amount of polymer adsorbed, influences the strength of the repulsion.

Steric repulsion is commonly used to stabilize suspensions in organic solvents. Electrostatic repulsion is not very effective in organic solvents because organic solvents have low dielectric constants compared to water and are not good media for creating surface charge on particles. On the other hand, there is a wide selection of polymers that are soluble to varying degrees in most organic solvents; hence one can find a polymer that is suitable for steric hindrance in most cases. Nonpolymeric additives, such as certain oils and surfactants, can also adsorb on particle surfaces, creating a steric layer and leading to repulsion.

Lastly, a very effective means of stabilization is known as electrosteric stabilization. As the name implies, it is the combination of electrostatic and steric. This type of stabilization comes about with the adsorption of polyelectrolytes on the particle surfaces. The polyelectrolytes ionize to create charge and electrostatic repulsion. At the same time, their polymeric nature results in a steric repulsion.

Total Potential Energy of Interaction. The total potential energy of interaction is the sum of the attractive and repulsive components (U_A and U_R). The idea of making this summation and using it as a predictor of the tendency for aggregation is attributed to four scientists: Derjaguin, Landau, Verwey, and Overbeek. Hence, it is called the DLVO theory. Figure 6.9 shows the features of the total potential energy of interaction schematically. One important feature is an energy barrier, the height of which is important to the stability of the suspension. The energy barrier prevents the particles from approaching close enough to fall into the deep primary minimum. Another feature of DLVO plots is a shallow secondary minimum that appears in some cases at a greater separation distances. Particles can become weakly agglomerated at a distance

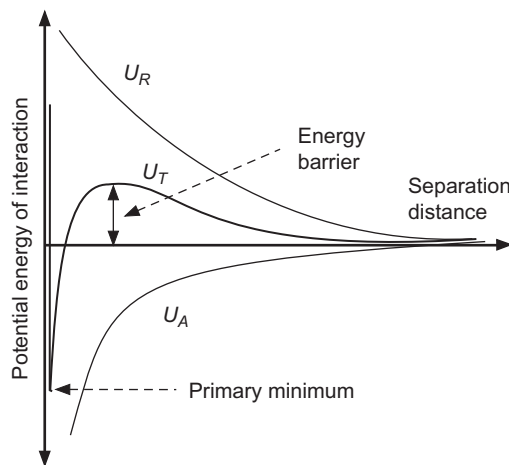


FIGURE 6.9 Schematic diagram showing total potential energy of interaction as the sum of the attractive and repulsive components.

defined by the secondary minimum; however, these agglomerates are easily broken in the suspension by stirring, for example.

Figure 6.10 shows the effect of varying surface potential and double layer thickness on the total potential energy of interaction. The potential barrier height is sensitive to both parameters: higher surface potentials and larger double layer thicknesses lead to stronger repulsion and hence higher barriers. One rule of thumb states that a barrier of about $25 kT$ is sufficient to prevent aggregation. Another factor to consider is the strength of attraction on the total potential energy of interaction. Particles with higher Hamaker constants have stronger attractive interactions, which brings down the height of the energy barrier (not shown).

The total potential energy of interaction for particles stabilized by a steric layer cannot be calculated easily. Experimental measurements of the force between flat surfaces covered with polymer as a function of separation have revealed that the shape of the total potential energy of interaction is a bit different than those plotted in Figure 6.10. The repulsive potential from the polymer steric layer dominates if the polymer covers the particle well such that the total energy of interaction increases dramatically at a separation distance close to the polymer layer thickness.

Overall Colloidal Stability. Achieving colloidal stability is a typical goal for a dispersion-based process. A stable suspension can be used to make coatings or parts that are consistent. The appearance and properties of a “stable” suspension do not change over the required processing time interval. This apparent stability is influenced by many factors, including the particle size and density, the particle-particle interactions, the mechanism of stabilization, and the particle concentration in the suspension.

The simplest issue to address is gravity-induced sedimentation, which is particularly important for larger and denser particles. The time scale for the development of a sediment is predicted using Eq. (6.3). This equation assumes that the particle is surrounded an expanse of liquid, and so it overpredicts the terminal velocity in suspensions containing more than a few volume percent. For example, one correlation for “hindered settling” in suspensions shows that the sedimentation velocity of a 30 vol% suspension of spherical particles has a terminal velocity one-tenth of that for a very dilute suspension. Nonetheless, a quick calculation with the terminal velocity equation can reveal the time frame over which a suspension might be expected to be stable to sedimentation.

The second consideration is aggregation, which is also called flocculation. The first step in aggregation is particle encounters or collisions due to Brownian motion. From Eqs. (6.4) and (6.5), the mean distance traveled by a particle in 3D Brownian motion in time t is given by:

$$\bar{x} = \sqrt{\frac{(kT)t}{\pi R \eta_L}} \quad (6.24)$$

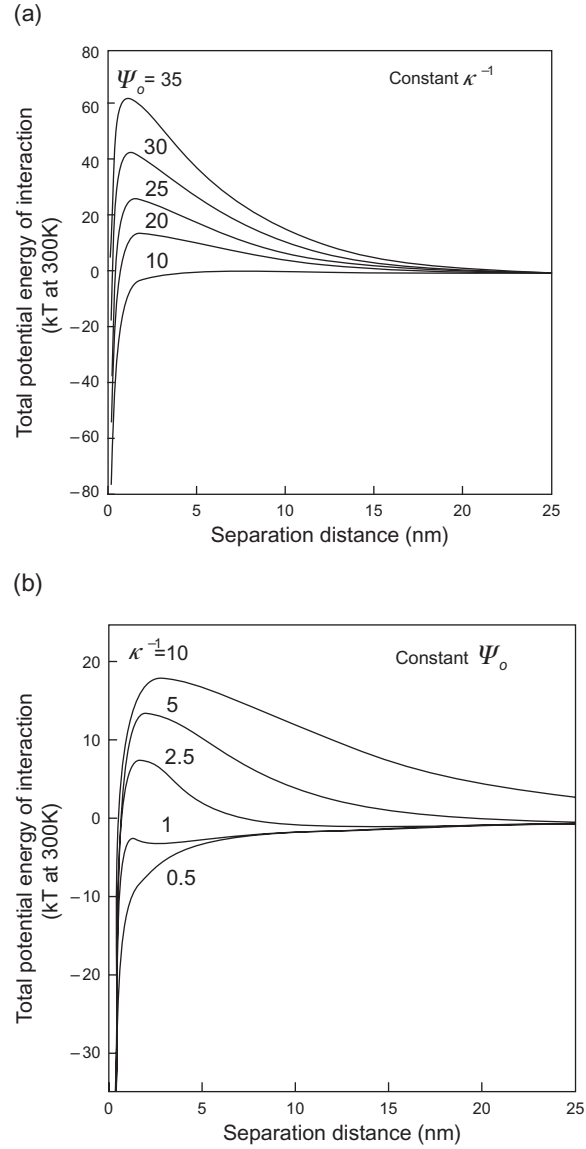


FIGURE 6.10 Calculated total potential energy of interaction (in units of kT at 300 K) as a function of separation distance for: (a) spherical silica particles ($R = 100$ nm) dispersed in water with double layer thickness of 5 nm and varying surface potential from 10 to 35 mV, as labeled and (b) spherical silica particles ($R = 100$ nm) with a surface potential of 20 mV dispersed in water with varying double layer thickness from 0.5 to 10, as labeled. The repulsive potential is calculated with Eq. (6.21).

From this equation, it is clear the distance traveled in time t is greater for smaller particles moving in liquid media with low viscosity. Now we can compare this length scale with the separation distance between particles to find a characteristic time to an encounter. Clearly as the concentration of particles in the suspension increases, the separation distance decreases and the time to an encounter becomes shorter. Less obvious is that for a given volume % of particles in a suspension, the time to an encounter gets shorter as the particle size gets smaller. [Example 6.5](#) compares the time scale for micron-scale particles to nanoparticles.

The next consideration is the energy barrier—the magnitude of the barrier determines the probability that the encounter leads to aggregation. That is,

EXAMPLE 6.5 Consider two suspensions of spherical silica particles in water: one has a particle diameter of 10 nm and the other has a particle diameter of 1 μm . Each suspension has a concentration or loading of 10 volume %. For each, find the spacing between particles and the time between encounters based on Brownian motion (Eq. (6.24)). Assume particles are arranged on a cubic lattice for simplicity. The viscosity of water is $\sim 1 \text{ mPa}\cdot\text{s}$.

Let's start with the 10 nm particles. The suspension is 10 vol% so that is equivalent to 10 cm^3 of particles in 100 cm^3 total. Each 10 nm particle has a volume of $\frac{4}{3}\pi R^3 = 5.236 \times 10^{-19} \text{ cm}^3$. Therefore, the number of particles is:

$$\frac{10 \text{ cm}^3}{5.236 \times 10^{-19} \text{ cm}^3/\text{particle}} = 1.91 \times 10^{19} \text{ particles}$$

These particles are in 100 cm^3 total volume, which we can envision as a box with an edge length of $(100 \text{ cm}^3)^{1/3} = 4.64 \text{ cm}$. Each particle is a cube in the box and so there are 1.91×10^{19} little cubes inside the box. So if each particle is a cube, then there are $(1.91 \times 10^{19})^{1/3} = 2.67 \times 10^6$ boxes on edge and each box is $4.64 \text{ cm} / 2.67 \times 10^6 = 1.736 \times 10^{-6} \text{ cm}$ on its edge. Considering that there is one particle in the center of each little cube, the separation between particle centers is the same as the edge length, 17.36 nm. Given that the particle diameter is 10 nm, we can conclude that the surface-to-surface separation distance is 7 nm.

Now, let's find the distance traveled by Brownian motion:

$$\bar{x} = \sqrt{\frac{(kT)t}{\pi R \eta_L}} = \sqrt{\frac{(1.38 \times 10^{-23} \text{ J/K} \cdot 300 \text{ K})t}{\pi(5 \times 10^{-9} \text{ m})(0.001 \text{ Pa}\cdot\text{s})}} = 1.62 \times 10^{-5}(t)^{1/2} \quad [\text{m}]$$

So, we can find the time between encounters as:

$$1.62 \times 10^{-5}(t)^{1/2} = 7 \times 10^{-9} \rightarrow t = 1.9 \times 10^{-7} \text{ s}$$

The time between collisions is extremely short for the 10 nm particles.

Repeating this exercise with the 1 μm diameter particles, we find the center-to-center separation distance is 1.74 μm and the surface to surface separation is 0.74 μm . The time between collisions is 0.21 s. This time is also quite short, but it is six orders of magnitude longer than the collision time for the nanoparticles.

without a barrier, when two particles that approach each other, van der Waals attraction pulls them close and prevents their separation. In other words, the particles are stuck in the primary minimum shown schematically in [Figure 6.9](#). However, with a barrier the particles must approach each other with an energy greater than the energy barrier in order to contact one another and aggregate. With a higher energy barrier, the probability of such encounters decreases. Typically, barrier heights in excess of $\sim 25 kT$ or so are best for reducing the aggregation rate.

When aggregation or flocculation occurs, it takes on different forms depending on the nature of the dispersion. If the particle concentration is low, then multiparticle aggregates tend to form. These aggregates remain suspended and continue growing until they sediment due to their larger size or interconnect to form a network or “gel” with other aggregates. Aggregate morphologies can be tightly packed or open and fractal-like. In concentrated suspensions, the tendency is for gelation, the formation of an interconnected network of particles. As can be imagined from [Example 6.5](#), nanoparticle suspensions have a tendency to gel due to the close proximity of particles.

6.2.2 Polymer Solutions

Polymeric solutions consist of a polymer dissolved in a solvent, either water or an organic liquid. Unlike particulate dispersions, polymer solutions can be formulated to be at thermodynamic equilibrium and so they are stable. One key to developing a polymer solution for a process (i.e., to make a coating) is to find the appropriate solvent. Many factors, including cost, environmental effects, and boiling point, might be important for solvent selection for any given process. In this section, a short introduction to the structure of the polymers in solution and the thermodynamics of solubility is provided along with a general picture of how solution structure changes with polymer concentration.

Polymer Structure in Solution. To illustrate the behavior of a flexible polymer chain, like polyethylene, in a solvent, the beads-on-a-spring model is often used. Polymer chains have many flexible, elastic elements that are in constant motion, just like springs. Polymer chains, like particles, are also subject to hydrodynamic forces and undergo Brownian motion, represented by the beads. Additionally, the beads act as pivot points where the springs can freely rotate. The motion of each bead is often imagined as a random walk, where the physical conformation of each joint is equally likely at any given time. In reality, the accessible rotations of polymer segments are restricted by how flexible the bonds are in the polymer backbone. For example, a polymer that contains many double bonds or benzene rings in its backbone is much less flexible than a chain that contains only carbon-carbon single bonds. Chain branches can also hinder motion by sterically restricting the available conformations of the polymer chain. Furthermore, interactions between the polymer and the solvent bias the chain to interacting more with

itself or with the surrounding fluid, causing the polymer to be either tightly coiled or more extended and flexible.

Because a polymer chain can adopt many different conformations in a solvent, the size of a chain and, consequently, its volumetric concentration, is difficult to define. The most common specification of size is the molecular weight, or average mass per individual chain. The molecular weight can either be a number average or a mass average, and can be measured by numerous ways including gel permeation chromatography, membrane osmometry, or light scattering. Because all polymer chains in a certain sample are not always the same length, the polydispersity index (PDI) is also cited. The PDI quantifies the broadness of the molecular weight distribution. A perfectly monodisperse polymer has a PDI of 1, a common free radically polymerized polymer has a PDI of about 2, and a polymer with a very broad molecular weight distribution has a PDI greater than 10.

Another description of size is the end-to-end length of the polymer chain, which can be estimated from its composition and molecular weight. First, the number of monomer repeat units in a polymer or the degree of polymerization, n , can be found by dividing the molecular weight by the monomer molecular weight. If a is the number of carbon-carbon bonds along the backbone of a single monomer, the total number of bonds in the polymer is $n_b = an$. Knowing that the length of a single carbon-carbon bond, l , is about 0.154 nm, the end-to-end distance of a polymer chain if it were stretched out completely, h , would be $h = n_b l$. For high molecular weight polymers, chain lengths can be longer than you would naively expect. In reality, diffusion causes polymers to coil into a messy sphere, as illustrated in Figure 6.11. For a freely jointed, flexible chain coiled in a solvent the mean square end-to-end distance is $\langle h^2 \rangle = n_b l^2$. This is a statistical quantity, calculated considering all of the possible chain conformations.

A more useful measure of a polymer size in solution is the radius of gyration, R_g , which is the average radius of the polymer with respect to its center of mass. The radius of gyration is directly related to the chain length:

$$R_g^2 = \frac{C_\infty n_b l^2}{6} = \frac{n b^2}{6} \quad (6.25)$$

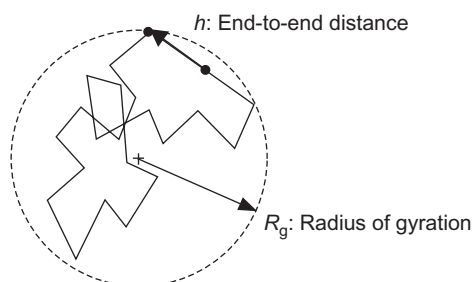


FIGURE 6.11 Polymer chain dimensions defined.

Here, n is the number of monomer repeat units in the chain (i.e., the degree of polymerization) and b is the statistical monomer length in the solvent. Recall that a monomer can contain many carbon-carbon bonds along its backbone, so b is often larger than the bond length l . This expression can also be extended by noting that $n = M/M_o$, where M_o is the monomer molecular weight. Hence $(R_g)^2$ is proportional to the molecular weight, M .

In a good solvent, the interactions between the solvent and the polymer are favorable, the chain avoids itself, and the coil expands. Steric effects become important, and the chains undergo what is termed a self-avoiding random walk instead of a pure random walk, which does not include steric effects. In this case, R_g is proportional to $n^{3/5}$ (rather than $n^{1/2}$). A special case is a polymer in what is called a theta solvent. Adding a polymer to a theta solvent requires no entropy of mixing (see below), and the attractions between polymer chain segments exactly cancel the steric exclusion effect. Polymers in theta solvents do undergo pure random walk motion with R_g is proportional to $n^{1/2}$ and have smaller radii of gyration than in good solvents.

Solvent Quality and Solution Thermodynamics. The ability of a solvent to dissolve a polymer can be predicted based on thermodynamic principles. Dissolution occurs when the change in Gibbs free energy on mixing, ΔG_m , is less than zero.

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (6.26)$$

where ΔH_m and ΔS_m are the change in the enthalpy on mixing and the change in the entropy on mixing, respectively. Entropy always increases on mixing ($\Delta S_m > 0$), which favors mixing. Therefore solubility is most closely connected with ΔH_m , which is sometimes referred to as the heat of mixing. If $\Delta H_m < 0$, then mixing the polymer and solvent together releases heat (exothermic) and dissolution occurs ($\Delta G_m < 0$). However, if $\Delta H_m > 0$, then the mixing is endothermic and dissolution may occur if $\Delta H_m < T \Delta S_m$. Flory-Huggins theory gives insights into this balance.

The Flory-Huggins theory considers the statistical distribution of n_s moles of solvent molecules and n_p moles of polymer segments on lattice sites. It predicts that the entropy change on mixing arises from configurational entropy change:

$$\Delta S_m = -R[n_p \ln \phi_p + n_s \ln \phi_s] \quad (6.27)$$

where ϕ_p and ϕ_s are the volume fractions of polymer and solvent, respectively ($\phi_p + \phi_s = 1$). Since volume fractions are less than one, the term in the brackets is a negative number. The enthalpy change on mixing depends on the number of contact points between polymer and solvent on the lattice, the interaction energies between solvent and solvent, polymer and polymer, and

solvent and polymer, which define the energy polymer-solvent contact, and the composition of the solution.

$$\Delta H_m = n_s \phi_p \chi RT \quad (6.28)$$

where χ is the Flory-Huggins interaction parameter. This interaction parameter contains the interaction energies mentioned above. Therefore,

$$\Delta G_m = RT[n_s \ln \phi_s + n_p \ln \phi_p + n_s \phi_p \chi] \quad (6.29)$$

For solubility, $\Delta G_m < 0$, and hence smaller values of χ favor solubility. Values for the χ parameter can be found in tables in reference volumes.

The Flory-Huggins theory provides a good starting point for understanding the factors that affect solubility. The χ parameter decreases with temperature, which means that solubility is favored at increased temperature. A theta solvent is a solvent that has a χ of $\frac{1}{2}$ at the temperature of interest. Likewise, the theta temperature of a solvent is the temperature at which χ is $\frac{1}{2}$. Polymer solubility is also influenced by molecular weight. Intuitively, higher molecular weight polymers would seem to be more difficult to dissolve. This is indeed the case, as shown in [Example 6.6](#).

A related route to understanding polymer solubility in various solvents is through the solubility parameter, which is derived from an empirical energetic analysis. The main premise of the analysis is that polymers dissolve in solvents that share chemical similarity. The solubility parameter, δ , is a measure of the cohesive energy density, which is related to the heat of vaporization and molar volume. The heat of mixing found from this approach scales with the square of the difference in solubility parameters between the solvent and polymer $(\delta_s - \delta_p)^2$. Hence, to reduce the heat of mixing and encourage dissolution, the solvent should have a solubility parameter that is similar to the polymer. [Table 6.3](#) gives solubility parameters for common solvents and polymers. It is clear from this table that the common thermoplastic polymers on the list require organic solvents for dissolution.

Effect of Concentration on Structure. When a polymer solution is dilute, individual polymer chains are separate from each other. Each coil has a size equal to its equilibrium radius of gyration in that solvent. Adding more polymer to the solution causes the coils to become closer together until C^* is reached, the concentration at which the polymer chains begin to overlap. The structural changes are shown schematically in [Figure 6.12](#). At concentrations greater than C^* , polymer chains interact with one another and with a further increase in concentration become entangled. As discussed in the next section, polymer concentration affects the viscosity considerably.

Since dilute and concentrated polymeric solutions act very differently from each other, C^* is an important concentration to know for a polymer/solvent system. The volume of one polymer coil in a solvent is:

$$V_C = \frac{4}{3} \pi R_g^3 \quad (6.30)$$

EXAMPLE 6.6 Calculate ΔG_m for a 5 vol% solution of polystyrene in toluene at 25°C for polymers with a molecular weight of 10,000 g/mol and 50,000 g/mol. The χ parameter for polystyrene – toluene is 0.37. The density of PS is 1.06 g/cm³ and the density and molecular weight of toluene are 0.867 g/cm³ and 94.14 g/mol, respectively.

