Joseph L. Keddie · Alexander F. Routh

Fundamentals of Latex Film Formation

Processes and Properties

Springer

Springer Laboratory Manuals in Polymer Science

For other titles published in this series, go to
www.springer.com/series/3721

Joseph L. Keddie • Alexander F. Routh

Fundamentals of Latex Film Formation

Processes and Properties

Springer

Joseph L. Keddie
Department of Physics &
Surrey Materials Institute
University of Surrey
Guildford
UK

Alexander F. Routh
Department of Chemical Engineering
and Biotechnology & BP Institute
University of Cambridge
Cambridge
UK

Printed on acid-free paper

Preface

This book has emerged out of our long-time research interests on the topic of latex film formation. Over the years we have built up a repertoire of slides used in conference presentations, short courses and tutorials on the topic. The story presented in this book has thereby taken shape as it has been told and re-told to a mix of academic and industrial audiences.

The book presents a wide body of work accumulated by the polymer colloids community over the past five decades, but the selection of examples has been flavoured by our particular experimental interests and development of mathematical models. We intend the book to be a starting point for academic and industrial scientists beginning research on latex film formation. The emphasis is on fundamental mechanisms, however, and not on applications nor on specific effects of formulations. We hope that the book consolidates the understanding that has been achieved to-date in the literature in a more comprehensive way than is possible in a review article. We trust that the reader will appreciate the fascination of the topic.

We are very grateful to the many students and post-docs whom we have had the privilege of supervising, and from whom we have learned much about latex film formation. Several of them have provided artwork for this book, as is noted in the figure captions. Post-docs, in a rough chronological order of their time at the University of Surrey, include Jacky Mallégol, Jean-Philippe Gorce, Chun-Hong Lei, Diana Andrei, Yong Zhao, Elisabetta Canetta, and Carolina de las Heras Alarcón. Post-docs at Cambridge include Venkata Gundabala, Grace Yow and Milan Patel.

PhD students and visitors in Surrey, who have studied latex film formation, are Katerina Tzitzinou, Elisabetta Ciampi, Juan Salamanca, Peter Doughty, Nicki Kessel, Philippe Vandervorst, Tao Wang, Tecla Weerakkody, Alexander König, Argyrios Georgiadis, and André Utgenannt. A special mention goes to Tao Wang who contributed to the writing of Chapter 7. Students at Sheffield and Cambridge are Wai Peng Lee and Venkata Gundabala and at Cambridge are Richard Trueman and Merlin Etzold.

Athene Donald and Richard Jones first introduced JLK to the topic of latex film formation and provided guidance in his early studies. Paul Meredith and Ruth Cameron were his first academic collaborators in studies of film formation at the Cavendish Lab in Cambridge. The Soft Matter Group members at Surrey, includ-

<div align="right">
Joseph L. Keddie, Guildford
Alexander F. Routh, Cambridge
</div>

Contents

Symbols

Generic symbols used throughout this book

Symbol	SI units	Meaning
E	m s^{-1}	Evaporation rate (units of velocity)
H	m	Film thickness (wet)
R	m	Particle radius
P	N m^{-2}	Pressure
T	K	Temperature
T_g	K	Glass Transition Temperature
η	N s m^{-2}	Dispersion viscosity
μ	N s m^{-2}	Solvent viscosity
ϕ	–	Particle volume fraction
ϕ_m	–	Close packed volume fraction

Chapter 1

A	Nm = J	Hamaker Constant
D_0	m^2 s^{-1}	Stokes-Einstein Diffusion coefficient
kT	Nm = J	Thermal energy
R	m	Particle radius
r	m	Spacing between particle centers
U	Nm = J	Interaction potential
ε	–	Permittivity
ε_0	A^2 s^4 kg^{-1} m^{-3}	Permittivity of free space
κ^{-1}	m	Debye length
Ψ	V	Electrostatic potential on particle surface

Chapter 2

A_0, A_{sp}	m		Tapping amplitudes for AFM
B	T (or V s m^{-2})		Magnetic field strength
d_I	m		Interpenetration distance
D_0	m^2 s^{-1}		Stokes-Einstein diffusion coefficient for a particle
D_{app}	m^2 s^{-1}		Apparent molecular self-diffusion coefficient
d_p	m		Path length for light through sample
d_b	m		Beam thickness
e_p	m		Average spacing between particles
E_d	Nm = J		Energy dissipation in tapping mode AFM
E_p	N m^{-2}		Storage modulus (obtained from DWS)
f	s^{-1}		frequency
$g_2(t)$	–		Correlation function for light scattering
G	T m^{-1} (V s m^{-3})		Gradient in the magnetic field
G' G''	N m^{-2}		Shear moduli (storage and loss)
h_{unit}	m		Height of fcc/hcp unit cell
H_{dry}	m		Average thickness of dry film
I	–		Intensity of radiation
I_0	–		Intensity of incident radiation
I_B	–		Background scattering intensity
K_P	–		Porod constant
K_B	–		Constant of proportionality
L	m		Length of beam
L', L''	N m^{-2}		Longitudinal moduli
m	–		Ratio of refractive indices
n	–		Refractive index
n_p	–		Refractive index of particle
Q	m^{-1}		Scattering wave vector
q	–		Quality factor for AFM cantilever
$<r^2>$	m^2		Mean-squared displacement
R_f	m		Förster radius
R_g	m		Radius of gyration (particle or molecule)
s	s^{-1}		Speckle rate
t	s		time
t_D	s		Fluorescence decay time
t_0	s		Initial time
T_f	-		Transmitted fraction of radiation
w	s		Interfacial width between two phases
Y	N m^{-2}		Young's modulus (of beam)
z	m		Void radius
α	–		Constant of proportionality (for DWS)
β	–		Exponent in stretched exponential
γ	s^{-1} T^{-1}		Magnetogyric ratio
λ	m		Wavelength of radiation
λ_{min}	m		Wavelength of minimum transmitted radiation
ν	–		Poissons ratio
θ	–		Scattering angle
$\Delta\sigma_f$	N m^{-2}		Change in film stress
τ_A	s		Auto-correlation time

| φ | – | Angle of deflection of beam |
| ω | s^{-1} | Angular frequency |

Chapter 3

D	m^2 s^{-1}	Diffusion coefficient
E	m s^{-1}	Evaporation rate (units of velocity)
H	m	Film thickness (wet)
H_{dry}	m	Film thickness (dry)
k_m	m s^{-1}	Mass transfer coefficient
k_p	m^{-2}	Permeability of particle bed
$K(\phi)$	–	Sedimentation Coefficient
L	m	Capillary length
L_b	m	Boundary layer thickness
P	N m^{-2}	Pressure
P^*	N m^{-2}	Characteristic pressure
P_{cap}	–	Dimensionless capillary pressure
Pe	–	Peclet number
t_{evap}	s	Time for evaporation
t_{diff}	s	Time for diffusion
y	m	Vertical distance
$Z(\phi)$	–	Compressibility
ϕ	–	Particle volume fraction
γ	N m^{-1}	Surface tension

Chapter 4

a_0	m	Radius of contact between two particles
E	N m^{-2}	Young's modulus
F	N	Force pushing particles together
G	N m^{-2}	Shear modulus
δ	m	Approach of particle centers
ε_R	–	Strain along particle centers
ε	–	Strain
γ_{wa}	N m^{-1}	Water – air interfacial tension
γ_{pw}	N m^{-1}	Polymer – water interfacial tension
γ_{pa}	N m^{-1}	Polymer – air interfacial tension
η_0	N s m^{-2}	Polymer low shear viscosity
$\overline{G}$	–	Dimensionless group comparing polymer relaxation time to evaporation time
$\overline{\lambda}$	–	Dimensionless group controlling particle deformation
ν	–	Poison's ratio
$\overline{\sigma}_t$	–	Dimensionless stress at top of film
θ	–	Angle of contact between sintering spheres