For this solution, the volume fractions are $\phi_p = 0.05$ and $\phi_s = 0.95$. To solve this problem, it is convenient to assume that we have 100 cm³ total volume—5 cm³ of PS and 95 cm³ of toluene. From there, the number of moles of each component can be found. Starting the toluene,

$$n_s = \left[\frac{0.867 \text{ g/cm}^3}{94.14 \text{ g/mol}} \right] \cdot 95 \text{ cm}^3 = 0.875 \text{ moles}$$

For the PS, the number of moles depends on the molecular weight. Starting with the lower molecular weight:

$$n_p = \left[\frac{1.06 \text{ g/cm}^3}{10000 \text{ g/mol}} \right] \cdot 5 \text{ cm}^3 = 5.3 \times 10^{-4} \text{ moles}$$

Now, ΔG_m is calculated:

$$\begin{aligned} \Delta G_m &= RT[n_s \ln \phi_s + n_p \ln \phi_p + n_s \phi_p \chi] \\ &= [8.314 \text{ J/(mol} \cdot \text{K)} \cdot 298 \text{ K}] [0.875 \ln(0.95) + (5.3 \times 10^{-4}) \ln(0.05) \\ &\quad + 0.875(0.05)(0.37)] \\ &= -75.0 \text{ J} \end{aligned}$$

So dissolution is favored. Repeating the calculation with the higher molecular weight polymer, we find that there are fewer moles of polymer (1.06×10^{-4}) and ΔG_m is less negative (−71.2 J). Toluene is a very good solvent for PS and dissolves both molecular weights.

and as a rough estimate we can assign C^* as the concentration for which the volume of the polymer coils equals the volume of the solution, V_T . The typical units of concentration are grams of polymer per unit volume of solutions (e.g., g/cm³ or g/dL, where 1 dL = 100 mL). (Note that while the units appear to be the same, C is a concentration and not a density.) With this definition:

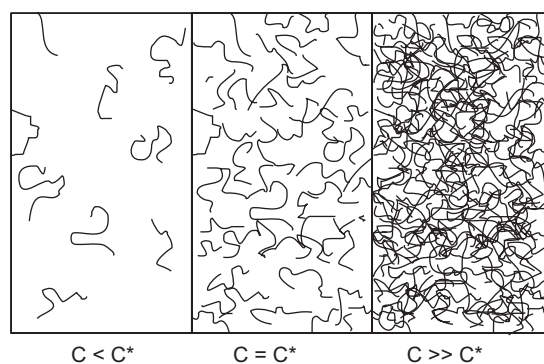
$$V_T = NV_C = N \left[\frac{4}{3} \pi R_g^3 \right] \approx N \pi R_g^3 \quad \text{at } C = C^* \quad (6.31)$$

where N is the number of polymer molecules in the solution. Rearranging and recognizing the connection between the N/V_T and C ($N/V_T = CN_A/M$), where M is the molecular weight and N_A is Avogadro's number:

$$C^* \approx \frac{M}{N_A \pi R_g^3} \quad (6.32)$$

TABLE 6.3 Solubility Parameters for Solvents and Polymers^a

Solvent or polymer	Solubility parameter $[(\text{J}/\text{m}^3)^{1/2} \times 10^3]$
Cyclohexane	16.8
Carbon tetrachloride	17.6
Xylene	18.0
Toluene	18.2
Tetrahydrofuran	18.6
Chloroform	19.0
Ethanol	26.0
Methanol	29.7
Water	47.9
Polytetrafluoroethylene (PTFE)	12.6
Polyethylene (PE)	16.4
Polystyrene (PS)	18.5
Polypropylene (PP)	19.0
Polymethyl methacrylate (PMMA)	19.0
Polyvinyl chloride (PVC)	20.0

^aData from Brandrup et al. (1999).**FIGURE 6.12** Schematic showing the changing structure of a polymer solution with concentration. From Evans, D. F., & Wennerstrom, H.: *The Colloidal Domain*. Page 295. 1994. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

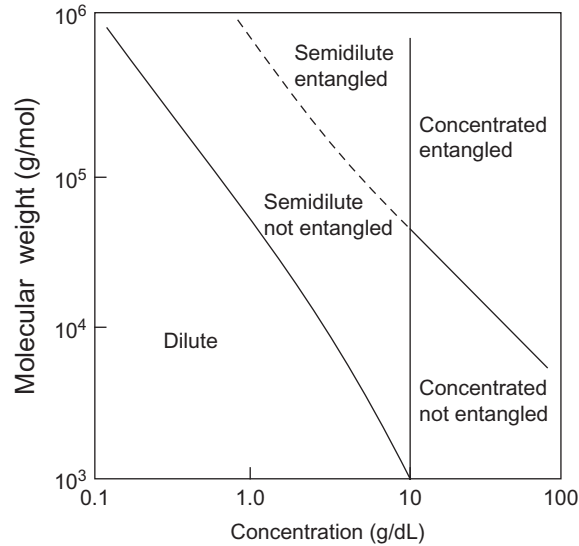


FIGURE 6.13 Effect of molecular weight and concentration on the structure (viscoelastic regimes) of polybutadiene in a good solvent. The regimes in the figure are based on rheological data. Reprinted from *Polymer*, 21/3, Graessley, W. W., *Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power*, 258–262, Copyright (1980), with permission from Elsevier.

According to Eq. (6.25), the radius of gyration is proportional to $(M)^{1/2}$, and so C^* is proportional to $M^{-1/2}$. Therefore, larger molecular weight polymers have lower C^* values.

Figure 6.13 shows how both molecular weight and concentration affect the solution structure. The dilute regime with separated coils occupies the lower left portion of the plot, where both concentration and molecular weight are below some limits. Considering moving from left to right on the diagram for a solution of a polymer of a certain molecular weight, the transition from dilute to semi-dilute occurs at C^* . With further increase in concentration, a concentrated regime is encountered along with entanglements if the molecular weight is high enough. Consistent with the rough model above, C^* gets smaller and smaller as molecular weight increases, indicating that making concentrated solutions of high molecular weight polymers is a challenge.

6.2.3 Rheology of Dispersions and Solutions

Fluid rheology, or flow behavior, is introduced in Chapter 3. As in melt processes, the rheological properties of solutions and dispersions are very important to the design of process steps. In initially formulating the dispersion or solution, rheology is often a rewarding method for characterizing particle and polymer interactions, and microstructure in the liquid. X-ray and

light scattering as well as optical and confocal microscopy are other methods to obtain interaction information, but, unlike rheological methods, the solutions must often be diluted for these techniques to be possible. Rheology is also useful in designing the forming or additive process itself. For example, the fluid flow can dictate which coating dies are chosen, the speed that the process can run, or the feasible dimensions of the final part. Additionally, the viscosity changes by orders of magnitude during solidification. Controlling the rate at which solidification occurs can be crucial to the final microstructure of the product. Finally, once a process has been implemented, rheology is an excellent diagnostic tool for confirming that a process liquid behaves similarly between batches or lots.

The rheological behaviors of dispersions and solutions are complex. As these liquids become concentrated, interparticle forces and hydrodynamic interactions become important and more complicated behavior emerges. The dispersion or solution can act like a solid or have behavior that is time or shear rate dependent. The variety in the rheological responses is evident in familiar dispersions and solutions, such as toothpaste, shampoo, applesauce, mud, and paint. Some appear solid-like until a shear is applied and others flow readily. The qualitative behaviors of both particulate suspensions and polymeric solutions are predictable in most cases, even when they are not dilute. These behaviors, as well as the microstructures that create them, are discussed in this section.

Rheology of Particulate Suspensions. When solid particles are dispersed in a liquid, the viscosity and rheological properties of the mixture are altered from that of the liquid alone. The presence of the particles interrupts and disturbs the flow of the liquid; the liquid is forced to move around the particles, and thus the viscosity increases. The simplest case is the addition of particles to a Newtonian liquid under conditions where the particles do not interact with each other (i.e., in dilute suspension). Einstein showed that the following relationship holds for dilute suspensions of spherical particles:

$$\eta = \eta_o(1 + [\eta]\phi)$$

$$\eta = \eta_o(1 + 2.5\phi) \quad \text{for spherical particles} \quad (6.33)$$

where η_o is the viscosity of the liquid without any particles, ϕ is the volume fraction of particles, and $[\eta]$ is the Einstein coefficient or intrinsic viscosity. This relationship holds only for low volume fractions (less than around 0.10) of noninteracting particles.

The meaning of the intrinsic viscosity is discerned when the relative viscosity (η/η_o) is plotted as a function of ϕ . See [Figure 6.14a](#). In this figure, the slope of the linear increase is the intrinsic viscosity, the increase in viscosity per unit of concentration. The intrinsic viscosity is formally defined as:

$$[\eta] = \lim_{\phi \rightarrow 0} \frac{\eta - \eta_o}{\eta_o \phi} \quad (6.34)$$

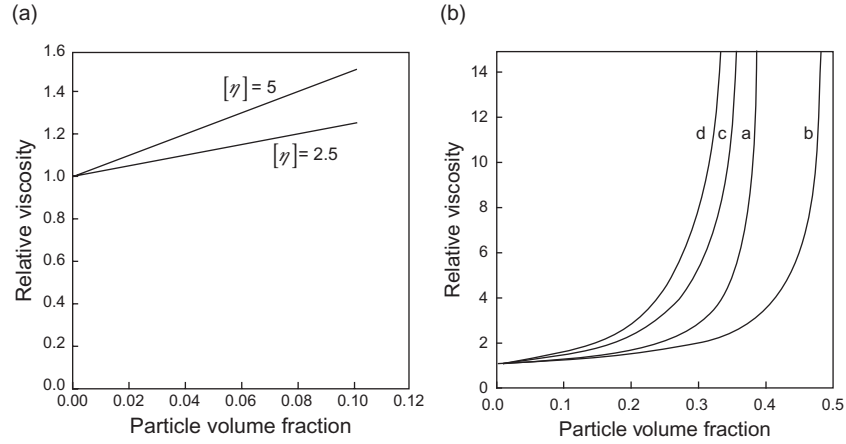


FIGURE 6.14 (a) Increase in relative viscosity (η/η_o) with addition of particles to a liquid. Data is plotted for $[\eta] = 2.5$ and 5 using Eq. (6.33). (b) Increase in relative viscosity (η/η_o) with addition of particles for dispersions with different maximum packing fractions ϕ_m and intrinsic viscosities: a. $\phi_m = 0.4$, $[\eta] = 2.5$ (spheres), b. $\phi_m = 0.5$, $[\eta] = 2.5$, c. $\phi_m = 0.4$, $[\eta] = 4$, and d. $\phi_m = 0.4$, $[\eta] = 5$. Results are calculated using the Dougherty-Kreiger relationship (Eq. 6.35).

A value of 2.5 is used for $[\eta]$ of spherical particles to recover Eq. (6.33). Higher values of $[\eta]$ represent asymmetric particles that, by virtue of rotation, appear to take up more volume and hence create an effect similar to a higher volume fraction of particles.

As more and more particles are added into the liquid, the distance between particles decreases. The chance that they physically collide increases as they crowd into the liquid. At some point, flow ceases because particles are unable to move around each other. This critical volume fraction of particles depends on particle packing, particle shape, and interparticle interactions. For now, we will ignore the last factor and assume that particles do not form agglomerates.

A useful concept in the rheology of more concentrated dispersions is the maximum packing fraction, ϕ_m , the highest volume fraction that the suspension can achieve and still flow. Monodisperse spheres, for example, can pack to a fraction of 0.74 if they are arranged in face-centered cubic or hexagonal close-packed geometries. Random close packing, on the other hand, leads to a maximum packing fraction of only 0.64. Particle size distribution plays an important role in packing, as discussed in Chapter 5. Mixing in fine particles increases the packing fraction as these fill interstitial spaces between larger particles. A broad particle size distribution typically results in a maximum packing fraction of 0.55–0.65.

Dougherty and Kreiger proposed the following expression for the effect of higher volume fractions of particles on viscosity.

$$\eta = \eta_o \left(1 - \frac{\phi}{\phi_m} \right)^{-[\eta]\phi_m} \quad (6.35)$$

Figure 6.14b shows calculated results from this equation, illustrating the effects of the maximum packing fraction and $[\eta]$ on the viscosity. The figure shows how the viscosity increases with ϕ as ϕ_m is approached and the fact that higher values of $[\eta]$, representing asymmetric particles, raise the viscosity more than spheres at a given ϕ . Note that in the limit of low dispersion concentration, Eq. (6.35) reduces to Einstein's equation (Eq. (6.33)).

Dilute suspensions of particles in a Newtonian liquid tend to display Newtonian behavior; however, at higher volume fractions these suspensions become non-Newtonian. Both shear thinning and shear thickening may be observed with increasing rates of shear. The shear thinning behavior results from particle alignment in the flow direction. Increasing the shear rate further can cause a shear thinning suspension to become shear thickening as higher shear rates disturb the particle alignment. Particle size and size distribution influence the shear thickening behavior. The shear rate at which shear thickening begins increases as the particle size decreases. That is, a larger particle size favors shear thickening. In addition, suspensions with narrower particle size distributions tend to shear thicken. In terms of processing ease in operations that require high shear rates, such as mixing and coating, shear thickening is not desired.

How do particle-particle interactions and agglomerates affect the viscosity and rheology? When attractive forces dominate, particles tend to agglomerate. The presence of agglomerates has the practical consequence of decreasing the suspension stability. That is, the larger agglomerates tend to settle over time. The tendency to agglomerate also reduces the maximum packing fraction, because particles cannot rearrange into favorable positions. In addition, large or oddly shaped agglomerates themselves trap liquid or immobilize liquid in their interiors. In effect, this results in the particle having a larger hydrodynamic size and the liquid in the agglomerate is therefore not available to assist flow. These effects lead to higher viscosity for agglomerated suspensions.

Flocculated suspensions have rheological behavior that is shear rate dependent. At low shear rates, the flocculated structure spans and connects large volumes of the fluid, causing the viscosity to be relatively high. As the shear rate increases, the flocculated structure breaks down and the viscosity drops. Therefore, flocculated suspensions are shear thinning. Increasing the shear rate on stable suspensions can also cause shear thickening. At these conditions, the particles do not have time to move relative one another and therefore, the particles “jam.”

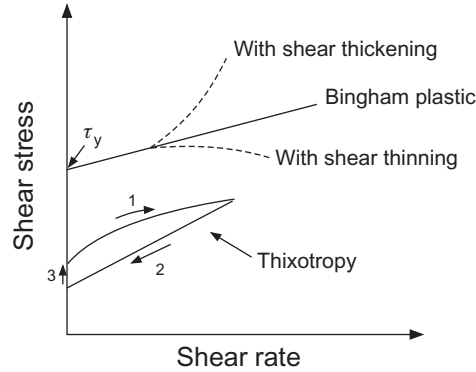


FIGURE 6.15 Schematic diagram of the shear stress versus shear rate behavior of several suspensions. The response of a suspension with a yield stress (Bingham plastic) is shown together with responses of those with a yield stress and shear thinning or shear thickening behavior. Thixotropy is also demonstrated in a suspension with a yield stress: 1: increase in shear rate, 2: response does not follow the same path on decrease in shear rate (hysteresis), and 3: with time the yield stress increases.

As particle concentration increases, suspensions rheology becomes more complex, including the appearance of yield stress, time dependence in the rheological response, and viscoelasticity. Figure 6.15 shows the response of a suspension with a yield stress, including possible responses that have shear thinning and shear thickening after the yield stress is surpassed. If the suspension flows as a Newtonian liquid after the yield stress is surpassed, then the suspension is called a Bingham plastic. The yield stress is sometimes convenient for processing methods as it assists in shape retention after the shear stress causing flow is removed (e.g., as in extrusion). An example of this behavior from everyday life is mayonnaise, which holds a shape with peaks and valleys in the jar, but flow easily under a knife. The high stresses applied by the knife break the microstructure of fats in the mayonnaise, allowing it to flow. Time dependence is also a possibility. A thixotropic suspension is one that is shear thinning, but experiences hysteresis and thickening as it sits undisturbed. For these materials, the history of shearing or stirring influences their rheological behavior.

Rheology of Polymer Solutions. Just as adding particles to a liquid causes the viscosity to rise, so does dissolving a polymer in a solvent. Factors such as polymer concentration, molecular weight, solvent/polymer interactions, and temperature all have a large effect on the viscosity of polymeric solutions.

When the solution is dilute, below the overlap concentration C^* , the separated chains can be modeled as noninteracting hard spheres of radius R_g . Just like particles, these spherical polymeric chains move in solution under Brownian motion and Einstein's equation (Eq. (6.33)) is valid to describe the relative viscosity of the solution. The volume fraction of polymer in solution is given by:

$$\phi = \frac{NV_C}{V_T} = \left(\frac{V_C N_A}{M} \right) C \quad (6.36)$$

This relationship makes use of the connection between the number of molecules in the solution volume and the concentration in grams polymer per volume of solution ($N/V_T = CN_A/M$). Now, substituting into Eq. (6.33) for spherical particles reveals:

$$\eta = \eta_o \left(1 + 2.5 \left(\frac{N_A V_C}{M} \right) C \right) \quad (6.37)$$

Using this, the intrinsic viscosity of a polymeric solution can be defined as:

$$[\eta] = \lim_{C \rightarrow 0} \frac{\eta - \eta_o}{C \eta_o} = \lim_{C \rightarrow 0} 2.5 \frac{V_C N_A}{M} = 2.5 \frac{4\pi R_g^3 N_A}{3M} \quad (6.38)$$

Therefore, this intrinsic viscosity, $[\eta]$, is different from the one used with particles; it has units of inverse concentration (e.g., cm^3/g). As in the particle case, $[\eta]$ gives the effectiveness of a single polymer chain in raising the solvent viscosity and therefore, the intrinsic viscosity can also be thought of as a measure of the size that a polymer chain takes up in a solvent, assuming that the dissolved polymer is a collection of non-interacting spheres.

Because the radius of gyration is proportional to $M^{1/2}$ (Eq. (6.25)), Eq. (6.38) can be re-written as:

$$[\eta] = \frac{A_2(A_1 M^{1/2})^3}{M} = A_3 M^{1/2} \quad (6.39)$$

Here, A_1 , A_2 , and A_3 are constants used to simplify the expression. Eq. (6.39) shows that the intrinsic viscosity depends on the molecular weight of the polymer. This makes intuitive sense; a greater molecular weight polymer chain is physically larger and impacts the polymer solution viscosity to a greater extent.

Equation (6.39) was derived assuming that the volume of a polymer chain in solution scales with $M^{3/2}$, which is not always true. A generalized version of Eq. (6.39) is the Mark-Houwink-Sakurada equation:

$$[\eta] = K_{MH} M^\alpha \quad (6.40)$$

where α and K_{MH} are the Mark-Houwink-Sakurada parameters. These parameters give some indication of the polymer conformation within the solvent, which is directly dependent on the affinity of the polymer to the solvent and also the polymer flexibility. They are also a function of temperature, with most polymers becoming more flexible with heat. If $\alpha = 0.5$, the polymer is dissolved in a theta solvent and Eq. (6.39) is followed exactly. In good solvents, polymer chains expand and contribute more to the rheology, and $0.5 < \alpha < 0.8$. Values of $\alpha > 0.8$ are possible for very rigid polymers. Mark-Houwink-Sakurada parameters are found in reference volumes, such as the *Polymer Handbook*, listed at the end of the chapter.

Polymer solution viscosity and rheological parameters change dramatically with concentration. In the limit of dilute solutions, the viscosity is linear with polymer concentration with a slope of the intrinsic viscosity:

$$\frac{\eta}{\eta_o} = 1 + [\eta]C \quad (6.41)$$

As the concentration of the polymer increases, polymer chains begin to interact in the solution. Equation (6.33) no longer holds as C^* is approached and the polymer chains overlap. Above C^* , polymer chains may also become entangled and their motion in the solvent becomes further restricted. The solution viscosity rises dramatically (see Figure 6.16 for an example). The viscosity of polymer solutions above C^* cannot quantitatively be predicted from polymer and solvent properties; instead, simple rheological experiments are conducted to properly characterize the polymer solution behavior. These data can then be fit to empirical models. For example, a power law of the type $\eta = BC^b$, where b and B are constants, is frequently successful.

Whereas dilute polymer solutions are relatively Newtonian like the solvents that are within them, the viscosity of concentrated polymer solutions is most often shear rate dependent. As a concentrated solution is sheared, polymer chains elongate in the velocity gradient direction and become disentangled. The elongated chains can move past each other more easily and the viscosity drops. Like polymer melts, solution viscosity is found to follow

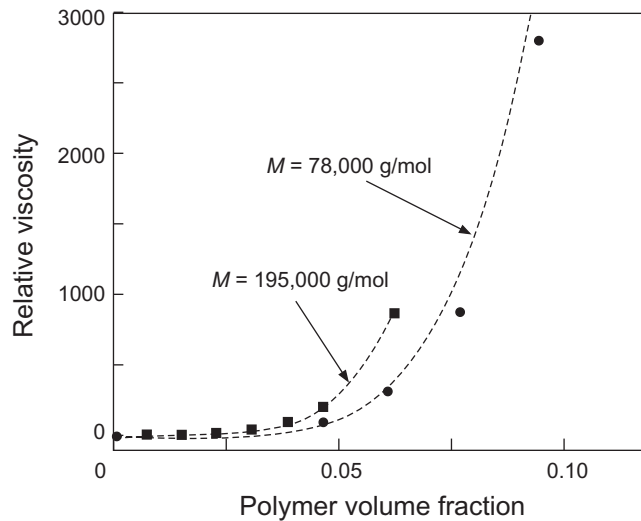


FIGURE 6.16 Relative viscosity of aqueous polyvinyl alcohol solutions made from polymer with $M = 195,000$ g/mol and $M = 78,000$ g/mol at 25°C . Empirical fits to the data are given as dotted lines. The relative viscosity is reported at zero shear but the solutions were only mildly shear thinning. Data from Buss *et al.* (2011).

power law behavior over a range of shear rates after initial Newtonian plateau (see Chapter 3). Like particulate suspension rheology, solution rheology is complex. Viscoelasticity is common in concentrated solutions and yield stresses and time-dependent responses can also be present.

6.2.4 Characteristics of Volatile Liquids for Dispersions and Solutions

Simple, volatile liquids play important roles in dispersion and solution processes. In a dispersion, the volatile liquid is a medium for dispersing particles, while in solutions, the volatile liquid is the solvent for polymer. As described above, these liquids play a central role in making the dispersions and solutions as well as in their rheology. Additionally, the liquid is removed by evaporation and so the volatility of the liquid is also important. Lastly, the surface tension and wetting behavior of dispersions and solutions are determined to a large extent by the surface tension of the liquids. [Table 6.4](#) gives some useful parameters for common liquids. Not included in the table are environmental, health, and safety factors. Organic solvents have varying exposure limits and most require control conditions for handling, such as fumehoods. Materials safety data sheets (MSDS) should be consulted for each solvent.

6.2.5 Drying

Drying is a critical step for coatings and three-dimensional parts made from particulate suspensions and polymer solutions. Considering the amount of water or solvent present in a slip cast piece after removal from the mold or a polymer coating after deposition onto a substrate, the drying step is frequently both time consuming and energy intensive. Also, for continuous processes, such as roll-to-roll coating operations, the rate of the entire process can be limited by the drying step. Lastly, drying leads to shrinkage and if this shrinkage is not allowed to occur freely then stress and defects may result.

There are many common features in the drying process for ceramic particle suspensions, high T_g polymer latexes, and polymeric solutions. Low T_g latex suspensions are a special case, where the polymer latex particles actually deform into a nonporous polymer coating during the drying process. Although most of what follows is focused on drying of coatings, the same principles apply to drying of bulk shapes. The description below begins with an exploration of general phenomena and ends with comments on drying of coatings and pieces from dispersion and solution processes.

General Features of Drying. There are three steps in any drying process. See [Figure 6.17](#). First, the volatile liquid is transported to the free surface of the coating or object. Of course, early in the drying process this step is

TABLE 6.4 Parameters for Some Volatile Liquids Used in Dispersion and Solution Processes^a

Liquid	Boiling point (°C)	Evaporation rate ^b	Heat of vaporization (J/g)	Permittivity	Viscosity at 25°C (mPa•s)	Surface tension (mN/m)
Acetone	56	7.70	524	21	0.3	25
Butyl Acetate	127	1.00	310	5	0.5	26
Cyclohexane	807	5.60	392	NA	1.0	26
Ethanol	78	2.65	860	24	1.2	23
Ethylene Glycol	198	< 0.01	800	37	20	48
Isopropyl Alcohol	82	2.08	578	18	2.4	22
Methanol	63	3.70	1100	33	0.6	23
Methyl Ethyl Ketone	80	4.59	444	18	0.4	25
Tetrahydrofuran	66	6.3	444	7.5	0.47	NA
Toluene	110	1.96	352	2	0.6	29
Water	100	0.16	2260	80	1	72
Xylene	140	0.55	327	2	0.7	28

^aData are from [Hellebrand \(1991\)](#) or [Weast \(1980\)](#).^bRelative to butyl acetate; NA = not available.