Chapter 5

a_T	–	Time-temperature superposition shift factor
b	m	Kuhn length for polymer segment
C_1, C_2	-, K	WLF equation factors
D_b	$m^{-2} s^{-1}$	Fickian diffusion coefficient
E_a	$J\ mol^{-1}$	Activation energy
G_c	$J\ m^{-2} = N\ m^{-1}$	Critical energy release rate
K_{IC}	$N\ m^{-3/2}$	Fracture toughness
M	–	Polymer molecular weight
M_e	–	Entanglement molecular weight
N	–	Degree of polymerisation
Λ	m	Interpenetration distance
σ_f	$N\ m^{-2}$	Failure stress
Σ	m^{-2}	Density of polymer chains crossing interface
τ_e	s	Rouse entanglement time
τ_R	s	Rouse relaxation time
τ_d	s	Reputation time
τ_{XL}	s	Time for cross linking reaction
w_I	m	Interfacial width for interdiffusion
χ	–	Flory Huggins interaction parameter

Chapter 6

A	$mol\ m^{-3}$	Critical concentration in Langmuir isotherm
C_s	$mol\ m^{-3}$	Surfactant concentration in solution
D_p	$m^2 s^{-1}$	Particle diffusion coefficient
D_s	$m^2 s^{-1}$	Surfactant diffusion coefficient
k, k'	s^{-1}	Reaction rate constants for surfactant adsorption and desorption
Γ	$mol\ m^{-2}$	Adsorbed amount in Langmuir isotherm
Γ_∞	$mol\ m^{-2}$	Maximum adsorbed amount
Pe_p	–	Particle Peclet number
Pe_s	–	Surfactant Peclet number

Chapter 7

D	m	Filler diameter
L_c	m	Critical length of inclusion
σ_f	$N\ m^{-2}$	Fracture strength
τ	$N\ m^{-2}$	Interfacial shear strength

Appendix A

F_{drag}	N	Drag force
G	m s^{-2}	Acceleration due to gravity
P	N m^{-2}	Pressure
$P*$	N m^{-2}	Characteristic pressure
$\Delta\rho$	N m^{-2}	Difference in density
ρ	kg m^{-3}	Fluid density
U	m s^{-1}	Velocity
$U*$	m s^{-1}	Characteristic velocity

Appendix B

$\Delta\Omega$	s^{-1}	Pulse bandwidth
Δy	m	Pixel resolution in a profile
γ	s^{-1} T^{-1}	Magnetogyric ratio
G_y	T m^{-1}	Magnetic field gradient
N	–	Number of echoes in a train
N_{acq}	–	Number of points acquired in an echo
N_S	–	Numbers of scans
τ_D	s	Time interval between points in an echo
t_{pd}	s	Time duration of an RF excitation pulse
τ	s	Pulse gap (delay time between RF pulses)
τ_R	s	Repetition delay time (before sequence repeats)
T_1	s	Spin-lattice relaxation time
T_2	s	Spin-spin relaxation time

Appendix C

H	kg/kg	Humidity
M_w	kg mol^{-1}	Molar mass
P_w	N m^{-2}	Partial pressure of water
P	N m^{-2}	Pressure
R	J mol^{-1} K^{-1}	Gas constant
V	m^3	Volume

Appendix D

a	m	Crack length
Δ	m	Thickness of sample
E	N m^{-2}	Elastic (Young's) modulus
G_c	J m^{-2} = N m^{-1}	Energy release rate
h, b	m	Specimen dimensions
K_I	N m$^{-3/2}$	Stress intensity factor
K_{IC}	N m$^{-3/2}$	Fracture toughness (critical K_I)
P	N	Applied load
r_y	m	Radius of crack tip
Σ	N m^{-2}	Applied stress
W_B	J	Fracture energy
Y	–	Geometric factor

1 An Introduction to Latex and the Principles of Colloidal Stability

1.1 What is Latex?

Latex is an example of a colloidal dispersion. It consists of polymeric particles, which are usually a few hundred nanometres in diameter, dispersed in water. The particles typically comprise about 50 percent by weight of the dispersion. Depending on the particular application, there will also be a complex mixture of pigments, surfactants, plasticising aids and rheological modifiers. The whole dispersion is colloidally stable, meaning that it can sit on a shelf for years and remain dispersed, without sedimentation of particles making 'sludge' at the bottom. In this book, the word 'latex' will be used as shorthand for a wet dispersion. Sometimes, however, latex is used as an adjective, as in 'latex film'. The plural of 'latex' is 'latices', not to be confused with 'lattices'! (An alternative is to say 'latexes', but 'latices' will be used through this book.)

Although colloids have been used since ancient times in Egypt and Greece, colloidal dispersions have been studied scientifically only since the nineteenth century when Thomas Graham first coined the term 'colloid'. It is derived from the Greek work *coll,* meaning 'glue'. A major advance in colloid science was made by Robert Brown, who observed pollen particles 'dancing' randomly when dispersed in a fluid. This phenomenon is now termed Brownian motion and is a defining characteristic of a colloidal dispersion. The effect is the result of an imbalance of forces between the colloidal particles and the surrounding molecules of the solvent, and it provides evidence for the existence of molecules. A dispersion in which Brownian motion is present is described as colloidal. An alternative definition, from the International Union of Pure and Applied Chemistry (IUPAC), is that colloidal particles have at least one dimension between 1 nm and 1 μm (IUPAC 2009).
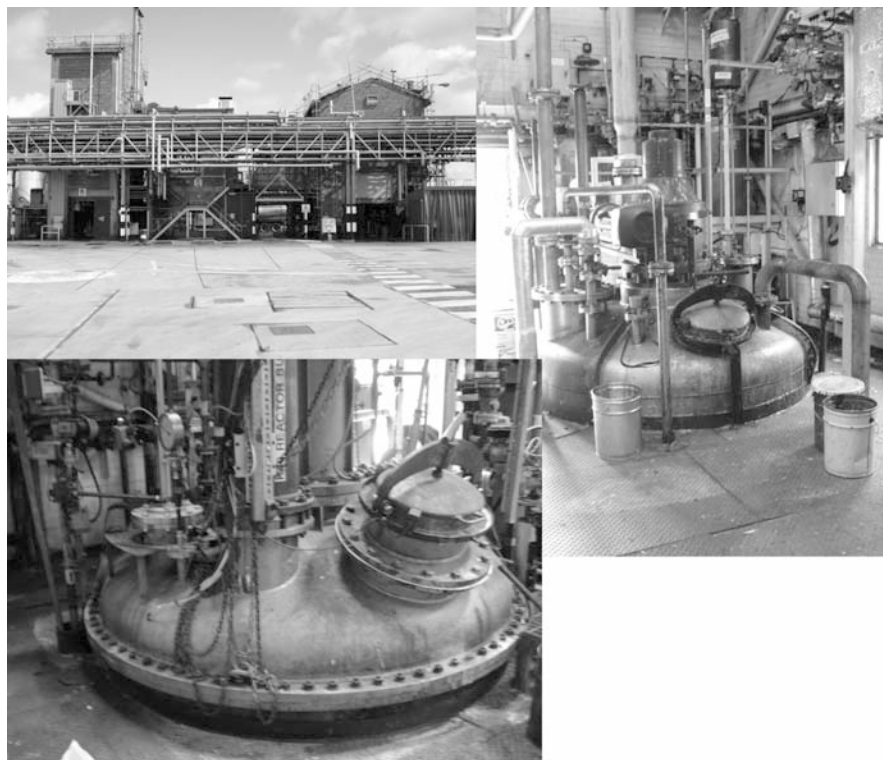
Fig. 1.1 An emulsion polymerisation reactor. The structure spans an entire building and covers two floors. The top of the reactor houses the stirring motor**. (**Photographs courtesy of AkzoNobel)

1.2   Latex Synthesis and Uses

Industrially and in the laboratory, latex is most often made by a reaction called 'emulsion polymerisation'. The process can be scaled up to large quantities, such as is demonstrated by the large reactors in Fig. 1.1. The scale of the structure, which spans two storeys, is indicated by the top two photographs. The top of the reactor and the stirring motor are shown in the bottom photo. The emulsion polymerisation process and newer developments, such as miniemulsion polymerisation, are described in numerous sources elsewhere (Lovell and El-Aasser 1997). A discussion of the polymerisation process is beyond our scope here.