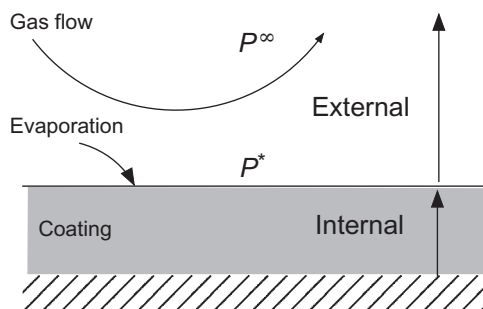


FIGURE 6.17 Schematic of a drying coating. The coating can be a polymer solution or a dispersion of particles in a volatile liquid.

instantaneous. Second, the liquid evaporates (i.e., it changes phase from liquid to vapor). Third, the vapor is transported away from the free surface. We can consider the first step as *internal*, dependent on transport processes inside the coating or object, and the second and third steps as *external*, dependent on conditions and transport processes in the surrounding gas phase. The three steps occur in series—the slowest step controls the rate of the drying process.

Initially, most drying processes are rate limited by external phenomena since most coatings are designed to be relatively dilute when deposited. So, as drying begins, the solvent or volatile liquid is plentiful at the free surface of the coating and the internal process that brings the volatile species to the surface (e.g., diffusion in the polymer/solvent system) is fast. Therefore, we do not expect internal factors to control the rate. Instead external factors, related to the driving force for the transport in the vapor phase or mass transfer coefficient, dominate. As drying continues, however, and the solvent content drops, eventually internal transport slows and becomes rate controlling until the end of the process.

External solvent vapor transport rates are affected by both the liquid-vapor equilibrium and gas phase conditions. An equilibrium between the liquid and the vapor is established at the free surface of the coating, and this equilibrium sets the partial pressure of the vapor adjacent to the free surface, P^* . An important point to remember here is that P^* increases with temperature. At some distance away from the surface, the partial pressure of the solvent vapor is set by the conditions far from the coating at P^∞ . The “driving force” for the removal of solvent vapor away from the coating surface is therefore the difference of these two values, $P^* - P^\infty$. For any drying to occur, P^* must be greater than P^∞ . The driving force is manipulated by temperature and solvent vapor concentration in the oven. Raising the temperature increases P^* ; an obvious limitation is boiling, which should be avoided. Solvent vapor concentration in the oven is kept low by flowing solvent free air through the oven. In the special case of aqueous coatings and

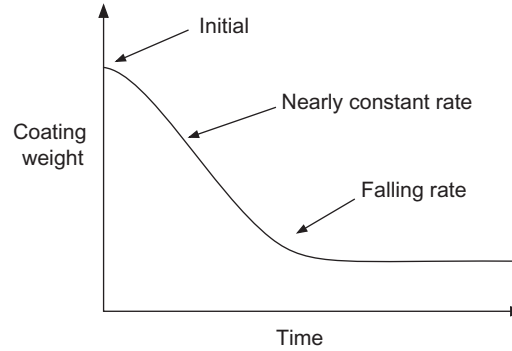


FIGURE 6.18 Schematic of weight loss from a drying coating. In the initial stage the drying rate (slope of the curve) is low as the coating or cast piece is heated to the temperature of the dryer. During the nearly constant rate period, the drying rate is nearly constant and external factors, such as airflow control the rate. In the last stage, the rate decreases as the supply of volatile liquid is depleted and internal factors, such as diffusion, limit the process.

water-saturated cast pieces, the drying rate is very much influenced by the relative humidity.

Drying is characterized by measuring coating weight as a function of time. Figure 6.18 shows a schematic representation. Usually, the data is normalized to the area of the coating, so that the slope of the curve, the drying rate is given in mass per area per time (e.g., $\text{kg}/(\text{m}^2 \cdot \text{s})$). (*Note:* such normalization of the drying rate is not relevant in drying of 3D objects as the exposed surface area changes with time.) By convention, this drying rate is stated as a positive number. Considering the external control of drying, the drying rate represents the flux of the volatile species in the gas phase away from the coating surface, $J_{S,g}$:

$$J_{S,g} = k(P^* - P^\infty) \quad (6.42)$$

The flux is the product of the driving force and k , the mass transfer coefficient, an empirically derived parameter that increases with the rate of airflow. Increasing the airflow, with air jets or fans, for example, increases the mass transfer coefficient. Hot air flow with jets impinging on the coating surface is one of the most important modes of drying. The drying rate (i.e., $J_{S,g}$) is constant in the early stages of drying because the driving force is constant. That is, a coating or cast article with high volatile liquid content has a reasonably constant P^* so long as the temperature is constant.

Heat transfer is required for drying. Heat must be transferred to the drying material to supply the latent heat of vaporization and also to raise the temperature of the material in order to speed the drying process. If heat is not supplied or not supplied fast enough, then evaporation lowers the temperature of the material. Evaporative cooling is a familiar phenomenon; evaporation of sweat keeps our bodies cool. Heat may be carried to the surface by

hot air (i.e., convection), transferred from hot solid that is in contact with the drying material (i.e., conduction), or absorbed from infrared radiation (IR) emitted by a hot solid nearby or an IR heater. Heat supplied to the surface of the drying material is then transferred to its interior by conduction.

Transient effects from evaporative cooling can also play a role in the drying rate. The heat of vaporization must be supplied for the phase change from liquid to vapor. So if the heat delivery to the drying coating or piece is not sufficient to raise the temperature of the drying material and supply this latent heat, then the temperature drops and P^* drops along with it. Typically, this phenomenon happens as the drying coating or piece first enters the drying oven. With time, temperature climbs to the temperature of the oven and P^* increases.

As drying continues, the content of the volatile liquid in the coating or part drops and the drying rate falls. The onset of falling rate period marks the beginning of the phase of drying that is controlled by internal factors. That is, the limiting step is getting the volatile liquid to the surface for evaporation and eventual removal in the gas phase. In this phase, drying is mainly controlled by diffusion. In the case of polymer-solvent coatings, the solvent must diffuse through the concentrated coating to the surface, and for coatings and cast pieces, the diffusion is of the vapor through the porous particulate material to the surface. More details are below.

Drying of Particle Dispersions. The course of events during the drying of a coating made from a particulate dispersion is shown in Figure 6.19. After the dispersion is applied to the substrate, evaporation begins at the liquid-air interface. As the volatile liquid evaporates, the liquid-air interface descends toward the substrate. As discussed above, it is likely that the coating liquid is relatively dilute so that it dries initially with a constant rate. The

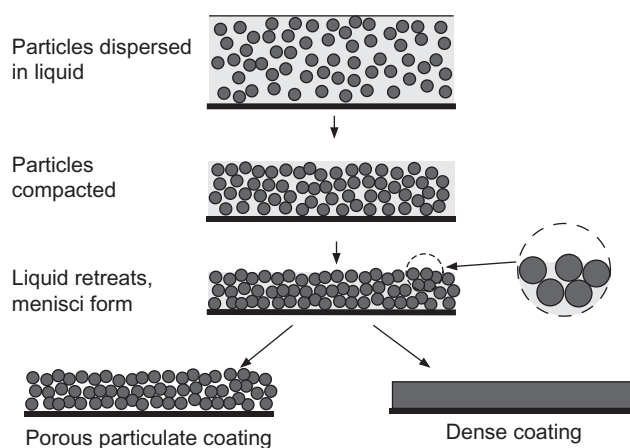


FIGURE 6.19 Stages of structure development in coatings made from particle dispersions.

evaporation rate (in grams per area of coating per time) found by a weight loss experiment can be converted to a rate of free surface descent (e.g., $\mu\text{m/s}$) during this phase. If the particles are colloidal in size or smaller, Brownian diffusion of the particles maintains a constant concentration of solids all of the way through the liquid. The decreasing amount of water brings the particles closer together and concentrates any soluble components that may be in the liquid phase. Increasing salt concentration can decrease the double layer thickness that surrounds particles, which may destabilize and possibly flocculate them.

Eventually, enough water is removed that a connected particle network is formed. At this point, the coating is quite similar in microstructure to a 3D part made by a slip casting process just as it is removed from the mold. Water evaporation and shrinkage continue, and the drying rate remains constant as long as particles remain submerged in water. The particles must rearrange into increasingly high packing fractions to remain completely saturated. At some point, the rearrangement stops and any further evaporation requires that the liquid-air interface retreat into the solids packing. Air invades into a particulate coating, creating curved menisci that, through surface tension and capillary forces, pull the particles toward each other. If the particles are colloidal in size, the pockets of air between them are sized for maximum light scattering and the coating turns from translucent to opaque.

As the air-liquid interface falls below the top surface of particles, the area for evaporation decreases and the effective evaporation rate is reduced. The “falling rate” drying period begins. The evaporation rate is reduced even further as the air-liquid interface recedes into the particle packing. In order for evaporation to occur, water-laden vapor must diffuse out through the pore space and fresh air must diffuse in. In the falling rate period, the evaporation rate is dominated by these diffusion processes, so later stage dryers often focus on heating the coatings to increase diffusion rates. Modifying convection (i.e., airflow), an external factor, is less effective. Likewise the same process occurs in a drying 3D part.

Just as the air-water interface is curved in a macroscopic glass capillary, the microscopic air-water interface is curved as it exists in the space between particles. The presence of curved liquid surfaces creates a pressure gradient in the packing, which is known as capillary pressure (see [Section 6.3.2](#)). When the particles are colloidal in size or smaller, the pressure difference across this interface can be an atmosphere or more. Even after most of the water has left the particle packing, some may be left behind at particle-particle contact points in what is termed a “pendular ring.” Here, the low pressure in the liquid as well as van der Waals and surface tension forces cause the particles to be pulled toward each other. The resulting stress is measureable and can also manifest itself in cracking. In 3D parts, drying stresses can cause warping as well. In the special case of a low T_g polymer latex, the particles are soft polymer spheres that deform. During drying,

particles flatten against each other at their contact points and the pore space shrinks until a dense coating is formed.

Drying Polymeric Solutions. Like particulate suspensions, polymeric solutions also dry with constant rate and falling rate periods. Initially, if the solution is below the concentration C^* , polymer chains distribute evenly in the suspension due to Brownian motion. The evaporation rate is constant, but it should be noted that P^* drops as the concentration of polymer near the free surface increases. Sometimes the drying rate still appears constant as this occurs because concurrently the coating is warming up to the oven temperature after experiencing evaporative cooling.

The falling rate period begins as further evaporation increases the polymer concentration to a critical level. Structurally, the polymer chains may start to entangle at this point and coating viscosity increases dramatically. The polymer solids now at the air-coating interface hinder evaporation. To complete the drying process, the remaining solvent must diffuse through the concentrated polymer-solvent network to the free surface. Again, the falling rate period is most affected by drying temperature and boosting the temperature of the dryer at this stage is effective at increasing the rate of evaporation.

Drying Stage Design Considerations. The drying stage takes up the most floor space and requires the most energy in a coating line, so mindful dryer design is essential for profitability. Since the drying process is multistage, dryers themselves are often sectioned into zones to target constant and falling rate drying differently. The atmosphere is most commonly air, but can be an inert gas, which can have the advantage of controlling explosive limits in the case of nonaqueous solvents. The gas flow can be either laminar or turbulent. Turbulence increases mass transfer but can affect surface flatness. The gas can also be heated, which is determined both for safety and energy considerations. Convection can be nonexistent, natural due to the evaporation process itself, induced (spin coating), or forced (tunnel dryers, flotation dryers, or impingement dryers). Finally, the gas can be recycled, which can decrease cost but also decrease the evaporation rate as compared to fresh air.

Although for economic reasons most drying processes are designed to dewater the product as quickly as possible, this can cause quality issues with the final part. Because the coating is effectively a solid during the falling rate period, stresses can build within it. In a particulate-based coating and slip-cast parts, stresses, as mentioned above, develop. If the coating dries unevenly the stresses are not balanced and cracks can develop. Gradients in the solvent concentration can develop both in the thickness direction and parallel to the substrate, and in various portions of a 3D part. Additionally, the constraint of the substrate prevents a coating from shrinking in the plane of the substrate and stress-induced curl or cracking is possible. One method to reduce cracking in 3D parts is to lower the evaporation rate, allowing the solvent time to redistribute when stresses develop.

Finally, drying multicomponent systems that contain both polymer and particles can often be a challenge; however, this is probably the most industrially common situation. Some polymer (called “binder”) is often added to particulate suspensions to act as a soft glue to hold the particles together. Particles are often added to polymeric solutions to act as a pigment or to modify the final hardness of the coating. When drying particulate suspensions reach the maximum particle packing fraction, dissolved binder in the solvent is still mobile. Depending on the drying rate and the viscosity of the liquid medium, a gradient of polymer can develop in the particle packing. Likewise, in drying particulate suspensions large, dense particles can sediment toward the substrate if the coating is dried too slowly. The resulting layered composition can either be desirable or a process challenge.

6.2.6 Curing of Liquid Monomers

Liquid monomers and oligomers are converted to solid polymers by reactions driven by heat or exposure to UV radiation or other energetic sources, such as electron beams. The process of solidification by chemical reaction is typically called “curing”. There are a host of chemistries designed for curing, including epoxies, polyurethanes, vinyl ethers, polyesters, and acrylates. Similarly the reaction mechanisms vary from condensation polymerization to free radical to cationic, for example. Given the richness and complexity of this topic and the processes that follow, the emphasis here is UV curing, a method used in the coating and 3D printing processes.

UV curing of liquid monomers and oligomers occurs in stages as the resin is exposed to UV light. [Figure 6.20](#) shows an example for free radical curing of acrylates. The first step is the formation of free radicals from dissociation of UV initiators. The initiators are UV absorbing chemicals dissolved into the resin. UV light covers a portion of the electromagnetic spectrum from a wavelength of 10 to 400 nm, but most UV curing is carried out in the ~200–400 nm range where many UV initiators absorb energy. The primary free radicals react with monomers, forming reactive groups on the monomer, which then launch continued reactions. The chain length grows by these propagation reactions, and additionally cross-links form with other chains as well as within themselves to form cycles. An important distinguishing factor in the monomers and oligomers that are used in UV curing is the functionality. That is, each reacting unit—monomer or oligomer—is capable of extending in multiple directions. For example, a trifunctional monomer has three sites for reaction. This feature leads to highly cross-linked networks. The process ends with the termination of these reactive groups, for example, by combination or disproportionation. To understand how to design a process to cure a coating or use curing to make a 3D printed shape, the effect of variables on the reaction rate and conversion from monomer to polymer should be understood.

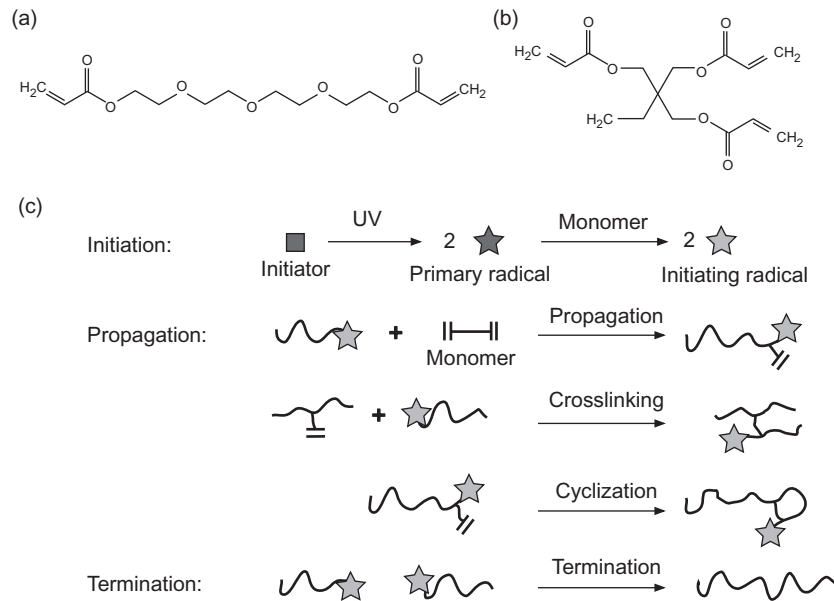


FIGURE 6.20 Acrylate monomer examples: (a) tetraethylene glycol diacrylate and (b) trimethylolpropane triacrylate. (c) Stages of reaction in UV curing of a diacrylate, neglecting chain transfer. *Courtesy of the A. V. McCormick research group, University of Minnesota.*

The initiation step is affected by the intensity of UV light, the concentration of photoinitiator, PI , in the resin, and the system geometry. Initiators can dissociate into two primary free radicals as they absorb light of a specific wavelength. The rate of initiation is a function of the light intensity absorbed, I_A . The intensity of incident light, I_o (in W/m^2 , for example), is a function of the specifications of the UV lamp and its proximity to the curing material. The light intensity transmitted, I_T , to a particular depth, z , is found with the Beer Lambert law:

$$I_T = I_o(e^{-\alpha[PI]z}) \quad (6.43)$$

where $[PI]$ is the photoinitiator concentration and α is the molar absorption coefficient of the PI (at the wavelength of illumination). The term $\alpha[PI]z$ is called the absorbance. The light intensity absorbed at a particular depth is:

$$I_A = I_o(1 - e^{-\alpha[PI]z}) \quad (6.44)$$

This relationship indicates that the gradient in intensity (and hence rate of initiation) is stronger in resins with high photoinitiator concentration. Absorbance increases with $[PI]$ and hence lower photoinitiator concentration must be used if thicker coatings or deeper cure depths are needed.

Dropping $[PI]$, however, slows the overall rate of conversion; an increase in I_o can compensate for this problem.

The free radicals generated in the initiation step react with monomers or oligomers to form initiating radicals and then these go on to react with monomers (or pendant groups on other chains) to propagate (or cross-link) the chains. Chains grow by monomer addition. Additionally, due to the multifunctional nature of the monomers, cross-linking between chains occurs and cycles can form. The rates of these reactions depend on the diffusion and so as the reactions proceed, their rates diminish. Further, there are termination reactions that result in the annihilation of the reacting sites. Overall the extent of conversion of the monomer to polymer can be monitored by a number of characterization tools. This extent of cure depends on the total amount of energy absorbed per unit area, which is known as the dose. The dose is the intensity multiplied by the illumination time.

Similar to drying, UV curing for coatings made on flexible webs is done continuously. After the resin is applied, the coated web passes under a UV lamp or several lamps. The speed of the process can be limited by this step and so the conditions for the resin and lamps are chosen for fast reactions and a high degree of conversion and cross-linking. Usually, high intensity lamps are used together with resins having an optimized photoinitiator content. For some resins, inert gas blankets the coating to prevent oxygen from inhibiting the cure by reacting with free radicals. This issue is experienced by acrylates, for example.

6.3 SHAPE CASTING

6.3.1 Process Overview

Shape casting from dispersions is a forming method to produce intricate and complex parts such as ceramic crucibles, toilets, and turbine blades. As a liquid, the dispersion is able to fill the fine features of porous and nonporous molds. Since ceramics are not made into complex shapes by melt casting, shape casting from a dispersion of ceramic particles is sometimes the only route to 3D ceramic shapes on an industrial scale. Since other, arguably more efficient methods of making metal and polymer shapes are available, shape casting from dispersions is almost exclusively a ceramic process.

There are several general steps in a shape casting process. The first step is the formulation and preparation of the dispersion. The dispersion must not only have the proper flow properties for casting, but also be composed of particles with the best characteristics for the process and other components to aid in the development of structure during and after solidification in the mold. The dispersions have a low enough viscosity to be poured under gravity into a mold. Next solidification occurs in the mold by extraction of the liquid medium of the dispersion into a porous mold (slip casting) or by

reaction (gel casting). After this “casting” step, the part is removed from the mold, dried, heated to remove binder if necessary, and then sintered at high temperature to develop a dense microstructure.

Slip casting, which is the main topic of this section, begins with proper formulation and mixing of a high solids loading slip and the preparation of porous mold with the desired final shape. Several considerations go into the selection of the powder starting materials for slip, as discussed more below. Most molds are made from gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$). Gypsum has a natural microstructure composed of needles and plates, which create a highly porous structure that is strong given the mold porosity. Molds are typically 50% porous, with a pore size of about $1\text{--}5\text{ }\mu\text{m}$ in diameter and up to $20\text{ }\mu\text{m}$ in length. Gypsum is also hydrophilic, so it takes up water easily. To protect the gypsum from acidic slips that degrade the material, the mold surface may be coated with a layer of inert material such as silica. In some high pressure casting operations, polymer molds are used.

After the slip is poured into the mold it is allowed to cast or solidify. See Figure 6.21. Capillary action draws water into the mold, leaving behind a consolidated layer of particles on the mold surface. This solid layer increases in thickness with time. Slip casting times vary greatly depending on the particle size, degree of flocculation, and part thickness. The casting time ranges from a few minutes for some parts to hours or even days. When the desired consolidated layer thickness is achieved, the excess liquid is drained from the center of the part, if a hollow part is desired. The part must then be removed from the mold. Separation from the mold may occur naturally as the part dries and shrinks. Parts are often removed as soon as they are robust enough to resist deformation and fracture during handling. Once the green part is removed, post-processing operations, including drying and sintering, are performed.

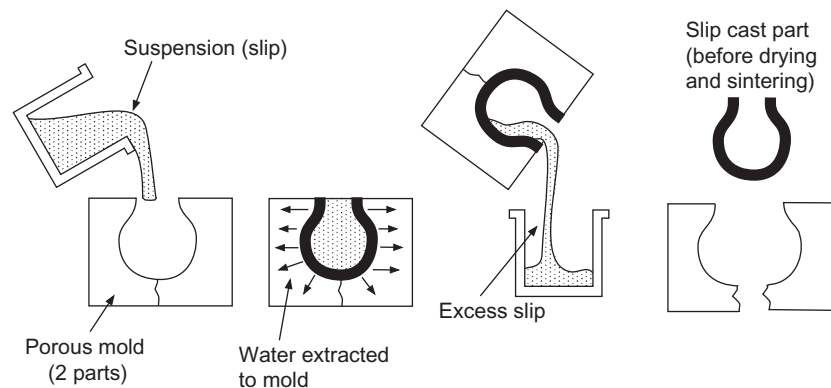


FIGURE 6.21 Schematic of the slip casting process. Adapted from Richerson (1992).

There are several variations of slip casting. Figure 6.21 shows “drain casting,” the process variation for a hollow part; after a specific amount of time, slip is poured off and the hollow part is removed from the mold. Another variation is “solid casting,” which produces a completely solid piece by filling the entire mold with slip. The mold is replenished with more slip as the liquid level falls until a completely solid piece is formed. After the part is removed from the mold, it is still “wet”; the pore space in the ceramic is filled with water. Therefore drying is required, followed by high temperature sintering for densification.