Latex may be synthesised from a range of monomers, the typical ones being acrylates (methyl methacrylate, butyl acrylate, ethylhexyl acrylate), styrene, vinyl acetate and butadiene. Copolymers are used extensively. The molar ratio of the monomers in the copolymer determines its glass transition temperature (T_g), the point at which a solid polymer changes into a liquid-like polymer, because long

range motion of the molecule's backbone is enabled. A polymer's viscosity falls sub-exponentially as the temperature increases above the T_g. As we shall see in our discussions in Chapter 5, the temperature at which a latex film is formed should be greater than the (co)polymer's T_g.

Anyone who coats a house with a modern, waterborne paint uses latex to their benefit. The largest household use of latex is for architectural or decorative paints, which typically comprise acrylic or styrene-acrylic copolymers. Most readers will be familiar with commercial latex paints, such as those shown in Fig. 1.2.

Fig. 1.2 Latex paint is marketed in the UK and other countries under the trade name of Dulux, as seen in this advertising material, showing a well-recognised mascot. (Photographs courtesy of AkzoNobel)

Table 1.1 Typical formulations for gloss, silk and matte paints.

Component	Function	Gloss Paint (Schuler et al. 2000) (wt.%)	Silk Paint (Murray 2009) (wt.%)	Matte Paint (Murray 2009) (wt.%)
Polymer particles (latex)	Acts as a binder for the pigment	26.5	20	15
Titanium dioxide	Pigment to create opacity	23.0	16	10
Defoamer	Prevents bubble formation during use	0.15		
Thickener	Adjusts viscosity	12.0		
Pigment dispersant	Stabilizes the pigment in the water phase	1.0	3 (total for all four)	3 (total for all four)
Coalescent	Lowers the film formation temperature and increases the interdiffusion rate	2.35		
Extender	Inexpensive filler, typically minerals such as calcium carbonate		2	32
Water	Carrier for the wet paint	35.0	59	40

Household paints and varnishes are usually applied over relatively small areas and allowed to dry. Viscosity control is particularly important for paints. Under a low shear rate, such as when coated vertically on a wall, the paint should not flow or drip: the viscosity should be high. When applied with a brush at a higher shear rate, the viscosity should be low to allow even spreading. Hence, rheology modifiers are a key ingredient of commercial paints. Shear thinning behaviour, meaning that the viscosity decreases as the shear rate increases, is desirable to ensure good spreading with a brush or applicator. Film thicknesses for household paints are typically one hundred micrometers. Typical formulations for three types of commercial emulsion (i.e., latex) paint are shown in Table 1.1, and other recipes are found in literature (Heldmann et al. 1999). Gloss paints are highly reflective of light, matte paints are poorly reflective, and silk paints have an intermediate reflectivity.

You might be surprised to see that the latex polymer makes up less than 30% by weight in the paint formulations. Note the presence of rheology modifiers and defoamers. Wetting agents are also often added to ensure full coverage of hydrophobic surfaces. Extenders, which are inexpensive minerals used as fillers, are added to matte paints to 'extend' how far the more expensive polymers can go. Extenders introduce light scattering and so are not added to gloss paints.

Increasingly, latex is being used as a binder in *industrial* coatings (applied in factory production) and various types of *protective* coatings for automobiles, aircraft, ships, appliances and more. The demands on industrial and protective coatings are high and go beyond improving the appearance of an object. The coatings need to provide resistance against corrosion, abrasion, wear, fire and chemical attack.

Beyond paints and coatings, the uses for latex include pressure-sensitive adhesives, sealants, carpet backings, construction additives (such as in cements and mortars), paper coatings, inks, and latex gloves and condoms. Each will be considered briefly here.