This section begins with a description of capillarity and an exploration of the casting rate, the rate at which solid ceramic particles accumulate on the mold wall. The casting rate is one of the important considerations when designing a slip composition and mold features. These and other process considerations are then discussed. The section concludes with comments on the post-processing of the parts made by shape casting.

6.3.2 Capillary Action

The flow of water into the porous mold is central to the slip casting. In Chapter 3, we learned that the liquid surface tension causes a pressure difference across curved liquid interfaces and that liquids wet surface based on a balance of interfacial energies. These phenomena are coupled in capillary action or capillary-driven flow into porous media.

Capillarity can be understood by considering a capillary tube plunged into a liquid, as shown in Figure 6.22. If the liquid wets the walls of the tube, then the liquid surface curves and a low pressure is established beneath the curved meniscus. The pressure difference for a spherical meniscus of radius, r , is:

$$\Delta P = \frac{2\gamma_{LV}}{r} \quad (6.45)$$

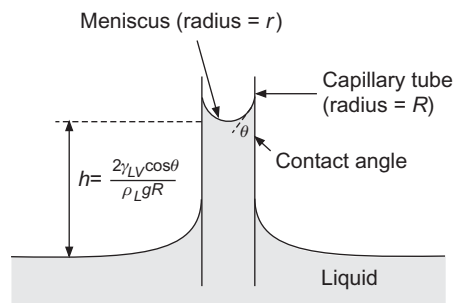


FIGURE 6.22 Schematic of rise of a wetting liquid up a capillary tube.

where γ_{LV} is the surface tension of the liquid and ΔP refers to difference in pressure between a flat liquid surface and the curved surface. The pressure causes flow of the liquid and the liquid rises until the hydrostatic pressure created by the column of liquid equals the capillary pressure given in Eq. (6.45). In slip casting, the pores are very tiny, commonly less than a micron in size and so the pressure difference is large across the meniscus. Therefore, the driving force for the liquid to enter the pores of the gypsum mold is very strong.

6.3.3 Predicting Cast Layer Thickness

After the slip or suspension is poured into the porous gypsum mold, water begins to move from the slip into the porous mold, leaving behind a layer of ceramic particles. Predicting how this cast layer thickness grows with time is essential to process design. In a drain casting operation, for example, this prediction is needed to select the time to pour off the excess slip. In general, the slip cast thickness increases with the square root of the casting time. In order to explain this observation and understand the factors that control the casting rate, a model is introduced for cast layer thickness.

There are two essential features of this model. The first is the motion of water from the slip into the mold. The driving force for this movement is a pressure difference set up by the curvature of menisci in the pores of the gypsum. One way to think of the mold is as a network of tiny capillary tubes, as described in the last section. Water wets the interior walls of the tube, forming a curved meniscus and the low pressure created by this curvature pulls water into the mold. This action is the same as a paper towel wicking up a spill. The second feature is accumulation of the ceramic particles; by tracking the water movement volumetrically the thickness of the stranded particles on the mold wall is found.

First, to understand the role of the mold alone, consider the simplified one-dimensional process illustrated in Figure 6.23, where water (with no particles) is drawn into a porous gypsum mold. At time $t = 0$, water is filled into a reservoir up to a level $x = L_s^0$, and contacts the mold. At the mold surface ($x = 0$), the pressure in the water is P_i and assumed to be independent of the water level (i.e., hydrostatic effects are not important). Water wets the hydrophilic gypsum and is drawn into the mold by capillary action. At time, t , some water has left the reservoir and entered the mold. In this model, there is no drying from the top surface so all of the water that leaves the reservoir enters the pores in the mold, saturating the mold to a level $x = -L_m$. The water within the mold is called the “filtrate.”

Conservation of volume gives the relationship between the position of the wet/dry interface in the mold, $x = -L_m$, and the height of the remaining water in the reservoir, $x = L_s$. Essentially, all of the water missing from the reservoir is in the pores of the mold. If the volume fraction of pores in the

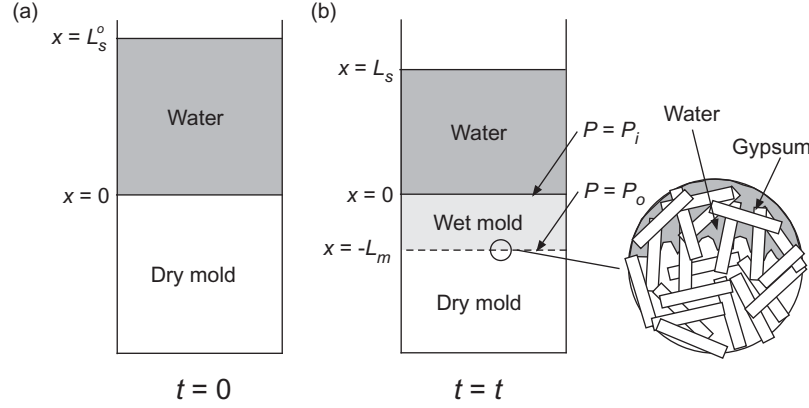


FIGURE 6.23 Schematic of the coordinate system for simple one dimensional water wicking from a reservoir into a porous mold. (a) At time $t = 0$, the water just make contact with the mold. (b) At time $t = t$, some water has moved from the reservoir into the pores of the mold. The inset shows water in the pores of the gypsum. Notice that the water wets the pore walls, creating a curved meniscus.

mold is ε_m and the area of contact between the mold and the water is A , then conservation of volume requires:

$$\int_{-L_m}^0 A \varepsilon_m dx + \int_0^{L_s} A dx = AL_s^o$$

$$\varepsilon_m L_m = L_s^o - L_s \quad (6.46)$$

The volume of filtrate V_F inside of the mold at time t is:

$$V_F = \varepsilon_m AL_m \quad (6.47)$$

Where water fills a pore between gypsum particles, the water-air interface is shaped as a curved meniscus. The pressure in the liquid under the curved interface, P_o , is lower than atmospheric due to capillary effects. Capillarity is especially strong given that the pore size in the gypsum is on the order of a micron, so the radius of curvature of the meniscus is very small. A pressure gradient is therefore imposed between the bulk of the liquid and the filtrate, as illustrated in Figure 6.24. Under the influence of this pressure gradient, water flows into the mold. The flux of a liquid, J_F , through a porous network is modeled using Darcy's Law:

$$J_F = -\frac{1}{\alpha_m \eta_F} \left[\frac{dP}{dx} \right] \quad (6.48)$$

Here, α_m is the resistance of the mold (units m^{-2}) and η_F is the viscosity of the filtrate. The mold resistance can be estimated using the Kozeny-Carmen approximation for the specific resistance

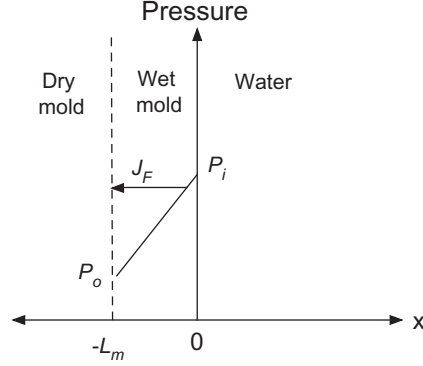


FIGURE 6.24 Pressure gradient established by the low pressure beneath the curved menisci in the porous mold.

$$\alpha = \frac{B(1-\varepsilon)^2 S^2}{\varepsilon^3} \quad (6.49)$$

In this expression, B is a constant (e.g., ~ 5 for many porous materials) and S is the specific surface area of the gypsum, which is the total surface area per unit volume. Note that the specific resistance depends on both the size and quantity of pores in the porous material. As the void size increases, S decreases, and therefore α also decreases. With respect to the volume fraction of pores in the mold, α decreases as ε increases. So molds with high porosity and large voids allow faster flow of the filtrate. However the flux, J_F , also depends on the pressure gradient driving flow, and this gradient is also a function of pore size. The curvature of water menisci in small pores is extreme, and the capillary pressure driving the flow depends on the inverse of the meniscus radius.

To derive an expression for the wet/dry interface L_m as it progresses in time, the water flux J_F is defined in terms of the change in the filtrate volume with time. A negative sign is added to account for the direction of the volume removal, which is in the $-x$ direction.

$$J_F = \frac{1}{A} \frac{dV_F}{dt} = \frac{1}{A} \frac{(\varepsilon_m A dL_m)}{dt} = \varepsilon_m \frac{dL_m}{dt}$$

$$J_F = -\varepsilon_m \frac{dL_m}{dt} \quad (6.50)$$

By setting this expression and Darcy's law equal to each other, an expression for the position of the wet/dry interface as a function of time is found:

$$-\frac{1}{\alpha_m \eta_F} \left[\frac{P_i - P_o}{0 - (-L_m)} \right] = -\varepsilon_m \frac{dL_m}{dt}$$

$$\frac{P_i - P_o}{\varepsilon_m \alpha_m \eta_F} dt = L_m dL_m$$

$$\int_0^t \frac{P_i - P_o}{\varepsilon_m \alpha_m \eta_F} dt = \int_0^{-L_m} L_m dL_m$$

$$L_m = \left[\frac{2(P_i - P_o)t}{\varepsilon_m \alpha_m \eta_F} \right]^{1/2} \quad (6.51)$$

This expression for the capillary flux of water into the gypsum mold shows that the water interface position increases with $t^{1/2}$. Even without particles in the water, the $t^{1/2}$ dependence is apparent as are the roles of the pressure difference, specific resistance of the mold and viscosity of the filtrate (water) on the advance of the wet/dry front.

In slip casting, particles are suspended in the water phase. Therefore as water is pulled into the mold the particles suspended in that water are left behind on the mold surface (i.e., by design they are too large to be carried into the pores). The situation is shown in Figure 6.25. The cast layer becomes another porous layer that water must pass through before it reaches the mold. This layer has its own specific resistance, α_c and void fraction, ε_c . Because the cast layer resistance is not equal to the mold resistance, the pressure drop through the cast layer and mold are not equal. However, the minimum pressure in the system, P_o , that drives the water flux through both layers is the same capillary pressure that was used in the simplified case.

The derivation of the cast layer thickness, L_c , as a function of time follows the same general ideas as above, but is more complex. The volume

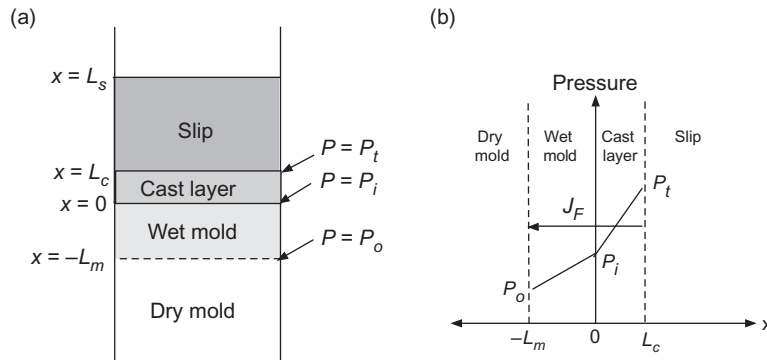


FIGURE 6.25 (a) Schematic of a one-dimensional slip casting process and (b) the pressure gradient established in the porous mold and altered by two resistive layers—the cast layer, which is a dense packing of ceramic particles, and the porous mold.

conservation must include not only the water but also the particles, and one more interface position must be tracked. Aksay and Schilling (1984) present the derivation in detail. The main result is the following equation for the cast layer thickness as a function of time:

$$L_c = \left[\frac{2(P_t - P_o)t}{\beta \eta_F \left(\alpha_C + \frac{\beta \alpha_m}{\varepsilon_m} \right)} \right]^{1/2} \quad \text{where} \quad \beta = \frac{1 - \phi_p - \varepsilon_c}{\phi_p} \quad (6.52)$$

where ϕ_p is the volume fraction of particles in the slip, which is assumed to be constant throughout the casting process, and β is a constant that arises from the conservation of volume that is carried out on the water and the particle phases. For a constant ε_c , β decreases as solids loading of the slip (ϕ_p) increases. The equation shows that the cast layer thickness grows with a $t^{1/2}$ dependence. In other words, to double the cast layer thickness, the casting time has to be increased by four times.

Typically, the cast layer resistance is greater than the mold resistance. The mold is designed to conduct the liquid away and is optimized for that purpose. The cast layer, on the other hand, is frequently composed of small particles packed with a small void fraction. Under these conditions, Eq. (6.52) simplifies to:

$$L_c = \left[\frac{2\Delta P t}{\beta \eta_F \alpha_C} \right]^{1/2} \quad \text{when} \quad \alpha_C \gg \alpha_m \quad (6.53)$$

where ΔP is used for the pressure drop across the cast layer and the wet mold.

By analyzing Eqs. (6.52) and (6.53), the important design principles of slip casting are illustrated. The casting rate can be increased by increasing the pressure difference between the slip and the dry mold ($\Delta P = P_t - P_o$). This can be done by increasing the surface tension or decreasing mold pore size, which decreases the capillary pressure P_o , or by imposing an external pressure on the slip, which increases P_t . Another option is vacuum casting, which drops the pressure in the mold further. Increasing the solids loading of the slip also increases the casting rate by decreasing the parameter β . With higher solids, less water removal is necessary to deposit an equivalent cast layer as a lower solids slip. Also, decreasing the viscosity of the filtrate also speeds slip casting. (Note that the viscosity of importance here is the water viscosity and not the slip viscosity.) However, since the filtrate is most often water, this parameter is not adjustable. Finally, the specific resistance of the cast layer can be decreased. Such a change could be accomplished by increasing the particle size or by increasing the void fraction of the cast by introducing a destabilizer. Such changes, however, must be made in consideration of the entire process and the requirement for the final ceramic.

6.3.4 Slip Casting Process Considerations

In designing a slip casting process, multiple factors are considered and trade-offs made. A change that enhances the casting rate may lead to a slip that is not stable with time or too viscous to pour. Ultimately some compromises are necessary.

Successful design of a slip casting process relies on proper formulation of the ceramic slip. Casting rate, drying shrinkage, green strength, and sinterability all rely largely on the slip formulation. Unfortunately, optimizing some of these parameters means that others are detrimentally affected. Slip casting begins with proper formulation and mixing of a high solids loading slip. Viscous slurries of ceramic particles are challenging to mix and homogenize. Ball mills and vibratory mills are often used. Additives that might lead to foaming or degrade during the first mixing process are often incorporated to the mixed slurry in a second, less energy intensive process. If air bubbles are formed in the milling process, they are removed from the slip before the casting process.

One major consideration is the slip viscosity, which must be chosen so that the slip is easily poured into the mold and fills the detailed sections of the part. Typical slip viscosities range from 100 to 1000 mPa · s. High solids loading slips contain less water to remove into the mold, but they are also very viscous and possibly difficult to work with. Therefore, most slips contain 40–50 vol% particles. Water is the most common solvent, although in cases where the particles may become hydrolyzed or gelled (MgO, CaO) or form an undesirable oxide layer in water, other solvents such as an alcohol may be used. Binders (<1 vol%) such as carboxymethyl cellulose or low T_g latex can be necessary to give the green part enough strength so that it can be removed from the mold and handled when completely dry. The trade-off is that many binders increase the suspension viscosity and decrease the rate of the water flow rate into the mold.

Designing the particle size distribution is also a challenge that affects both dewatering of the slip as well as the sintering process. Smaller particles can be pulled into the pores of the mold, clogging the gypsum. Pore spaces between small particles are tortuous and constricting, leading to low dewatering rates. Larger particles, however, may sediment during the casting process and the resulting green ceramics sinter less efficiently. A typical slip contains powder particles ranging from 1 to 5 μm in size, although either smaller or larger particles can be used by making concessions in the process design.

One effective method for controlling dewatering rates is adjusting the stability of the slip. Highly flocculated slips form fractal, porous particle gel networks in the cast layer that allow water to pass through quickly, reducing casting time. Conversely, particles in highly deflocculated slips rearrange during the casting process into a dense packing. Water flows through the particle packing more slowly, increasing the casting time, yet the resulting green

part is very dense, which is advantageous for the sintering process. Deflocculated slips pour and fill the mold easily, so one strategy is to add a coagulant just before casting so that the particles aggregate once the slip has filled the mold.

There are several ways to increase the casting rate without making trade-offs with the slip composition. “Vacuum casting” and “pressure casting” are other process variations that speed up the solidification process by applying a vacuum to the outside of the mold or pressure to the slip, respectively. In “centrifugal casting,” the part is spun to create centripetal forces to consolidate and pack particles at the mold walls.

Slip casting is advantageous due to the high level of detail that can be produced in the green structure, relatively low expense of the process, and the level of homogeneity that is gained in the green part. Disadvantages include the time required to produce a single part, and the limits placed on the process by the porous mold and the capillary action. Namely, slip casting of submicron particles, which have considerable technical importance is a challenge due slow casting rate and clogging the mold.

6.3.5 Post-Processing Operations

Once the part is cast and the excess slip is poured from the mold, post-forming or post-processing operations are performed. The part is removed from the mold and dried completely. Although slip casting in general produces a green part with a smooth surface, there can be a ridge that is left behind at the seam between the two mold halves. This defect is sanded off in the green state. The organics in the part, including any binder, are then decomposed at a low temperature (300–600°C). Next, the part is sintered at a high temperature (900–1500°C) to form a dense, strong final product. Finally, surface coatings such as paints, glazes, or other decorations can be applied to complete the operation.

6.4 COATING AND TAPE CASTING

6.4.1 Process Overview

Thin, flat sheets of polymer, ceramic, or metal particles are produced from coating dispersions, solutions, and liquid monomers. Tape casting is a special type of coating process in which a dispersion containing ceramic particles with polymer binder is coated onto a substrate. In all cases, a liquid dispersion is deposited, spread onto a substrate, and subsequently solidified. In tape casting, the solidified sheet is stripped from the substrate and then heated to remove the polymer and sinter the ceramic sheet. Adhesive tapes, capacitor layers, displays, recording media, decorative varnishes, and

protective barriers are all examples of functional coatings created from dispersions, solutions and liquid monomers.

There are a tremendous variety of coating operations, ranging from those designed to coat flexible substrates (webs) at high speeds to those that coat discrete objects like ophthalmic lenses or silicon wafers. The fundamental steps in a liquid coating process are: (i) preparing the liquid, (ii) feeding or transporting the liquid to the coating apparatus, (iii) distributing the coating liquid on the substrate, (iv) metering the coating liquid such that a uniform liquid layer is achieved, and (v) solidifying the liquid layer, typically by drying, curing, or chilling.

Figure 6.26 shows an example of a continuous operation for preparing polymer coatings on flexible substrates (webs). The flexible substrate comes in a roll and the apparatus unwinds it and controls its motion and tension during the process. Polymer solution is pumped at a controlled rate into a slot die, which is stationed over the web at a precise position beneath a back-up roll. The details of the die are shown in a later figure, but given that the solution enters the die in a central location a distribution chamber similar to the one shown in Chapter 3 for extrusion of polymer sheets would be used to assist the delivery. This chamber allows easy flow cross web so that the polymer solution exits the slot at a constant rate across the web. The next step is metering, creating a liquid layer with a uniform thickness. Slot coating is “pre-metered”—thickness is determined by the flow rate into the die and the substrate velocity. The coated substrate is carried through a dryer, where solvent is removed, and the final coated product is then collected in a roll at the end of the production line. This sort of process is frequently referred to as a “roll to roll” (R2R) process.

As discussed previously, the drying step often is rate limiting in designing a coating process. For example, if the coating is applied at 20 m/min and

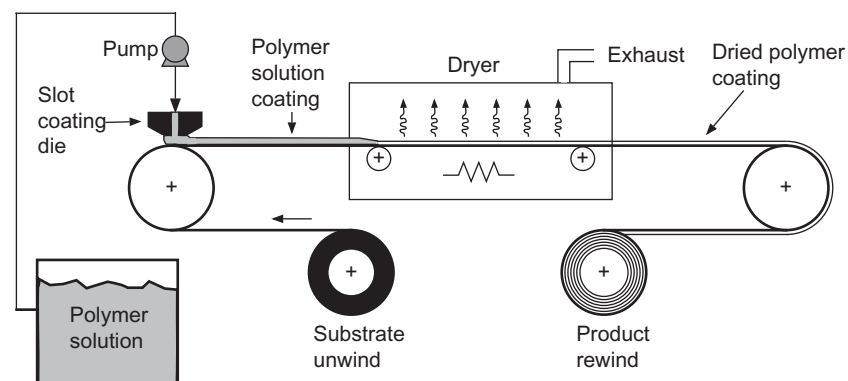


FIGURE 6.26 Schematic of a continuous process for coating a flexible substrate (web) slot coating of a polymer solution. This schematic shows some of the main features.

drying takes 2 minutes, a 40 meter long dryer section is required. If the dryer is impractically long and the drying process itself cannot be shortened, the coating or deposition speed must be decreased. Drying a coating too quickly can cause coating defects such as blisters and cracks. The drying section can also encompass annealing or curing for polymeric coatings.

Once a coating is dry, post-processing steps also occur at the speed of the web. For example, calendering is common in paper manufacturing. Most paper is coated to improve the surface characteristics and interaction with inks. This coating is calendered, or passed through a set of rollers that apply pressure to create a smoother, glossier surface finish. Laminates can also be applied in a separate step. In the case of ceramic tapes, the green tape must be sintered after it is dried of moisture and the binder removed.

Like all dispersion and solution processes, the liquid properties dictate the design of the coating process. Rheology is important for transporting, applying, metering, and leveling the coating liquid. High viscosity liquids are difficult to apply quickly to fast moving webs. Surface disturbances from coating liquid application may also take longer to level (by surface tension) and may be locked in by the drying stage. Low viscosity liquids may drip, pool, or be blown about in impinging air dryers. How the coating wets and spreads on the substrate is as important to understand as its rheology. In all cases, a coating liquid must replace air at a substrate interface without trapping bubbles or dewetting. Some advanced coating processes apply one liquid layer on top of another liquid layer before the drying stage. Here, the wetting of one liquid on another is important, as well as the surface tension between the adjacent liquids and their miscibility.

In this section, a brief overview of liquid coating methods followed by a discussion specific to how these processes are used to make polymer coatings and tape cast ceramic layers.