Pressure-sensitive adhesives (PSAs) are permanently tacky at room temperature, and provide permanent and nearly instant adhesion to almost any surface. They are well-known in their application as tapes and sticky labels. Pressure-sensitive adhesives have many specific applications in the household (Fig. 1.3) and in cars (Fig. 1.4). They typically have a glass transition temperature that is around –50°C, and hence are made from monomers such as butyl acrylate or 2-ethyl hexyl acrylate to reduce the copolymer's T_g.

Industrially, films are deposited onto long rolls of substrate material running at high speeds through industrial coaters. Most often the 'transfer coating' process is used for labels. A sandwich structure, as in Fig. 1.5a, is made. The latex is spread on a 'release liner' with a low-surface-energy surface, such as a silicone polymer, and then film-formed. The rate of drying is increased by drawing the film on the backing layer through a long oven or by blowing hot air across it. The dry film thickness for applications is typically 20 μm. Next, a 'face material' (or facestock) is pressed into contact with the latex adhesive surface. The air surface of the facestock is decorated appropriately for the adhesive's application. To use the adhesive, it is peeled off from the release liner and then pressed onto the surface of choice, such as a beer bottle. The final film should be uniform and not have defects, such as pinholes or surface ripples.
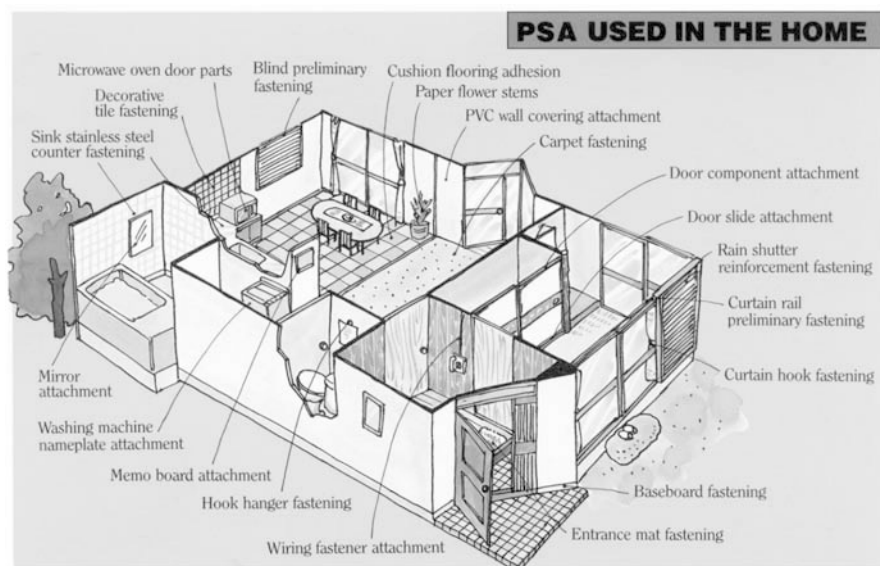
Fig. 1.3 Uses of pressure-sensitive adhesives in the home. (Image reproduced with permission of Cytec Specialty Chemicals)
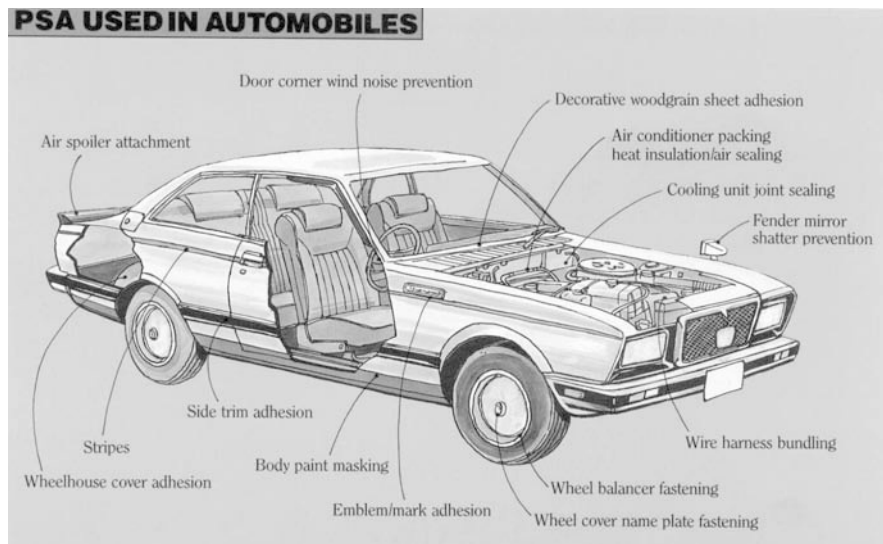
Fig. 1.4 Uses of pressure-sensitive adhesives in a car. (Image reproduced with permission of Cytec Specialty Chemicals)