6.4.2 Coating Methods

Several coating application methods are available for selection based on considerations including coating liquid properties, production speed, and cost. Whether the substrate is a continuous web or an irregularly shaped object also may limit options for coating operations. Figure 6.27 shows schematics of several common coating application methods that all involve coating onto moving substrates. They range from methods that involve plunging a substrate into the coating and then pulling it out without (Figure 6.27a dip coating) and with post-metering (Figure 6.27b knife coating) to a fixed or adjustable gap applicator that feeds liquid from a reservoir (Figure 6.27c doctor blade coating). Precision high speed coatings are frequently prepared with pre-metered processes such as slot coating (Figure 6.27d), slide coating (Figure 6.27e), which involves liquid flowing down an inclined plane after it exits at a controlled flow rate from a slot die, and curtain coating

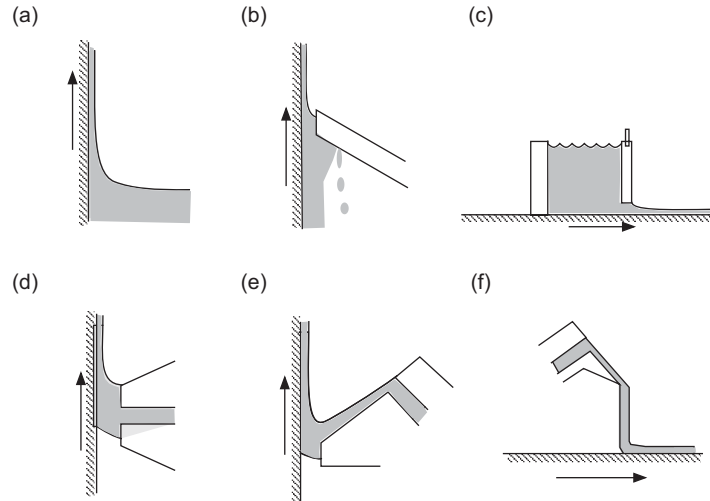


FIGURE 6.27 Different methods for applying liquid coatings onto moving substrates: (a) dip coating, (b) knife coating, (c) adjustable gap blade coating (doctor blade coating), (d) slot coating, (e) slide coating, and (f) curtain coating. In (a) and (b) the liquid is pulled from a vat or container; in (c) a liquid reservoir is kept full during coating and in (d)–(f) the liquid is pumped into the coating die. *Courtesy of M.S. Carvalho, Pontifical Catholic University of Rio de Janeiro.*

(Figure 6.27f), which is like a waterfall of coating liquid that impinges on a moving substrate.

Dip Coating. Perhaps the most obvious method of coating is dip coating. See Figure 6.28. A substrate is immersed in a pool of liquid and then removed at a fixed speed. The process can be conducted with a discrete substrate and or with a continuous substrate that plunges into the bath of coating liquid and then is pulled out and into a dryer.

Controlling the thickness of the as-deposited liquid entails a balance of forces. Liquid clings to the substrate as it exits the bath; a viscous drag pulls the liquid upward. This force is proportional to the product of the substrate speed and the viscosity and inversely proportional to the thickness, $\eta U/h$. At the same time, the liquid layer experiences the tug of gravity, which is proportional to ρgh , where ρ is the density of the coating liquid. Considering only these two forces, a simple estimate is derived by setting these two forces equal:

$$h_{\text{wet}} = \sqrt{\frac{\eta U}{\rho g}} \quad (6.54)$$

where the subscript “wet” is added to emphasize the thickness is that before drying or other solidification event. It represents the thickness of the liquid

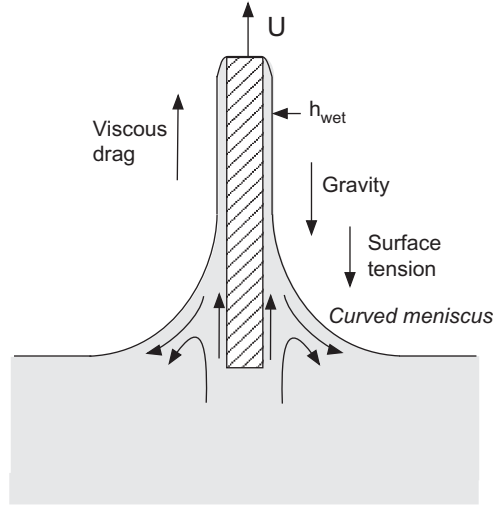


FIGURE 6.28 Schematic diagram of dip coating.

coating where it is flat, some distance away from the meniscus region near the bath. This simple relationship captures much of the action in dip coating. The viscous drag pulls liquid up and gravity forces it back down. The liquid attached to the substrate takes on the velocity of the substrate, moving upward, and the liquid at the free surface responds most to gravity, moving downward. Hence the velocity gradient between the substrate and the surface is complicated, especially near the bath. There is a stagnation point where the velocity is zero. Importantly, increasing the substrate withdrawal speed increases the thickness, making the prospect of depositing thin coatings time consuming.

In addition to viscous drag and gravity, yet another force comes from the curved liquid meniscus. The low pressure beneath this meniscus draws liquid from the newly deposited layer, which has a flat surface, downward back to the bath. This force is the result of surface tension. The relationship with all three forces included is:

$$h_{\text{wet}} = 0.944 \left(\frac{\eta U}{\gamma_{LV}} \right)^{1/6} \sqrt{\frac{\eta U}{\rho g}} \quad (6.55)$$

where γ_{LV} is the surface tension of the coating liquid. Equation (6.55) is frequently referred to the Landau-Levich equation, after the scientists who derived it. The new term, the ratio raised to the 1/6 power, is called the capillary number. The Landau-Levich equation was designed for low capillary number, less than about 0.01. Notice that as the capillary number increases toward unity, a trend consistent with increasing coating speed or coating

viscosity, Eq. (6.55) approaches the simpler Eq. (6.54). Also, the relationships for wet coating thickness do not account for non-Newtonian rheology or draining of the deposited liquid coating due to gravity. In practice, the second effect is usually not significant if thin coatings are prepared or if drying occurs immediately after deposition.

Dip coating has a number of applications, but the process also has a significant disadvantage. The technique is well-suited to coating discrete parts, exploring new coating materials and creating thin, uniform coatings. However, as Eqs. (6.52) and (6.53) show, the faster the substrate is drawn from the bath, the greater is the applied coating thickness. Therefore, the process is not well suited to high-speed, high-throughput coating operations. One solution is to dip coat and post-meter with a knife, as shown in Figure 6.27b.

Adjustable Gap Blade Coating (or Doctor Blade Coating). A second type of coating application method uses a rigid blade to establish a gap that meters coating liquid onto a moving substrate. The method is used extensively in tape casting of ceramics and the terminology in that field is “doctor blade coating.” A schematic of an adjustable gap blade coater or doctor blade coater is shown in Figure 6.29. The two main features of the applicator are the reservoir and the blade. The reservoir holds the coating liquid, supplying it to the gap established by the blade. Coating liquid can be replenished periodically or fed into the reservoir continuously. The blade establishes the gap; applicators may have a fixed gap or a gap that is adjustable by micrometers. The gap is of central importance to this coating operation and so substrate flatness and rigidity is also key. Lastly, the applicator must be rigidly held in the coating apparatus to prevent it from moving as the substrate travels beneath.

In doctor blade coating, the moving substrate drags coating liquid and the blade meters the coating liquid to produce a controlled thickness. The reservoir also plays a role, because hydrostatic pressure drives flow beneath the blade as well. To develop an understanding for the factors that control the wet coating thickness, let's consider the flow rate, Q , in two regions, as

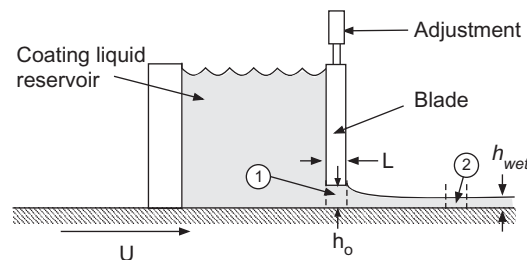


FIGURE 6.29 Schematic diagram showing the cross-section of an adjustable gap blade coating applicator. Two zones for flow analysis are noted: (1) directly under the blade and (2) the wet coating after exit.

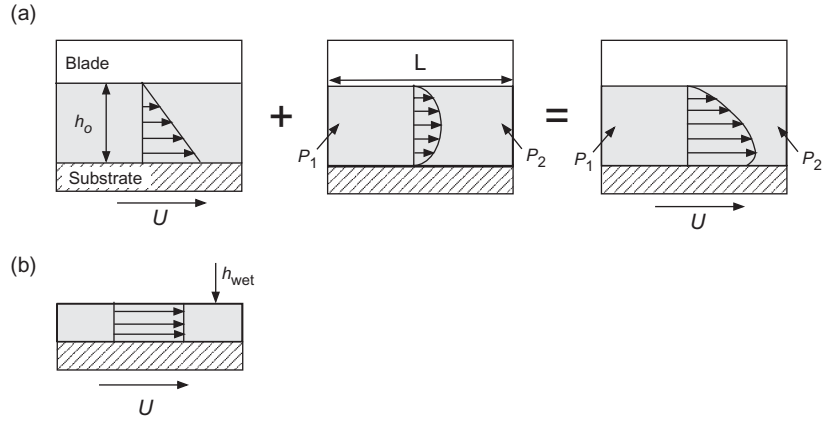


FIGURE 6.30 (a) Schematic diagram showing the velocity profiles under the blade in a doctor blade coating apparatus (region 1 in Figure 6.29). The drag portion of the flow (left) creates a linear velocity profile, the pressure-driven flow (middle) leads to a parabolic profile and flow with both drag and pressure-driven effects (right) is a summation of the two. (b) Schematic diagram of the coating after exiting the blade (region 2 in Figure 6.29), showing movement at the velocity of the substrate (plug flow).

noted in Figure 6.30. The first region is under the blade, where drag and pressure combine and the second region is the wet coating that is moving away from the blade with the substrate.

The action underneath the blade consists of two parts: a drag flow from the moving substrate and a pressure-driven flow from the hydrostatic pressure. Figure 6.30a shows the velocity profiles that develop from the drag and pressure effects separately and then added together. These two types of flow are explored in more detail in Chapter 3.

The drag from the moving substrate considered on its own (Figure 6.30a, left) produces a linear velocity profile in the liquid. Assuming that the liquid does not slip on any surface, the liquid in contact with the substrate moves with the velocity of the substrate, U , and the liquid in contact with the stationary blade is also stationary. Across the gap depth, the average velocity of the flow is $U/2$. Therefore, the volumetric flow rate in region 1 from the drag component, $Q_{1,d}$ is:

$$Q_{1,d} = \frac{U}{2} h_o w \quad (6.56)$$

where h_o is the gap and w is the width of the blade and coating. In this analysis, the width is assumed to be large so that it does not affect the flow.

For a stationary substrate, the only driving force for flow would be the pressure difference through the gap. In this case, the velocity profile would be parabolic, as illustrated in Figure 6.30a, middle. Since in this situation the blade and the substrate are not moving, the no slip condition causes the flow

to be stagnant at these two surfaces, and the greatest amount of flow is at the center of the gap. If the pressure in the liquid at the entrance to the gap is P_1 and the pressure at the exit of the blade is P_2 , the flow rate $Q_{1,p}$ across the blade of land length L , is given by:

$$Q_{1,p} = \frac{h_o^3(P_1 - P_2)}{12\eta L} w = \frac{h_o^3 w \Delta P}{12\eta L} \quad (6.57)$$

Notice that the pressure-driven flow has a stronger dependence on the gap height as compared to the drag flow component and is also influenced by the liquid viscosity η . Unless liquid curvature at the exit is considered, the pressure in the fluid exiting the die, P_2 , is assumed to be close to atmospheric. Here, we have assumed that the liquid is Newtonian. A somewhat more complicated expression for pressure-driven flow of non-Newtonian power law liquids is given in Chapter 3 and could be used in this analysis.

The total flow rate under the blade, Q_I , is then found by adding the individual components:

$$Q_I = \frac{U}{2} h_o w + \frac{h_o^3 w \Delta P}{12\eta L} \quad (6.58)$$

The velocity profile (Figure 6.30a, right) is the addition of the two components, a distorted parabola.

In the deposited layer, region 2, all of the coating moves with the velocity of the substrate:

$$Q_2 = U h_{\text{wet}} w \quad (6.59)$$

This type of flow is called plug flow. See Figure 6.30b.

Since all of the liquid flowing beneath the blade must also exit on the substrate (mass conservation), Q_I and Q_2 are equal:

$$\frac{U}{2} h_o w + \frac{h_o^3 w \Delta P}{12\eta L} = U h_{\text{wet}} w \quad (6.60)$$

Simplifying this expression, the coating thickness is:

$$h_{\text{wet}} = \frac{h_o}{2} \left(1 + \frac{h_o^2 \Delta P}{6\eta L U} \right) \quad (6.61)$$

In many processes, the speed and viscosity of the coating liquid are high enough so that the second term in the parenthetical expression in Eq. (6.61) is small and the coating thickness can be approximated as half of the gap.

Doctor blade coating is commonly used for viscous suspensions, such as those developed for tape casting. The method creates controlled thickness layers with high precision. A downside of the method is the contact between the applicator and the web and the use of gravity for feeding the liquid to the gap.

Slot Coating. Slot coating (also called slot die coating) is a pre-metered process; coating liquid is pumped through a slot die, with a controlled flow rate, Q , onto a moving substrate. The output of the process is a liquid layer of thickness h_{wet} traveling with plug flow at the substrate speed, U ; therefore, $h_{wet} = Q/U$ (on a per coating width basis). The ability to control the coating thickness by setting the flow rate and coating speed is a main advantage of slot coating as well other pre-metered methods, such slide and curtain coating.

Figure 6.31 shows a perspective schematic of a slot coating die as it applies coating liquid to a web. The coating liquid is pumped from a tank through a feed pipe located at the center of the die. To distribute the liquid across the length of the die and to ensure uniform output from the slot across the web, a distribution chamber with lower flow resistance is used. The die is spaced very close to the web, which is supported by a back up (or backing) roll. Because the process is very sensitive to the gap between the die and the substrate, this roll is designed to be smooth and have a highly circular cross-section so that no undulations occur as the roll rotates during the process. The coating “bead” is formed where the liquid meets the substrate.

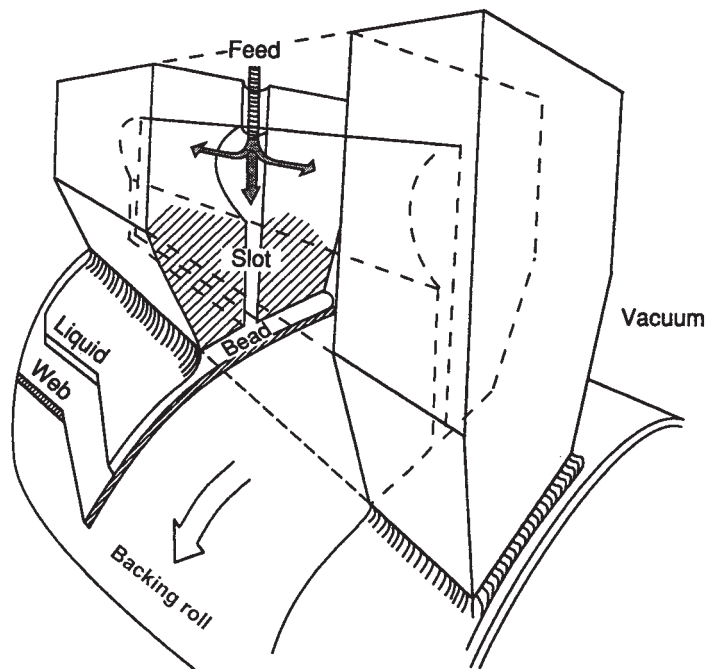


FIGURE 6.31 Schematic diagram of a slot coating die, web, applied liquid, and backing roll. The perspective of the drawing exaggerates the curvature of the roll. From Stokes, R. J. & Evans, D. F.: *Fundamentals of Interfacial Engineering*. Page 406. 1997. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

The shape of the bead depends on the process conditions. A vacuum box is placed on the upstream side of the die for extra control of the process, as discussed below.

The basic process analysis of slot coating has similarities to that of doctor blade coating; drag and pressure-driven flow combine to establish the conditions, but the fixed incoming flow rate leads to differences. A schematic of the lower part of the die, the coating bead, and the substrate is shown in Figure 6.32. Coating liquid is pumped in through a feed slot; the pressure in the bead at the entrance is noted as P_E . The shape of the die lips can vary considerably. In this example, the upstream and downstream die lips are parallel to the substrate surface and each is separated from the substrate by a gap, h_o . On the upstream side, the pressure in the gas phase, P_o , is either atmospheric or adjusted to be sub-atmospheric with a vacuum box. The downstream meniscus is bounded by gas at atmospheric pressure, P_{atm} . The pressures in the liquid at the upstream and downstream sides of the bead are noted as P_U and P_D . A first goal of the process analysis is to gain an understanding of the flow in the bead and the factors that control the coating thickness. To assist in this analysis, three zones are identified in Figure 6.32: 1. upstream, 2. downstream and 3. deposited coating.

Consider first the upstream side of the die (zone 1). Here, there is drag flow due to the moving substrate and pressure-driven flow. Again, we can add together the contributions of each. Combining the drag and pressure-driven terms as we did in the last section and assuming a unit coating width and a Newtonian liquid:

$$Q_1 = \frac{U}{2} h_o + \frac{h_o^3 (P_U - P_E)}{12\eta L_U} \quad (6.62)$$

where L_U is the contact length of the upstream die lip. To maintain a steady-state location of the upstream meniscus, the net flow in zone 1 is zero ($Q_1 = 0$) and therefore the second term in this equation must be less than zero, indicating that P_U , which is approximately P_o , is less than P_E (i.e., $P_U < P_E$). The velocity profile under these conditions is shown in

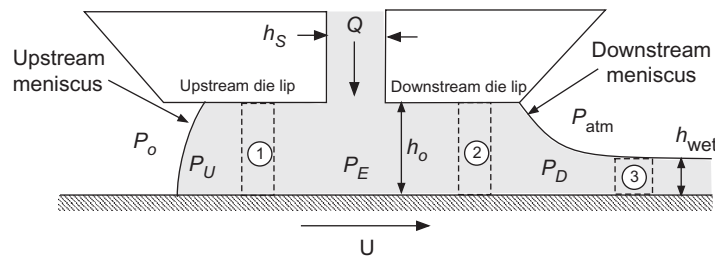


FIGURE 6.32 Schematic diagram of a slot coating die, coating bead and substrate. See text for description. Adapted from Romero et al. (2004).

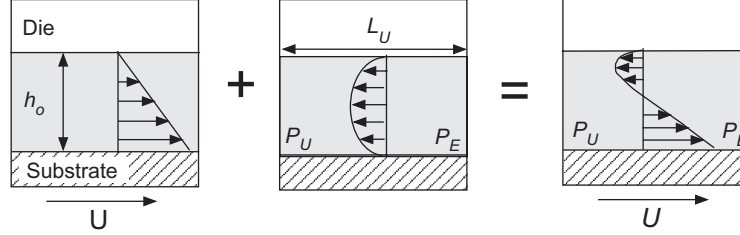


FIGURE 6.33 Schematic diagram showing the velocity profiles under the upstream die lip as a combination of drag and pressure-driven flow.

Figure 6.33. The direction of flow reverses across the gap and there is no net output.

In the downstream side of the die (zone 2), the liquid also experiences drag and pressure-driven flow, and last, the departing coating (zone 3) is transported by plug flow. By mass conservation, the flow rate in zone 2, Q_2 , is equal to the flow rate in zone 3, Q_3 , and both are equal to the flow rate from the feed slot. So, we can just use one “ Q ” for the process and set it equal to the plug flow output, assuming unit width:

$$Q = Q_2 = Q_3 = U h_{\text{wet}} \quad (6.63)$$

Analyzing now the flow rate in zone 2, we find that the wet film thickness follows the same expression as in doctor blade coating. Now, written with the variables of the slot die and on a unit width basis:

$$h_{\text{wet}} = \frac{h_o}{2} + \frac{h_o^3(P_E - P_D)}{12\eta L_D U} \quad (6.64)$$

where L_D is the contact length of the upstream die lip. Now the importance of the adjustable flow rate comes into play. If the flow rate Q is set (at fixed U) so that h_{wet} is greater than $h_o/2$ then P_E will be greater than P_D (i.e., the second term in Eq. (6.64) is greater than 0 and the pressure-driven flow is toward the deposited liquid layer). However, if the Q is decreased sufficiently so that h_{wet} is less than $h_o/2$, then P_E must be less than P_D ($P_E < P_D$) to maintain a stable coating bead. Since P_D is approximately atmospheric pressure, sub-atmospheric pressures are needed. To fulfill this requirement and achieve lower coating thicknesses, a vacuum is pulled on the upstream side of the die. The vacuum lowers P_U and P_E (but still maintains the requirement of $P_U < P_E$). The result of pursuing $h_{\text{wet}} < h_o/2$ and hence $P_E < P_D$ is that drag and pressure drive flows in opposite directions, as shown in Figure 6.33. When the thickness drops below a critical level ($h_o/3$), then recirculations appear in the downstream meniscus and these could have adverse effects as coating liquid is trapped in these circular pathways for some time.

As might be imagined, changing Q and the vacuum pressure (at a fixed U) results in different shapes for the coating bead. For example, starting from the conditions that lead the shape in Figure 6.32, increasing Q (and keeping all other conditions constant) would cause the bead to expand so that it contacts more of the upstream die lip. Likewise from the same starting point, lowering the pressure relative to ambient on the upstream side (i.e., increasing the vacuum) would lead to the same effect. Of course, variations in speed with Q and vacuum constant have similar effects. Under different conditions, the contact of the bead on the downstream die lip also changes. Based on these changing bead configurations and instabilities that come about in the exiting coating, a “coating window” can be defined.

Figure 6.34 shows a schematic of the coating window for slot coating. The coating window identifies regimes in process space that result in a stable coating bead and a high-quality liquid layer without defects. The axes on the plot are the main process variables. On the y-axis is the pressure on the upstream side of the beam represented as pressure below atmospheric. On the x-axis is $1/h_{wet} = U/Q$. This axis can be read in several of ways—increasing web speed or decreasing flow rate Q while keeping the other variable constant, for example. A good place to start is at the condition of no applied vacuum or $P_o = P_{atm}$ (y-axis is 0). Here, the coating window extends to a critical level of $1/h_{wet}$, where $h_{wet} = 1/2 h_o$. This value lies on the lower limit line (labeled 2 in Figure 6.34) where the bead pulls away from the

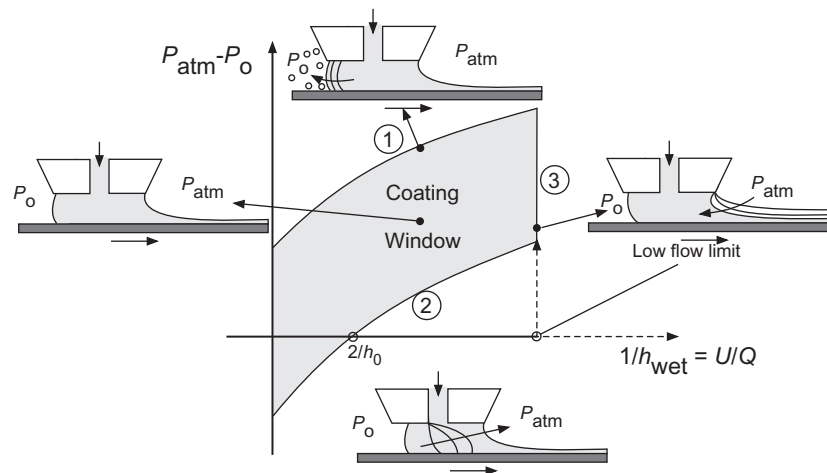


FIGURE 6.34 Schematic diagram of a slot coating window. Note that three limiting bounds are emphasized in this diagram: (1) an upper bound where coating liquid overflows the gap on the upstream side, (2) a lower bound where the coating liquid is depleted from the upstream side of the die, and (3) a low flow or high speed limit that occurs when attempting to coat very thin layers. Reprinted from *J. Non-Newtonian Fluid Mechanics*, 118, Romero, O. J., Suszynski, W. J., Scriven, L. E. & Carvalho, M. S., *Low-flow limit in slot coating of dilute solutions of high molecular weight polymer*, 137–156, Copyright (2004), with permission from Elsevier.

upstream die lip due to excessive drag relative to the rearward pressure-driven flow. The lower limit for the coating thickness is represented as the vertical line on the coating window (labeled 3 in Figure 6.34). This limit occurs in the extremes of low Q or high U , because the curvature at the downstream meniscus becomes extreme, causing the coating to breakup into rivulets or droplets. This limit is independent of vacuum. Lastly, the upper bound on the coating window (labeled 1 in Figure 6.34) is created by excessive vacuum, which leads coating liquid to be pulled out of the die and the loss of pre-metering action.

The analysis above takes into account only the viscous effects and neglects the role of capillarity (i.e., meniscus curvature) on the process. These effects are very important in slot coating and represent another process variable to contend with and adjust to achieve the desired coating thickness and uniformity. Hence the coating window is really a 3D coating space where a convenient third axis is the capillary number, $Ca = \eta U / \gamma_{LV}$.

Overall, slot coating is an excellent choice for coating thin liquid layers quickly. It finds application in the production of adhesives, magnetic tapes, and optical films to name a few. The process can be extended to two layers by including a second feed slot. Another variation is to remove the backup roll and use tension to support the web.

Curtain and Slide Coating. Curtain and slide coating methods are economical extensions of slot coating. Both methods have the possibility of coating multiple wet layers using only one die. In slide coating, the liquid is pushed through a slot and then slides down the die face and onto a substrate supported by a coating roll. Layers can be added sequentially to the bottom of the flow with the intention that the liquids remain distinct and unmixed even after encountering the coating web.

Curtain coating uses the same principles as slide coating. However, in curtain coating the liquid falls from the end of the inclined die onto the web. Although more difficult to design, curtain coating operations have many advantages including an extra gravity assist in wetting the substrate. Also, by changing the speed of the web, the thickness of the applied coating can be altered independently of the die design or liquid properties. These advantages apply whether the final product has single or multiple layers.

Multilayer coating applications were initially driven by the photographic industry to produce film that often had more than ten or more independent layers. By coating many liquids with one die, separate drying steps between each layer are unnecessary, resulting in great energy and space efficiency, and cost savings. However, a great deal of research and planning is necessary to implement a multilayer coating operation. The liquid surface tensions and miscibilities must be matched so that they can not only be coated but also dried without causing defects. Solvent migration between layers can cause precipitation of undesired solids and bare spots occur if one liquid does not wet another.

6.4.3 Polymer Coatings

Polymer coatings are thin layers of polymer applied to either flat substrates or irregular objects. Polymeric coatings can be functional (adhesives, photographic films), protective (anticorrosion), or decorative (paint). They are also used to modify surfaces (paper coatings, hydrophobic coatings). Although polymeric coatings are mostly organic, they can also include ceramic or metal particles to increase durability, functionality, or aesthetics.

Because polymer coating solutions are often expensive, coating methods are designed to produce as thin of a polymer layer as fast as possible. Polymeric coatings are typically on the order of 1–100 μm in thickness. Depending on the desired thickness of the coating, the rheology of the liquid and the speed of the web, polymeric coatings are applied many different coating methods, including those described in the last section. Multilayer coatings are also common.

Although all polymeric coatings are designed to be an impervious, homogeneous thin layers of polymer when dry, there are three unique starting liquid types that can be used to produce this outcome: polymer solutions, monomer liquids, and polymer latexes.

Polymer solutions. To reduce the viscosity of a polymer so that it becomes a coatable liquid, polymer is dissolved in a solvent. The rheology of the coating solution is tailored to the coating and drying method by altering the amount of solvent in the solution, as described in [section 6.2.3](#). Once the liquid is deposited onto a substrate, the solvent must be removed in a drying process. As solvent is removed, the glass transition temperature of the solution increases, as shown in [Figure 6.35](#). Nominally, when the glass transition temperature is greater than the drying temperature, the coating is solid. If the drying temperature is higher than room temperature, the coating may continue to solidify or harden upon cooling. Additionally, some polymers

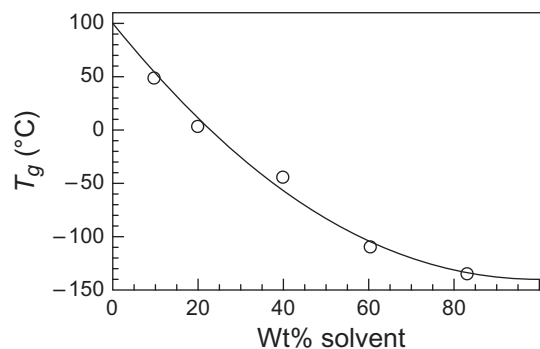


FIGURE 6.35 Glass transition temperature of polystyrene as a function of toluene content. Data from [Adachi et al. \(1975\)](#).

crystallize as solvent is removed or on cooling from the drying temperature, creating final polymer coatings that are semicrystalline.

Most polymers for functional coatings are not water soluble and so organic solvents are used. The solvent is chosen both for its ability to dissolve the polymer of interest but also for its cost and volatility, which influences the drying step. Frequently, the inclusion of additives or the need to reduce cost leads to the use of multiple volatile solvents. One potential issue with this practice is phase separation during drying if the more volatile solvent is also the better solvent for the polymers. Although usually undesirable, this possibility has been exploited to make porous polymer membranes.

Polymer solution coatings are advantageous because they can often be formulated to specifications at the processing site, applicable to a wide variety of polymers and tunable to create controlled thicknesses and properties in the final coating. Unfortunately, the amount of polymer that can be dissolved in a solvent and still maintain fluidity for coating is relatively small ($\sim 10\text{--}20\text{ wt}\%$) and hence a considerable amount of drying is required per unit of coating thickness. Complications related to solvent handling also present disadvantages, including environmental and safety concerns, solvent recycling, and the need for more expensive dryers that are capable of capturing flammable solvents.

Liquid Monomers. Many monomers are liquid at room temperature, so they can be coated directly often with no solvent or minimal solvent added to reduce their viscosity at the coating temperature. Oligomeric precursors are also in this category. Instead of a drying step, monomer liquids are solidified by curing reactions. As curing proceeds, the average molecular weight of the coating material increases until a solid polymer layer is formed. Curing reactions are initiated by heating or exposure to ultraviolet (UV) light or other energetic sources such as electron beams.

Compared to polymer solution coatings, a lesser variety of polymer chemistries are amenable to this route. One of the most popular curable coating materials is epoxy. Epoxies are not formed from monomers but rather by reaction of oligomeric resins with hardeners or curing agents. The coating liquids are made with solvent as well to improve the coatability. Among the liquid monomer alternatives, acrylates are common for UV curing.

Monomer liquids are attractive routes to coatings since they require little to no solvent and therefore a reduced or eliminated drying step. Final coating properties such as cross-link density can be controlled during the curing step by changes to the temperature and UV intensity as well as to the chemistry of the resin. Specialized, functional monomers and initiation agents may be more expensive than the materials used in polymer solution coatings, however. Also, achieving high degrees of cure and low residual monomer contents is sometimes a challenge in glassy polymers. The final product in many cases is brittle due to the high degree of cross-linking.

Polymer latex. A latex is a dispersion of polymeric particles in water. Given the low solubility of functional polymers in water, latex routes provide an environmentally attractive approach for creating durable polymer coatings. Particles ranging in size from ~ 10 nm to $1\text{ }\mu\text{m}$ can be produced from a variety of polymer chemistries by emulsion polymerization. Since they are synthesized as dispersions and stabilized in the process, they are particularly easy to use. For some application the latex is formulated with other phases, like ceramic particles.

The drying of latex particle suspensions is somewhat different from the drying of hard colloidal particles, which is described in an earlier section. The process known as “film formation” is shown in [Figure 6.36](#). As water is removed, particles become more concentrated in the suspension during a “consolidation” stage. As the falling rate period ends and the water begins to invade into the particle packing, surface tension, capillary, and van der Waals forces start to pull the particles toward each other. These forces are strong enough that the particles start to flatten at particle-particle contact points. See [Figure 6.37](#). Accordingly, the pore space between the particles shrinks. This stage is termed “compaction.” Finally, in the “coalescence” stage, polymer chains diffuse across the boundaries between particles, welding the particles together. This process creates a final coating that is devoid of pores or boundaries between what were once individual particles.

Since water is the liquid medium for latex coatings, this route is an environmentally friendly alternative to monomer and solventborne coatings. Many consumer coatings such as varnishes and paints begin as latex dispersions. Complex polymer blends or structures can be polymerized into a latex particle, which retains its identity during the latex film formation process. However, latexes are expensive to transport and purchase as raw products in commercial scales, and the drying of water is an energy intensive process.

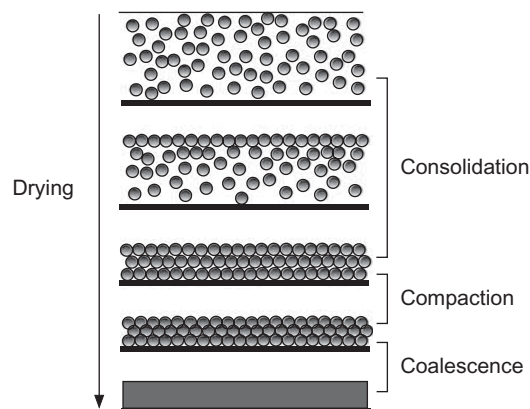


FIGURE 6.36 Latex film formation stages.

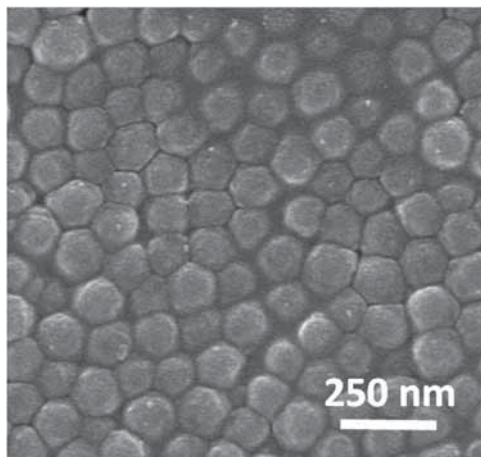


FIGURE 6.37 Top surface of a drying low T_g latex coating in the compaction stage. The coating was frozen and then imaged in a scanning electron microscope with a cryogenic stage to preserve the water in the pore space between the particles. Particles are flattened at their contact points. From C.C. Roberts (2010) reproduced by permission.

6.4.4 Tape Casting of Ceramics

Doctor blade coating of ceramic dispersions containing polymer binder is termed “tape casting.” The end result of tape casting is a thin ceramic sheet or multilayer ceramic product. The steps in a tape casting process are very similar to any other coating process. The suspension (coating liquid) is formulated and mixed. Ball milling may be used to first disperse the ceramic particles, and then binder, plasticizer, or other additives are introduced in a second step. The suspension is then de-aired to remove bubbles. Finally, the liquid is coated onto the substrate, usually with doctor blade coating, but slot coating is also used. As in Figure 6.26, the as-deposited tape cast layer is sent immediately into an oven for drying. The layers are deposited onto a flexible plastic substrate that is wound up after drying and sent to the next stage of the process. Green tape thicknesses in the range of $\sim 10\ \mu\text{m}$ to over $200\ \mu\text{m}$ can be prepared. As thickness increases, the length of the dryer increases to provide for more drying time and/or the speed is reduced for the same reason. Based on the stringent applications in electronic devices, for example, tape casters may be located in clean rooms or have filters for their air supplies to reduce dust and other extraneous particulates. Once dry, green tape cast sheets go through a number of steps depending on the part geometry and application, including cutting to size, punching holes for electronic conductors, metalizing, and stacking. Next the parts are heated to remove binder and sinter.

Suspensions for tape casting are formulated for easy coating onto the substrate and flexibility in the green tape after drying. There are three main components in these dispersions: ceramic particles, a liquid medium (water or organic solvent), and additives. As in slip casting, achieving a high particle content is desired; however, the need to work with fine particles and a considerable amount of binder limits the solids loading. A particle concentration of 20–35 vol% is typical. Particle sizes are finer than those in slips for slip casting (i.e., much less than 1 μm in diameter). Large particles degrade the surface roughness of the tape cast layer, a feature that is especially important for multilayer and electronic applications. Since aggregates are problematic for the same reason and others, additives are used to ensure colloidal stability, usually by steric or electrosteric means. The ceramic particles are dispersed in the liquid medium before organic binders are added, because binders increase the viscosity and may interfere with achieving a highly dispersed state.

The choice of a water or an organic solvent for the liquid medium depends on a number of factors, including the suitability for dispersion of the particles and compatibility with the binder. Water is the best choice in terms of environmental, health, and safety factors. Most oxide particles are easily dispersed in water, and latex (i.e., emulsion) based binders are suitable. However, water also requires a lot of energy to evaporate in the drying stage due to its high heat of vaporization. Organic solvents have the advantage of fast drying and easy dissolution of binders and plasticizers, but they often have to be recaptured, contained, and disposed of in the drying step.

To increase flexibility, the green tape usually contains high concentrations of binders and plasticizers. Up to 15–25 vol% of the dry tape can be polymeric binders. Polymers, including polyvinyl alcohol, polyvinyl butyral, cellulosic polymers and acrylics, can either be dissolved into the liquid medium or added as latex. Plasticizers, such as phthalates and glycerol (for aqueous slips), can be employed to further increase the flexibility of the tape. Plasticizers are short chain molecules that are soluble in the binders and designed to reduce the modulus of the binders. Because of their low molecular weight, plasticizers are removed during thermal treatment at a lower temperature than the polymer binder. This sequence is helpful because pore channels are created as the plasticizer leaves, which allows easier volatilization of the binder. With the binders added, the viscosity of a suspension for tape casting is typically in the range of 0.5–20 Pa $\cdot$ s with shear thinning characteristics.

Once the coating is applied and dried, flexible green tape casts can optionally be removed from the substrate and fired in plates or sheets in a furnace. The heating step removes the binder and other organics remaining in the tape cast as well as sinters the particles together into a durable final product. High binder concentrations present challenges, such as large amounts of shrinkage during the sintering step, leading to possible curling or cracking.

Tape casting methods are also used to make multilayer devices, such as multilayer capacitors, fuel cells, batteries and multilayer ceramic substrates, and multilayer composite materials. These processes involve multiple depositions and multiple materials, including metals. Co-firing is frequently a challenge as the conditions for sintering of the ceramics and metals are not easily made compatible and thermal expansion mismatches lead to warping and other stress-induced defects.

6.5 EXTRUSION AND INJECTION MOLDING

6.5.1 Process Overview

In this section, extrusion and injection molding of concentrated dispersions is introduced. This brief section builds on techniques described primarily in Chapter 3 in the context of polymer melts. The main idea is to incorporate high loadings of ceramic or metal powder into a polymer melt, extrude or injection mold, and then remove the polymer and sinter the part. The “melts” are not designed to be functional polymers but rather convenient vehicles for the shaping process. As such they are designed to allow incorporation of ceramic or metal powder particles and for decomposition. Solvent can also be added. A main challenge is achieving a high solids loading and a low enough viscosity for processing. To this end, engineered particle size distributions are useful. In addition to polymer-based processes, traditional ceramic products are extruded from a highly loaded aqueous paste with little or no polymer added. These materials make use of the natural plasticity in clay-based ceramics.

After extrusion or molding is complete, removal of the volatiles and binders is typically a long process that scales with the size of the article. Ordinarily this “burnout” step is indeed a thermal process in which the polymers are pyrolyzed in controlled environments. Chemical debinding is also an option.

6.5.2 Extrusion of Concentrated Dispersions

In Chapters 3 and 4, extrusion was described as a process for polymer melts and solid metals. Extrusion is also a method to produce parts from a concentrated slurry or paste. This method is commonly used to produce ceramic brick, bathroom and roof tile, catalytic supports, and also tube-shaped ceramic parts such as furnace tubes and electrical insulators. Not exclusive to ceramics, metal powder can also be extruded to form high density metallic shapes. By starting with a metallic powder heterogeneous in composition, alloyed parts can be formed. Extrusion of pastes shares some features with melt extrusion (i.e., thermoplastic polymers) and others with solid extrusion (i.e., metals).

The stages of an extrusion forming process include first mixing the feed material and de-airing. The extruder feed material must be viscous and moldable when moving in the extruder, and yet when expelled as extrudate, it must hold its shape like a solid. Therefore, a major challenge of this type of extrusion is to achieve plasticity in a concentrated, particulate suspension or paste. There are at least two routes. The first is to use the natural plasticity that occurs in clay-water mixtures at appropriate moisture levels. Those familiar with pottery know that plasticity is achieved with a water content in between a fluid slip and a dry and crumbly mass. The “plastic” ceramic can be shaped by hand or on a potter’s wheel. The plasticity is derived from thin layers of water on the clay platelets; under shear the platelets move relative to each other, but when the shear stress is removed, the water film and capillary effects hold the platelets in place. The second more universal route is to use polymer additives. In both routes, feed material can have up to 50 vol% particulates with the remainder water (or solvent) and binders. De-airing is carried out on its own, or the initial chamber in the extruder is designed for de-airing, possibly with a vacuum system. Because high concentration particulate slurries and pastes are often very viscous, removing bubbles is challenging but important for eliminating defects in the final part.

Once the extrudate is formulated, the material is then pressurized and forced through the extrusion die to make cylinders, hollow tubes, rectangular cross-sections, and even complex shapes like substrates and filters in automotive applications. See [Figure 6.38](#). After exiting the extruder, the wet piece is dried, its surface optionally treated or smoothed, and, finally, organic binders are burned from the component and it is sintered to create the final form.

The most common extruder type for particulate slurries and pastes is the screw auger, which is essentially a single screw extruder (see Chapter 3). However, both piston press extruders, which forcefully ram material through a die opening, and twin screw extruders are used. Piston press extrusion is a slow, batch process, because the piston ram must be retracted between the formation of each part. However, the pressures that are possible with a piston press are much higher than those with auger extruders. Both co- and counter-rotating twin screw extruders have a higher capital cost than single screw augers, but require less power to move the material through the barrel. Also, as discussed in Chapter 3, the throughput of a single screw (auger) extruder is pressure dependent, whereas it is pressure independent in a twin screw extrusion system. Lastly, the extrusion process can be horizontal or vertical.

Metal and ceramic particles are typically hard and abrasive, which, when in concentrated slurries, create a lot of friction both on the extruder walls and between individual particles. When the auger applies pressure to such a slurry, the solid particles jam to form a stress-bearing network. The water or other fluid redistributes in this network, and can sometimes separate from the particle packing. This phenomenon is similar to what happens when you



FIGURE 6.38 Example of honeycomb shaped ceramic for environmental technology applications, such as diesel filters. *Courtesy of Corning, Inc. www.corning.com.*

step on moist sand at the beach. To prevent the migration of water, small hygroscopic clay particles are sometimes added to slurries to fill in spaces between larger ceramic materials to restrict flow through the pore space. Particulate fines are also useful for this purpose. Organic binders such as polyvinyl alcohol, methyl cellulose, or polyethylene glycol can also be added which serve to reduce interparticle friction, increase viscosity, and reduce liquid migration. Finally, coagulants like acids or bases can be helpful to provide the desired viscosity in the extruder and to encourage the formation of the desired stress-bearing solid network. These additives can occupy up to 20 vol% of the feed material.

As the high solids extrudate is pushed through the extruder, wall friction can increase the power requirements and cause heating and wear. Augers are made from high grades of steel or other suitably hard and durable metal. Sometimes small amounts of lubricant are injected at the walls of the barrel in order to better move the material. Finally, increasing the temperature of the material in the barrel may reduce friction by reducing the viscosity of the extrudate organics. Stress near the barrel walls can serve to align the particles, creating a unique microstructure at the edges of the part.

Flow profiles in the particulate dispersion extrusion formation process mirror those described in detail for polymer extrusion. However, most highly concentrated particulate systems have the added complication that the dispersions are shear thinning or have a measureable yield stress. If the die-entrance region is improperly designed for the material, a dead zone may appear where the shear stress during operation is not sufficient for the material to yield and flow forward. This problem can be corrected by increasing the taper of the die-entrance region, which increases the shear stress in the extrudate. Poiseuille flow through a rectangular or circular die is altered when the extrudate is shear thinning. Shear at the walls creates an effective lower viscosity there, which decreases the total pressure needed to push the material through the area.

6.5.3 Powder Injection Molding

Powder injection molding is the general term for the process of injection molding of polymer melt-based mixes containing a high loading of ceramic or metal powders. This process is similar to injection molding of thermoplastics (see Chapter 3) except that metal or ceramic particles are compounded with polymer binder into pellets before the process. The injection unit can be based on a reciprocating screw type or a piston. The molding process follows the same principles as thermoplastic injection molding. Parts are solidified by cooling in the mold, and then heated to remove binder and sinter.

Ceramic or metal powder incorporation into the polymer melt can be accomplished by high shear mixing in a twin screw extruder, for example. The powders used in this process have particles in the micron size range for ceramics and less than 20 μm or so for metals. Lubricants are also added to lessen wear of machine from contact with hard particles. At least two polymer binders are used. The major binder is a higher molecular weight polymer that is responsible for the solidification and strength of the molded part. The minor binder is a lower molecular weight polymer that enhances flow behavior and assists in the binder burnout process. The minor binder decomposes before the major binder, which clears out some pore channels and allows easier removal of the major binder. Plasticizer or solvent is also added to assist in flow. The mixes can have up to 50–70 vol% particles.

Post-processing is the rate limiting step in the powder injection molding. Decomposition and removal of large amounts of polymer from the parts requires time and ovens with atmosphere control. Of concern is retention of the shape of the parts considering that the polymers are thermoplastic. The time needed to remove the polymer increases with part size and hence powder injection molding applications are restricted to small parts. Given the high content of polymer there is considerable shrinkage during the polymer removal and then final sintering steps. Nonetheless, the advantage of creating complex shapes drives the use of this process.