In a typical industrial coater, as in Fig. 1.5b, a steel roll is rotated through a reservoir of wet latex, picking it up as it rotates. The backing layer is then drawn at high speed across the rotating wet roll to deposit a thick film. The excess latex in the film is skimmed off by passing a grooved bar (called a 'Meyer rod') across it.

Another process, called 'gravure', uses a roll that has grooves engraved in it. When the gravure roll is passed through a reservoir of latex, its grooves pick up some of the latex. The roll is then pressed in contact with a backing layer onto which it leaves a wet film. Higher coating speeds are obtained with the gravure process compared to most other processes. Depending on the process, coating speeds can range from 100 to over 1000 meters per minute.

Textiles and carpet backings are often made from acrylic polymers. The coating provides durability to the material surface as well as a resistance to a number of solvents (Campos et al. 2006).

Construction materials often have hydrophobic polymer latices added to them. These reduce the water permeability of the final material and will lead to a life extension from reduced corrosion (Stancato et al. 2005).

Paper coatings use latex as a binder to enable the incorporation of clays and inorganic fillers. Latex coatings on paper are cheaper than wood pulp and also allow greater penetration of ink during the printing process (Zang and Aspler 1995, Alturaif et al. 1995).

Inks for printing on paper and card may use latex as a binder for the pigment or dye particles (Hutton and Parker 2008). There is growing interest in water-based inks to replace solvent-based materials. In inkjet printing, colloidal dispersions are used in inks (Calvert 2001), and the use of latex particles has been demonstrated in an inkjet printer (Wong et al. 1988).

(a)