6.6 LIQUID MONOMER-BASED ADDITIVE PROCESSES

6.6.1 Process Overview

Photocurable liquid monomers and resins naturally lend themselves to additive manufacturing. The conversion of liquid to solid is instigated by light and therefore one route is to selectively polymerize the liquid in a continuous liquid bath. The process of stereolithography (SLA—for stereolithography apparatus) is based on this premise. SLA uses a scanning laser to polymerize 2D layers; a moving platform and fresh layers of resin make it possible to build in the third dimension. Another route is to control the positioning of the liquid and illuminate broadly. This path is taken by an inkjet 3D printing method. Resin “ink” droplets are deposited and then illuminated to cure them into polymer. Again, a layer-by-layer approach creates the 3D object. This method lends itself to multiple materials and colors.

There are similarities and differences in the requirements for the photocurable liquid resins for these processes. The liquid itself must have a low enough viscosity so that it can be distributed onto the build platform or jetted into droplets easily. In addition, the inkjet process requires attention to the surface tension of the liquid. For both, fast curing is essential in order to increase the overall process speed. Moreover, for SLA in particular the curing process should not result in large amounts of shrinkage. For both, the resin and curing conditions should result in a final product with a required set of physical and mechanical properties. Other desirable features are insensitivity to atmospheric conditions, such as relative humidity and oxygen.

SLA and inkjet involve the same sort of preparation as other additive methods. The first step in is to create a CAD file of the part and convert the drawing to an STL format. The STL file is then used by the printer software to establish a sequence of scan patterns for the 2D slices of the 3D object.

It is worth noting here that there are additive manufacturing processes based on dispersions. In particular, lower viscosity dispersions can be inkjet printed directly and high viscosity dispersions can be extruded in processes that are similar to fused deposition modeling. In these processes, solidification is by drying, which can be encouraged using heated build plates. Of course, combining a curable polymer with particles is yet another variation. For the purposes of this section, however, the focus is on liquid monomer-based processes.

6.6.2 Stereolithography (SLA)

Stereolithography is a high-resolution additive process that uses photocurable liquid resin. The process begins with a thin layer of the liquid resin on a build platform. A laser scans over the layer to selectively polymerize a 2D pattern, a fresh layer of resin is added, and the process repeats to build a 3D object. SLA has a long history. The process was invented in 1986, in

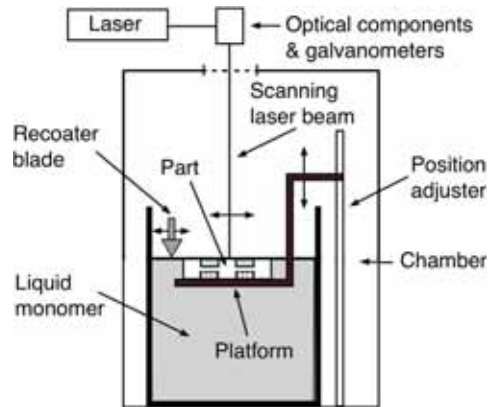


FIGURE 6.39 Schematic diagram of a stereolithography apparatus, showing the main components and analogies with selective laser sintering (see Chapter 5). Resin level height sensor is not shown. Adapted from [Venuvinod and Ma \(2004\)](#).

the same era as selective laser sintering (SLS) and fused deposition modeling (FDM).

[Figure 6.39](#) is a schematic of an SLA system. The system consists of an enclosed chamber, containing a vat or bath of resin, as well a platform and positioning system. The enclosure prevents escape of resin fumes. Additionally, since photocurable polymers are used, the chamber is either opaque or tinted to prevent ambient light from starting the curing process prematurely. The other major pieces of equipment are the laser, and components that control the beam. Lasers are chosen based on the photoinitiator systems. Wavelengths in the 320–360 nm range are common.

In SLA, 3D parts are built layer-by-layer using a scanning laser beam. A build platform is immersed in a liquid resin bath; the height is adjusted so that it is very close to the free surface of the bath and only a thin layer of resin exists on the platform. The laser scans over the surface, creating a cured 2D pattern and adhering the part to the platform. The platform then moves down and a layer of resin floods the surface. To speed this process and establish a uniform layer thickness, a blade passes over the surface and meters the liquid in a manner similar to doctor blade coating (i.e., the layer thickness is $\sim \frac{1}{2}$ the gap between the blade and the previous layer). Other recoating strategies are also used. The scanning laser beam then creates the next 2D layer and adheres it to the previous. Supports are built at the same time. These extra pieces of the same polymer are needed to stabilize the part and for overhangs. An alternative setup locates the laser and optics beneath the platform and begins with the platform at the bottom of the vat. The laser scans through the transparent bottom, curing a layer and then the platform moves up and resin is pulled into the gap.

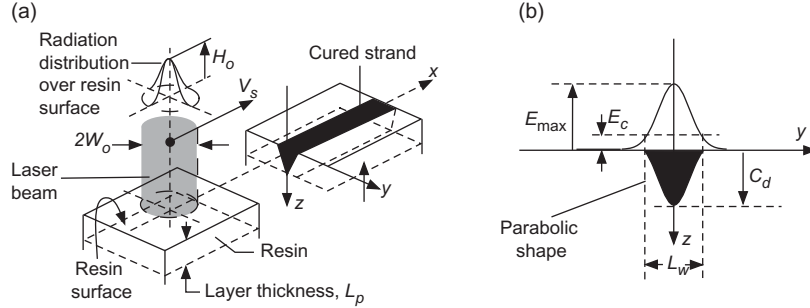


FIGURE 6.40 Schematic diagrams showing features of a laser line scan in a curing material. From *Venuvinod and Ma (2004)* with kind permission from Springer Science and Business Media.

The laser beam physics discussed in the last chapter as well as the introduction to UV curing are useful for understanding the SLA process. The laser beam spot has a Gaussian distribution in its intensity or irradiance, H . (In the context of UV curing, this parameter is equivalent to the intensity, I .) Considering the sketch of a scan track, the irradiance as a function of y is given by:

$$H = H_o \exp\left(\frac{-2y^2}{W_o^2}\right) \quad (6.65)$$

where H_o is the irradiance at the center of the scan ($y = 0$) and W_o is the value of y at which $H = H_o/e^2$. See Figure 6.40a. W_o is a measure of the radius of the scanning beam. The power is found by integration. Considering an instant in time when the beam illuminates a circular cross-sectional area of radius y , the total power, P_L , provided is:

$$P_L = \frac{\pi}{2} W_o^2 H_o \quad (6.66)$$

The power at the resin surface is typically specified by the SLA manufacturer. Equation (6.66) can also be rearranged to provide a convenient expression for H_o .

To understand the depth and extent of cure, we need to find the exposure, which is the energy absorbed per unit area. (In the context of UV curing, this would be called the dose.) The exposure, E (also known as the energy density) at the surface ($z = 0$) is found by integration of the irradiance:

$$E(y, 0) = \sqrt{\frac{2}{\pi}} \frac{P_L}{W_o V_s} \exp\left(\frac{-2y^2}{W_o^2}\right) \quad (6.67)$$

where V_s is the scan velocity in the x -direction. The integration requires several steps and converting an integration over time to one over distance,

using the definition of velocity. (Note that in the last chapter we did not consider the details of the Gaussian distribution in finding the energy density.) According to the Beer-Lambert law the irradiance, and hence the exposure, decreases with depth into the resin bath (i.e., with an increase in z).

$$\begin{aligned} E(y, z) &= E(y, 0) \exp\left(\frac{-z}{D_p}\right) = \sqrt{\frac{2}{\pi}} \frac{P_L}{W_o V_s} \exp\left(\frac{-2y^2}{W_o^2}\right) \exp\left(\frac{-z}{D_p}\right) \\ &= E_{\max} \exp\left(\frac{-2y^2}{W_o^2}\right) \exp\left(\frac{-z}{D_p}\right) \end{aligned} \quad (6.68)$$

D_p , the depth of penetration, is the depth z at which $E(y, z) = E(y, 0)/e$. Considering the terminology of UV curing, $1/D_p$ is equal to the product of the molar absorptivity of the photoinitiator and the concentration of the photoinitiator ($\alpha[PI]$). In other words, D_p is a constant for a given resin formulation. There is a critical exposure, E_c , needed for the liquid resin to solidify. This value is also a property of the resin material. The z and y values, where $E(y, z) = E_c$, define the dimensions of the solidified strand: C_d , cure depth, and L_w , line width, respectively:

$$C_d = D_p \ln \left[\sqrt{\frac{2}{\pi}} \frac{P_L}{W_o V_s E_c} \right] = D_p \ln \left[\frac{E_{\max}}{E_c} \right] \quad (6.69)$$

$$L_w = W_o \sqrt{\frac{2C_d}{D_p}} \quad (6.70)$$

From these relationships the required velocity for a scan to reach a certain cure depth can be found. See [Figure 6.40b](#). Or, given information about the laser (P_L , W_o) and the resin (E_c , D_p), the geometry of the cured strand can be predicted for a given velocity. See [Example 6.7](#). A complete derivation of these equations is found in Jacobs (1992).

The scan pattern involves overlap of adjacent tracks, resulting in increased exposure for the material in the overlap region. The spacing between adjacent strands or tracks is called the hatch spacing. The scan patterns are designed to create functional structures quickly. The cure depth is of particular importance as it relates to the layer of resin that is applied on the part. The layer thickness is less than the cure depth so that the laser penetrates to the previously deposited layer, creating a region of “overcure” that helps the layer-to-layer bonding. Due to the variable states of cure in the part, resins must have low shrinkage on cure to avoid strain and warping.

EXAMPLE 6.7 A resin designed for SLA has an E_c value of 10.1 mJ/cm^2 , a D_p of 4.8 mil (0.122 mm), a viscosity of $370 \text{ mPa}\cdot\text{s}$ and density of 1.16 g/cm^3 . The SLA machine provides a power of 100 mW at the resin surface a beam diameter at $1/e^2$ of $250 \mu\text{m}$. (a) From this information find the cure depth and line width as a function of scan speed as the speed varies from $0.1\text{--}1 \text{ m/s}$. (b) If the printer specifies a layer thickness of 0.10 mm , find the depth of the overcure region for a scan speed of 0.5 m/s

- a. Using Eqs. (6.70) and (6.71) and recognizing that W_o is $\frac{1}{2}$ of the $1/e^2$ diameter = 0.125 mm

$$\begin{aligned}
 C_d &= D_p \ln \left[\sqrt{\frac{2}{\pi}} \frac{P_L}{W_o V_s E_c} \right] \\
 &= (0.122 \text{ mm}) \ln \left[\sqrt{\frac{2}{\pi}} \frac{0.1 \text{ W}}{\pi (0.125 \text{ mm})(V_s [\text{mm/s}])(1.01 \times 10^{-4} \text{ J/mm}^2)} \right] = \\
 &= (0.122 \text{ mm}) \ln \left[\frac{6.32 \times 10^3}{V_s} \right] \\
 L_w &= W_o \sqrt{\frac{2C_d}{D_p}} = 0.125 \text{ mm} \left(\frac{2C_d [\text{mm}]}{0.122 \text{ mm}} \right)^{1/2} = 0.506 \sqrt{C_d}
 \end{aligned}$$

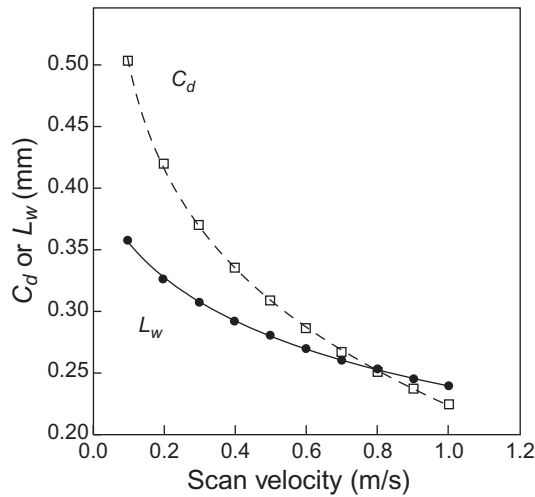


FIGURE E6.7

- b. For a scan speed of 0.5 m/s , the C_d is 0.31 mm , which results in a overcure region that is $\sim 0.2 \text{ mm}$ deep.

SLA post-processing. Post-processing for SLA begins with raising the part out of the resin bath and allowing it to drain. Removal of uncured monomer then proceeds with physical wiping and rinsing with solvent. The part is solid at this point, but due to the fast scanning speed, it is not completely cured. Hence it is placed in a UV chamber to finish the process. Support structures are also removed at some point during this process.

SLA has some interesting features relative to other additive processes. The laser scanning technology combined with the precision of curing leads to high resolutions and high scan speeds. Layer thicknesses are on the order of 25–100 μm and laser spot location is precisely controlled on higher end systems (e.g., within 10 μm) though the spot sizes are larger than that 50–300 μm . Experimental microSLA is reducing sizes further. Moreover, the curing technology can also be adapted to exposing through a mask so that an entire 2D layer can cure at once. Other innovative techniques for ultrahigh resolution and fast speed are also under development.

6.6.3 Inkjet Printing with Liquid Monomers

Another liquid monomer-based additive process involves creating a 2D pattern by inkjet printing, curing the pattern and repeating the process to build a 3D object. Figure 6.41 shows an example of a inkjet printing setup designed for delivery of monomers and curing. Multiple printheads are mounted on a carriage that moves in the x - y plane. Each printhead contains multiple nozzles for ink delivery (i.e., the nozzle array extends in the y -direction in Figure 6.41 with a single ink reservoir feeding the set of nozzles so that each pass in the x -direction deliver ink over a wide area). An inline UV lamp cures the drops after they are deposited. Like other additive methods a 2D pattern is created and then the platform descends (z -direction) and the next

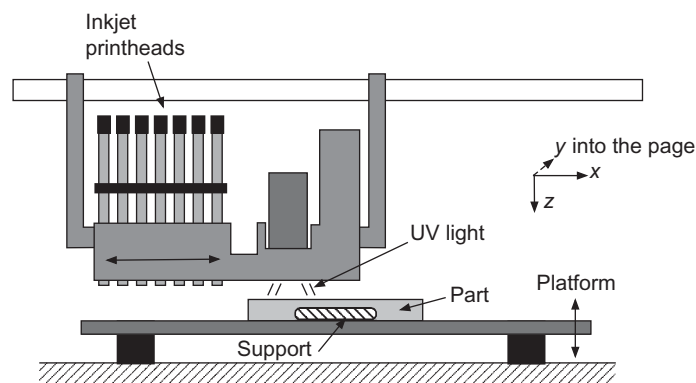


FIGURE 6.41 Schematic diagram of a multinozzle inkjet delivery system with inline UV curing. Cartoon show nozzles just after completing delivery with no ink dispensing. Adapted Stratasy's product information, www.stratasy.com.

layer is printed. Supports are obviously needed in this process. The multiple printhead design accommodates this need as well as providing the means to print multiple materials and color in the final part. To understand more about this process, the fundamentals of inkjet printing are first explored.

Inkjet Printing Principles. Inkjet printing is a method for depositing small amounts of liquid onto surfaces at precise locations. In general, the printing process consists of generating discrete droplets and depositing them onto a surface. The printed liquid then solidifies, often by drying, but in the case of liquid monomer printing, by curing. This technology can create very small drops on the order of 10s of microns in diameter at a rate of 10s of kHz, with exact positioning of each drop. There are two main methods of inkjet printing. The first, termed “continuous inkjet printing (CIJ),” uses the Rayleigh instability of a liquid jet to generate drops of ink. The second method, drop on demand (DOD), produces single drops. Figure 6.42 shows schematics of both options.

Continuous inkjet printing produces a steady stream of drops through the Rayleigh instability of a falling stream of ink. The Rayleigh instability is the tendency of a perturbed stream of liquid to break up into drops. Any jet of liquid is slightly irregular in diameter and, as the liquid falls, the thin sections tend to become thinner and eventually pinch off, while the thick sections grow into drops. This instability is familiar in everyday life, for example in the breakup of a slow flow of water from a sink faucet. In CIJ,

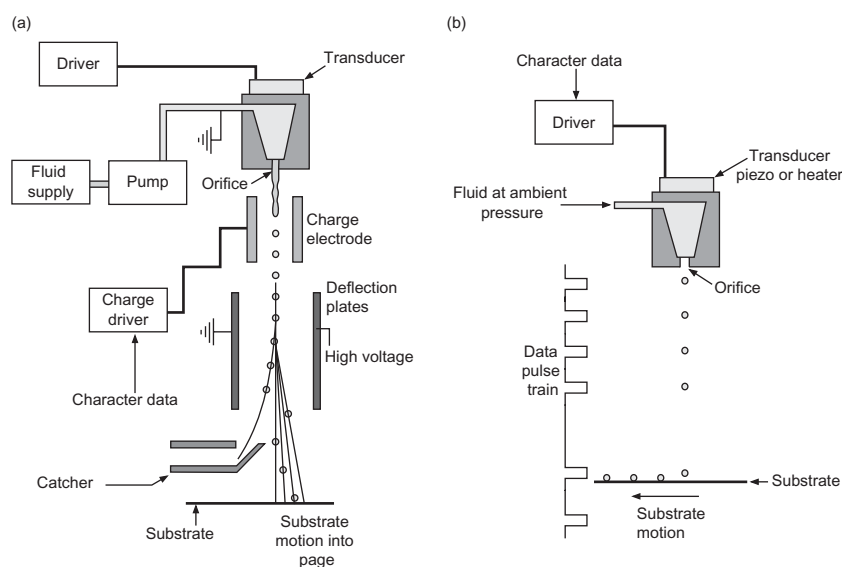


FIGURE 6.42 Schematic diagrams for (a) continuous ink jet printing and (b) drop on demand printing with the piezoelectric option. Courtesy of MicroFab Technologies, www.microfab.com; MicroFab Technote 99-01 (1999).

the liquid is perturbed with a sinusoidal pressure fluctuation while it is ejected from the nozzle to encourage the resulting drops to be regularly spaced and sized. Drops are slightly larger than the nozzle diameter, approximately 100 μm .

In continuous inkjet printing, drops are produced whether they are needed for printing or not. Therefore, drops are positioned either for printing or recycling as diagrammed in Figure 6.42a. This is done through electrostatics; each drop is charged as it falls and then its flight path is altered by deflector electrodes onto either the substrate or into a recycle stream. Drops that are not needed for the pattern or drops that are an abnormal size are deflected. Although drops are produced at high rates, typically only a small fraction are actually used for printing. The unused ink is recycled back to the nozzle, so as the printer operates the ink has the potential to become aged, contaminated, or dried, leading to printing defects.

By contrast, droplet on demand (DOD) printing creates only drops that are needed for the pattern. Here, drops are generated by a pressure pulse that forces just the desired amount of liquid from the nozzle when it is wanted. In bubblejet printers, the pressure pulse is created by locally heating and boiling a small amount of the ink solvent within the nozzle. The volume expansion of the vapor causes ink to be forced out of the nozzle. Pressure pulses can also be generated by using a piezoelectric transducer that mechanically deforms to squeeze the liquid out of the nozzle. The ejected drop, falling from the nozzle, remains connected to the fluid in the nozzle through a stretching ligament. See Figure 6.43. This ligament thins until it becomes so thin that it is unstable and detaches. As the drop falls, surface tension either draws the ligament back into the drop or the ligament forms a separate, smaller drop that falls independently and can cause printing defects.

Drop formation by DOD printers is bounded by operability limits that are defined by the Ohnesorge number, Oh , which is dimensionless number that represents the ratio of viscous forces to surface tension and inertial forces:

$$Oh = \frac{\eta}{\sqrt{\rho R \gamma_{LV}}} = \frac{\sqrt{We}}{Re} \quad (6.71)$$

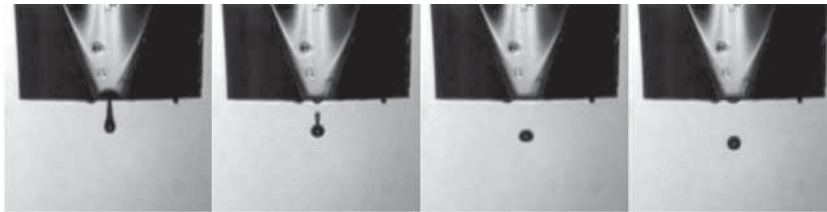


FIGURE 6.43 Images of a droplet emerging from a drop-on-demand nozzle captured at 25 microsecond intervals. The ink droplet is $\sim 40 \mu\text{m}$ in diameter. *Courtesy of A. Mahajan and D. Barton, University of Minnesota.*

Here, η , ρ , and γ_{LV} are the ink viscosity, density, and surface tension, respectively, whereas R is the nozzle radius. The Ohnesorge number is a combination of the Weber number, We , where $We = v^2 \rho R / \gamma_{LV}$ and the Reynolds number ($Re = v \rho R / \eta$). At high Oh , viscous dissipation prevents the drop from falling from the nozzle tip. At low Oh , small satellite drops tend to be present between the primary drops. For Newtonian inks, there is a process window that has been correlated to good inkjetting characteristics. If $1/Oh$ is less than ~ 1 , then the viscosity of the liquid is too high, but if $1/Oh$ greater than ~ 10 then forming a single, distinct droplet is an issue. See [Derby \(2010\)](#). If the ink cannot be changed, this criterion requires that the drop size is the only variable parameter. Like in continuous inkjet printing, drop diameters naturally are sized on the same order as the nozzle diameter, with some variability that is possible by changing the pressure pulse magnitude and frequency. Typical nozzle diameters range from 30 to 100 μm . The highest resolution printers can deliver 10 picoliter drops ($\sim 13.2 \mu\text{m}$ drop diameter) and even 1 picoliter drops ($\sim 6.2 \mu\text{m}$ drop diameter).

DOD printing has a few advantages over CIJ printing. Because DOD printers do not require a recycle gutter to catch unwanted drops, the nozzle head can be placed more closely to the substrate (2–3 mm), which reduces the likelihood of air currents to misplace the drop. The lack of a recycle stream also reduces the chance of contamination or aging of the ink. Drop generation frequencies in DOD printers are an order of magnitude slower (1–20 kHz) than CIJ printers, but since every drop is used the two technologies actually are comparable in drop print rates. DOD drop sizes are smaller than those created with CIJ printing.

Another issue with inkjet printing is drop interaction with the substrate. Upon impact, a high energy, high velocity drop may recoil upwards before capillary forces bring the drop back to a spherical shape. This sort of splashing is discouraged by limiting the exit velocity. The impact event also starts the spreading of the drop on the substrate. Once the energy from the impact has dissipated, capillary forces remain, which bring the drop toward its equilibrium shape. This shape is determined by the equilibrium contact angle of the liquid with the surface, but other factors also influence the final feature size. In monomer printing, curing reactions increase viscosity and halt any shape changes. Multiple drops dispersed close together can merge if the curing is not fast enough. Other phenomena occur in droplets that solidify by drying.

Liquid Monomer Printing. Inkjet printing of liquid monomers is a synergistic combination of inkjet printing and photocurable resin technology. Starting with the requirement for inkjet printing first, we can estimate Oh using values typical of liquid monomers. As an example, trimethylolpropane triacrylate, has a surface tension of $\sim 34 \text{ mN/m}$, viscosity of $\sim 45 \text{ mPa} \cdot \text{s}$, and a density of 1.1 g/cm^3 . For a nozzle of radius $50 \mu\text{m}$, Oh is ~ 1 . Therefore $1/Oh$ is also ~ 1 , which is right on the borderline for good droplet

formation. With a smaller nozzle this monomer might not form droplets very well. Likewise, mild heating to reduce the viscosity would assist the process.

The next consideration is curing. As in the SLA process, the conditions should provide fast cure and an adequate cure depth. The effect of process parameters on curing and structure development can be inferred from the previous discussions of SLA and UV curing. The cure depth can be estimated in a similar way as that for SLA. In the case of monomer printing, however, the UV source is not a concentrated beam but rather a broader area and this broad UV source moves over the printed pattern at some fixed velocity. We expect the cure depth to increase as the velocity decreases and as the incident intensity from the UV lamp increases. Overcure for enhancing the layer-to-layer bonding is desired, as is printing patterns that creates good in-plane bonds. No post-curing is needed and the only additional step after a part is build is dissolution of the support.

One advantage of liquid monomer inkjet printing is the ease of printing multiple materials. At the simplest level, delivery of the monomer that forms the part and another material for the support. The supports also solidify by curing, but they are designed to be washed away in water after the printing is complete. More than two materials can be printed, making multiple colors and multiple physical properties possible. The method affords excellent resolution with layer heights $\sim 20\text{ }\mu\text{m}$ and $\sim 40\text{ }\mu\text{m}$ in plane resolution.

6.7 SUMMARY

Dispersions and solutions can be cast and molded into shapes and made into functional coatings. Liquid monomers are also useful starting materials for the fabrication of coatings and 3D objects by polymerization. The fundamental topics of importance to designing these processes include colloidal interactions and stability, polymer solution behavior, rheology, radiation curing, and drying. Creating a stable dispersion requires attention to particle-particle interactions. Van der Waals attraction tends to aggregate particles in dispersions, leading to gels and sediments; however, engineering repulsion between particles by electrostatic or steric phenomena allows suspensions to be stable over the time span needed for further processing. Creating a useful polymer solution requires attention to molecular weight and solvent choice. Solidification by drying and curing both involve kinetics and conditions such as temperature and intensity of UV light.

Shape casting from dispersions is an important process for creating ceramics in complex shapes. In slip casting a ceramic dispersion is poured into a porous mold. A layer of ceramic particles builds on the interior surface of the mold over time due to capillary action. The rate of casting depends on the solids loading and particle size in the dispersion as well as the mold

characteristics. Predictions of casting time are necessary for engineering processes to create controlled thickness parts.

Coating processes create thin layers of dispersion, solution or liquid monomer that are then solidified by drying or curing. There are many coating application methods, including dip coating, blade coating, slot coating, and curtain coating. Coating processes require metering to ensure a controlled thickness. Pre-metered processes, such as slot coating, afford the best control as all of the coating liquid is deposited onto the substrate. Predictions of the effect of coating liquid properties, such as viscosity and surface tension, and coating speed on thickness allow processes to be engineered. In roll-to-roll processing, inline drying and curing occurs in series with the deposition. Hence, process speeds may be limited by the solidification equipment, such as the dryer length.

Ceramic and metal dispersions are also extruded and injection molded. Ceramic extrusion is carried out with thick pastes based on clays or dispersions containing polymers to assist in developing plasticity. Twin screw and single screw extruders operate on similar principles as polymer extruders to create extruded products. For injection molding, ceramic or metal particles are dispersed into polymer melts and then molded using techniques very similar to those used to mold thermoplastic polymers. Removal of the large amounts of polymer binder from these products is typically the rate-limiting step.

Liquid monomers are used in additive processes, including stereolithography and monomer inkjet printing. In stereolithography, the monomer is cured layer-by-layer with a scanning laser. Achieving high resolution and adequate bonding between layers requires attention to the laser energy density. The cure depth is a function of the laser specification, resin characteristics, and scanning speed. Liquid monomers have appropriate characteristics for inkjet printing. Scanning printheads deposit monomer droplets and UV light cures them. Multiple materials can be incorporated into the 3D printed object.

Chapter acknowledgment: Christine Roberts gratefully acknowledges helpful discussions with the late Professor L. E. Scriven as well as her coworkers at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

BIBLIOGRAPHY AND RECOMMENDED READING

Colloid science

- Evans, D.F., Wennerstrom, H., 1994. *The Colloidal Domain*. VCH Publishers, New York, NY.
- Heimenz, P.C., 1977. *Principles of Colloid and Surface Chemistry*. Marcel Dekker, New York, NY.
- Hunter, R.J., 1993. *Introduction to Modern Colloid Science*. Oxford Science Publications, New York, NY.

- Larson, R.G., 1993. *The Structure and Rheology of Complex Fluids*. Oxford University Press, New York, NY.
- Russel, W.B., Saville, D.A., Schowalter, W.R., 1989. *Colloidal Dispersions*. Cambridge University Press, Cambridge, UK.
- Shaw, D.J., 1980. *Introduction to Colloid and Surface Chemistry*. Butterworth & Co, London, UK.
- van Olphen, H., 1963. *Introduction to Clay Colloid Chemistry*. Wiley Interscience Publishers, New York, NY.

Polymer Solutions. Latex and Curing

- Blackley, D.C., 1997. *Polymer Latices: Science and Technology*, second ed. Chapman & Hall, New York, NY.
- Hiemenz, P.C., Lodge, T., 2007. *Polymer Chemistry*, second ed. CRC Press, Boca Raton, FL.
- Keddie, J.L., 1997. Film formation of latex. *Materials Science and Engineering* 21, 101–170.
- Macosko, C.W., 1994. *Rheology: Principles, Measurements and Applications*. Wiley - VCH, New York, NY.
- Pappas, S.P., 1992. *Radiation Curing: Science and Technology*. Plenum Press, New York, NY.
- Sperling, L.H., 1992. *Introduction to Physical Polymer Science*, second ed. Wiley Interscience, New York, NY.
- Young, R.J., 1981. *Introduction to Polymers*. Chapman & Hall, New York, NY.

Slip Casting, Coating, and Tape Casting

- Aksay, I.A., Schilling, C.H., 1984. Mechanics of colloidal filtration. In: Mangles, J.A., Messing, G.L. (Eds.), *Advances in Ceramics*, Vol. 9: *Forming of Ceramics*. American Ceramic Society, Columbus, OH, pp. 85–94.
- Cohen, E., Gutoff, E., 1992. *Modern Coating and Drying Technology*. VCH Publishers, New York, NY.
- Fries, R., Rand, B., 1991. Slip-casting and filter pressing. In: Brook, R.J. (Ed.), *Concise Encyclopedia of Advanced Ceramic Materials*. VCH Publishers, New York, NY, pp. 151–187.
- Mistler, R.E., 1991. Tape casting. In: Schneider Jr., S.J. (Ed.), *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*. ASM International, Materials Park, OH, pp. 161–165.
- Reed, J.S., 1995. *Principles of Ceramic Processing*, second ed. Wiley & Sons, New York, NY.
- Schilling, C.H., Aksay, I.A., 1991. Slip casting. In: Schneider Jr., S.J. (Ed.), *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*. ASM International, Materials Park, OH, pp. 153–160.
- Scriven, L.E., 2004. *Coating Process Fundamentals Short Course Notes*. University of Minnesota, Minneapolis, MN.
- Stokes, R.J., Evans, D.F., 1997. *Fundamentals of Interfacial Engineering*. VCH Publishers, New York, NY.
- Tormey, E.S., Pober, R.L., Bowen, H.K., Calvert, P.D., 1984. Tape casting — future developments. In: Mangles, J.A., Messing, G.L. (Eds.), *Advances in Ceramics*, Vol. 9: *Forming of Ceramics*. American Ceramic Society, Columbus, OH, pp. 140–149.

Extrusion and Injection Molding

- Handle, F. (Ed.), 2007. *Extrusion in Ceramics*. Springer-Verlag Publishing, Berlin, Germany.
- Mangels, J.A., Trela, W., 1984. Ceramic components by injection molding. In: Mangles, J.A., Messing, G.L. (Eds.), *Advances in Ceramics*, Vol. 9: *Forming of Ceramics*. American Ceramic Society, Columbus, OH, pp. 220–233.
- Mutsuddy, B.C., 1991. Injection molding. In: Schneider Jr., S.J. (Ed.), *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*. ASM International, Materials Park, OH, pp. 173–180.

Ruppel, I., 1991. Extrusion. In: Schneider Jr., S.J. (Ed.), *Engineered Materials Handbook*, Vol. 4: Ceramics and Glasses. ASM International, Materials Park, OH, pp. 165–172.

Monomer-based Additive Processes

- Basaran, O.A., Gao, H., Bhat, P.B., 2013. Nonstandard inkjets. *Annu. Rev. Fluid Mech.* 45, 85–113.
- Derby, B., 2010. Inkjet printing of functional and structural materials: Fluid property requirements, feature stability, and resolution. *Annu. Rev. Mater. Sci.* 40, 395–414.
- Gibson, I., Rosen, D.W., Stucker, B., 2010. *Additive Technologies*. Springer, New York, NY.
- Jacobs, P.F., 1992. *Rapid Prototyping and Manufacturing: Fundamentals of Stereolithography*. McGraw Hill, New York, NY.
- Martin, G.D., Hoath, S.D., Hutchings, I.M., 2008. Inkjet printing – the physics of manipulating liquid jets and drops. *J. Phys. Conf. Ser.* 105, 1.
- Venuvinod, P., Ma, W., 2004. *Rapid Prototyping: Laser-Based and Other Technologies*. Kluwer Academic Publishers, New York, NY.

CITED REFERENCES

- Adachi, K., Fujihara, I., Ishida, Y., 1975. Diluent effects on molecular motions and glass transition in polymers: I. Polystyrene-toluene. *J. Polym. Sci. Polym. Phys. Ed.* 13, 2155–2171.
- Aksay, I.A., Schilling, C.H., 1984. Mechanics of colloidal filtration. In: Mangles, J.A., Messing, G.L. (Eds.), *Advances in Ceramics*, Vol. 9: Forming of Ceramics. American Ceramic Society, Columbus, OH, pp. 85–94.
- Basaran, O.A., Gao, H., Bhat, P.B., 2013. Nonstandard Inkjets. *Annu. Rev. Fluid Mech.* 45, 85–113.
- Brandrup, J., Immergut, E.H., Grulke, E.A., 1999. *Polymer Handbook*, fourth ed. Wiley Interscience, New York.
- Buss, F.S., Crawford, K., Roberts, C.C., Peters, K., Francis, L.F., 2011. Effect of soluble polymer binder on particle distribution in a drying particulate coating. *J. Colloid Interface Sci.* 359, 112–120.
- Derby, B., 2010. Inkjet printing of functional and structural materials: fluid property requirements, feature stability, and resolution. *Annu. Rev. Mater.* 40, 395–414.
- Evans, D.F., Wennerstrom, H., 1994. *The Colloidal Domain*. VCH Publishers, New York, NY.
- Graessley, W.W., 1980. Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power. *Polymer* 21.3, 261.
- Hellebrand, H., 1991. Tape casting. In: Brook, R.J. (Ed.), *Concise Encyclopedia of Advanced Ceramic Materials*. VCH Publishers, New York, NY, pp. 190–265.
- Hunter, R.J., 1989. *Foundations of Colloid Science*, vol. I. Oxford University Press, New York, NY.
- MicroFab Technote 99-01, 1999. Background on ink-jet technology. < www.microfab.com > .
- Richerson, D., 1992. *Modern Ceramic Engineering*. Marcel Dekker, New York, NY.
- Roberts, C.C., 2010. *Understanding Particulate Coating Microstructure Development*, Ph.D. Thesis. University of Minnesota, Minneapolis, MN.
- Romero, O.J., Suszynski, W.J., Scriven, L.E., Carvalho, M.S., 2004. Low-flow limit in slot coating of dilute solutions of high molecular weight polymer. *J. Non-Newtonian Fluid Mech.* 118, 137–156.
- Russel, W.B., Saville, D.A., Schowalter, W.R., 1989. *Colloidal Dispersions*. Cambridge University Press, Cambridge, UK.
- Stokes, R.J., Evans, D.F., 1997. *Fundamentals of Interfacial Engineering*. VCH Publishers, New York, NY.

- Venuvinod, P., Ma, W., 2004. *Rapid Prototyping: Laser-Based and Other Technologies*. Kluwer Academic Publishers, New York, NY.
- Weise, G.R., Healy, T.W., 1975. Coagulation and electrokinetic behavior of TiO_2 and Al_2O_3 colloidal dispersions. *J. Colloid Interface Sci.* 51, 427–442.
- Yates, D.E., Healy, T.W., 1980. Titanium dioxide-electrolyte interface. *J.C.S. Faraday I* 76, 9–18.

QUESTIONS AND PROBLEMS

Questions

1. Why are van der Waals forces strong in particulate dispersions but only weak as a bonding mechanism in solids (i.e., compared to covalent and ionic bonding)?
2. Can electrostatic forces also lead to aggregation? Explain.
3. What factors related to the particles control the electrostatic repulsion? What factors related to the liquid medium control electrostatic repulsion?
4. What is an electrical double layer?
5. What is meant by “colloidal stability”?
6. What are the main factors that determine polymer solubility in a solvent?
7. How is the rheology of a colloidal dispersion similar to the rheology of a polymer solution?
8. What factors limit the solids loading in colloidal dispersions and solutions?
9. What are intrinsic viscosity and relative viscosity?
10. If a drying process is controlled by external factors, what does that mean? Internal factors?
11. How can the drying rate be increased early and late in the drying process?
12. What sorts of structure result from monomer curing? How are they the same and different from structure resulting from drying of a polymer solution?
13. Is the extent of cure always spatially uniform in UV cured materials?
14. List the steps in a slip casting process.
15. What factors control the thickness of the cast layer as function of time? Why is it frequently valid to ignore the resistance of the mold?
16. List several coating operations and determine if they are pre-metered.
17. How is a thin coating created in the dip coating process and why is the process not used widely in manufacturing of coating on continuous webs?
18. Why is slot coating a more controlled process compared to doctor blade coating?
19. What is latex film formation?

20. What are the chief advantages and disadvantages of powder injection molding?
21. In stereolithography, what is the importance of the Gaussian intensity distribution or irradiance?
22. What factors control the cure depth and line width in stereolithography?
23. What is the Ohnesorge number and how does it predict inkjet printing characteristics?
24. What are the advantages of monomer inkjet printing as a method of additive manufacturing?

Problems

1. (a) Consider a $1\text{ }\mu\text{m}$ diameter silica particle in water. Plot the distance traveled by sedimentation as a function of time and the distance traveled by Brownian motion as a function of time. Make your plot on the same graph. Assume $T = 25^\circ\text{C}$. (b) Repeat for particles $10\text{ }\mu\text{m}$ and $0.1\text{ }\mu\text{m}$ in diameter. Comment on the effect of particle size on the relative influence of gravity and Brownian motion.
2. (a) Consider an aluminum oxide suspension in water at 20°C . Find a particle size below which Brownian diffusion dominates for a time scale of 1 day. State assumptions. (b) Repeat for a temperature of 50°C . Comment on differences. (c) Repeat for a suspension in ethylene glycol at 20°C . Comment on differences.
3. Consider a suspension of particles (isoelectric point is at pH 6) in water at pH 2 and a NaCl concentration of 0.001 M . Describe how the strength of repulsion varies with the following changes, assuming all other conditions remain constant. Give a description (more than just increase or decrease) in terms of the effect on the double layer thickness and the zeta potential. (a) Change from 0.001 M NaCl to 0.1 M NaCl. (b) Change from 0.001 M NaCl to 0.001 M CaCl_2 . (c) Change from pH = 2 to pH = 5. (d) Change from 25°C to 50°C . (e) Change from water to methanol.
4. A silica suspension (40 vol% silica, average particle size = $0.5\text{ }\mu\text{m}$) in water is prepared at pH = 5 and 25°C . Assume 0.0001 M NaCl and a surface potential is 25 mV. (a) Plot the potential energy of attraction as a function of separation distance. (b) Calculate the double layer thickness. (c) Plot the potential energy of repulsion as a function of separation distance. (d) Plot the total interaction energy as a function of separation distance. (e) Do you think this suspension is stable (not prone to aggregation)?
5. A dispersion is made containing 50 g of alumina powder (average particle diameter = $0.5\text{ }\mu\text{m}$) and 50 g of water. The pH of the dispersion is adjusted with HNO_3 to a pH of 3.5. (a) Calculate the double layer

thickness for dispersions having three different concentrations of CaCl_2 : (i) 0, (ii) 0.001 M and (b) 0.01 M . Plot the total interaction potential vs. separation distance for the alumina dispersions. Assume a surface potential of 50 mV . Comment on the stability of these dispersions.

6. Consider two silica particles (spherical, radius $R_p = 10\text{ }\mu\text{m}$) with water at their contacts, as shown in Figure P6.6. The radius R_n is $0.1\text{ }\mu\text{m}$. The distance x is the distance between the center of the particle and the center of the radius of curvature at the ring of water at the neck. Drawing is not to scale. Calculate and compare the van der Waals force assuming a 1 nm separation distance (with water intervening) with the capillary force of adhesion. Assume room temperature and complete wetting ($\cos\theta = 1$). *Hint*: The principal radii of curvature are R_n and $x - R_n$. Also see Chapter 3. Comment.

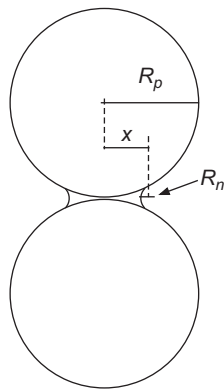


FIGURE P6.6

7. (a) Will the wetting of water on glass be improved as temperature increases? See Chapter 3 for discussion of wetting. State rationale for your answer and assumptions. (b) The capillary pressure pulling liquid A into a porous mold is twice that of liquid B. Liquid A has a surface tension 50 mJ/m^2 and a contact angle of 0° and liquid B has a surface tension of 73 mJ/m^2 . What is the contact angle for liquid B?
8. Consider a stabilized aqueous suspension of alumina ($\text{pH} \ll \text{isoelectric point, IEP}$) has volume fraction of particles of 0.4, a maximum volume fraction of particles of 0.6 and intrinsic viscosity (shape factor) of 3.5, and an average particle size of $0.4\text{ }\mu\text{m}$. (a) Calculate the viscosity of the suspension. (b) Graph the cast layer thickness as a function of time (use excel or other program). Assume the packing fraction in the cast is equal to the maximum packing fraction, Φ_m , the resistance of the cast layer is 10^{17} m^{-2} , the pressure drop from the mold is 140 kPa , and the mold resistance is much less than the cast layer resistance.

9. Consider your answer to problem 8. How would the time needed to form a 1 mm thick cast layer change (qualitatively relative to the original suspension) if: (a) the volume fraction of particle in the slip was 0.2, (b) the suspension has a pH near to the IEP, (c) 5 wt% polyvinyl alcohol is dissolved in the water, and (d) the average particle size of the alumina decreases to 0.1 μm .
10. An aqueous alumina slip containing 45 volume% alumina particles is cast into a gypsum mold. The ceramic particles are monodisperse with a size of 1 μm and they are well-stabilized. The as-cast layer is 65% of theoretical density. The gypsum mold has a specific resistance of $2 \times 10^{10} \text{ cm}^{-2}$ and a void fraction of 0.5. The total pressure drop from the slip to the saturation interface in the mold is 0.1 MPa. Plot the cast layer thickness as a function of time. Predict the time needed to cast a 1 mm thick layer and the position of the saturation front in the gypsum mold at that time
11. Polystyrene (PS) coatings are to be prepared on a polyester web using a blade coating apparatus like that used in tape casting. Two coating liquids are available: (1) polystyrene (MW = 100,000 g/mol) in toluene at a concentration of 15 wt% and (2) polystyrene latex particles in water at a concentration of 40 vol%. The coater has a land length (L) = 1 mm, a gap of 300 μm and the web speed is 100 m/min. (a) Estimate the viscosity of the suspension. State assumptions. (b) Estimate the as-deposited and final coating thickness. Assume that the latex coalesces completely. (c) Compare the advantages and disadvantages of making the coating from latex as compared with a solution of PS in an organic solvent.
12. (a) Find an expression for the wet thickness of a blade coated polymer solution, which is shear thinning and follows a power law expression with n and K as power law exponent and consistency index, respectively. (b) Find an expression for the dry thickness of a blade coated polymer assuming that the polymer solution has a polymer volume fraction of 0.1. State other assumptions.
13. Consider the preparation of a 5 μm thick polyvinyl alcohol (PVA) coating from deposition of a 7.5 vol% aqueous solution. Design processes based on dip coating and blade coating. Use the data in Figure 6.16 (lower M polymer) and assume that the surface tension of the solution is $\frac{1}{2}$ that of pure water. Which method would you use and why?
14. (a) Using your answer to question 13, specify the length of dryer needed for the coating process you selected. Assume that the process is “roll to roll” with a drying rate of 20 μm of thickness loss per minute in the constant rate period.
15. Research the cell casting process used to make polymethylmethacrylate (PMMA, plexiglass) sheets. (a) List the advantages and disadvantages of cell casting and continuous cell casting. (b) Describe the typical

formulation of “syrup” used to make PMMA sheets. Why is it not just the monomer and initiator? (c) Polymers are rarely cast into thick parts or shapes. Why?

16. Compare ceramic and polymer extrusion. Include (a) the starting materials for the processes, (b) the feeding process, (c) the effect of rheological characteristics on flow, and (d) shape retention.
17. An acrylate monomer (trimethylopropane triacrylate) is mixed with a photoinitiator with a concentration of 0.01 mol/liter. At the UV wavelength of interest, the molar absorption coefficient is 1.1×10^4 liters/(mol•cm). (a) What is the fractional transmitted light intensity (Eq. (6.43)) through a coating that is 50 μm thick? 100 μm thick? (b) What is the total dose of UV delivered (J/m^2) for an incident intensity is $1 \text{ W}/\text{cm}^2$ and illumination time of 1 s?
18. Consider problem 17 from the perspective monomer inkjet printing. Assume the same monomer and photoinitiator are used, droplet create a monomer thickness of 20 μm and the conditions in 17(b) result in adequate curing. What intensity of UV source is needed to achieve a print-head speed of 100 m/min? State assumptions.