1. = Release liner or backing
2. = Silicone release coating
3. = Adhesive coating
4. = Face material lamination
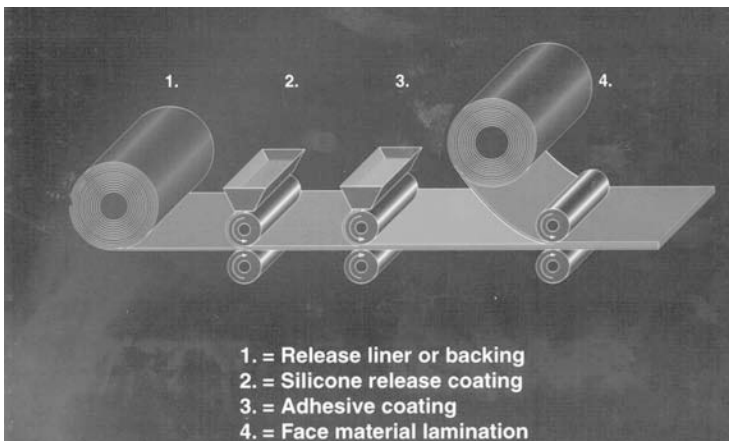
(b)
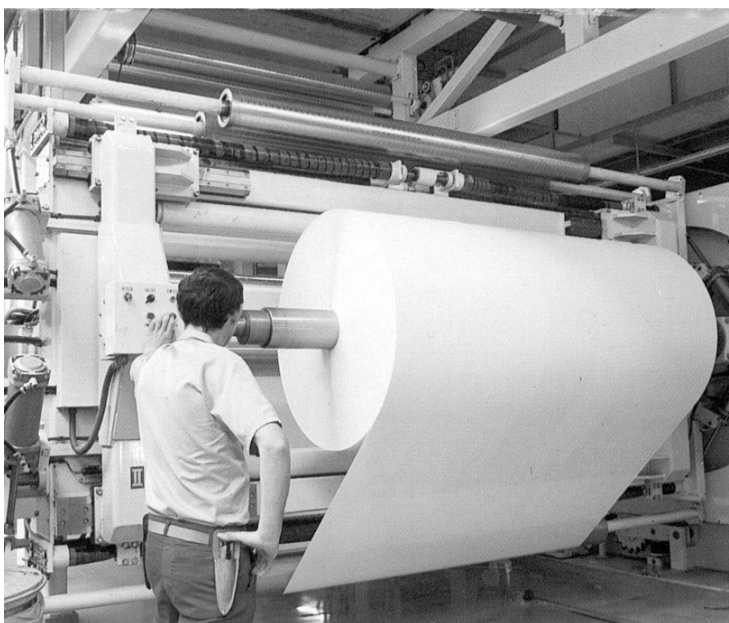
Fig. 1.5 Industrial coating of pressure-sensitive adhesive films. **a** In the transfer process, the latex adhesive **3** is deposited onto a silicone release coating **2** on a release liner **1**. Then the face material **4** is laminated onto the adhesive surface. Image courtesy of Cytec Specialty Chemicals. **b** An industrial coater. (Photograph used with permission of Cytec Specialty Chemicals)
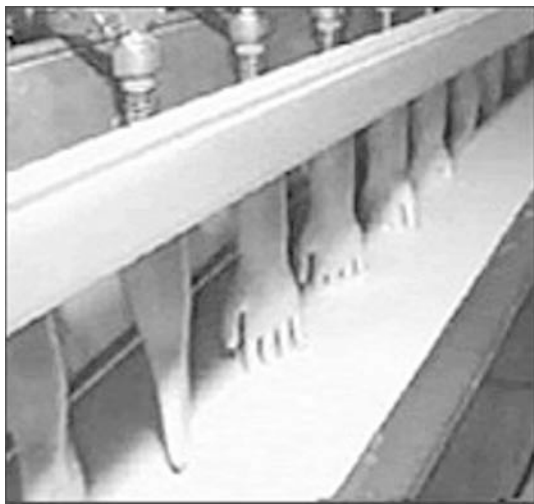
Fig. 1.6 Latex gloves are being made by dipping moulds into a natural latex dispersion and withdrawing. (Photograph used with the kind permission of Innovative Gloves Co. Ltd, Songkhla, Thailand)

Latex gloves are made by dipping a hand-shaped, ceramic mould into a latex dispersion and drying, such as shown in Fig. 1.6. Condoms are manufactured similarly – but of course with a different mould.

1.3   Historical Context and Economic Importance

There is a natural form of latex that is derived from a tree (*Hevea brasiliensis*), which – as its Latin name implies – originated in Brazil (Fig. 1.7). Plantations were developed in several Asian countries to support the growing rubber industry in the twentieth century. Natural latex is essentially cis-isoprene emulsified by a protein. During World War II, the supply of this latex from Malaysia was disrupted, and the resulting shortages spurred the development of synthetic latex made via emulsion polymerisation. The first commercially available latex was introduced by the Glidden Company in 1948. Consequently, a large synthetic latex industry grew through the remainder of the century. A second important factor is that some persons have an allergy to the protein in natural latex; about one in 10 persons show sensitisation (Turjanmaa et al. 1996, Liss et al. 1997). This drawback of natural latex has encouraged the growth of the synthetic latex market as an alternative, especially for applications in gloves.

Fig. 1.7 The white dripping liquid is the sap of the *Hevea Brasiliensis* tree, which provides the natural form of latex. It is being collected in a bowl at the bottom of the tree for later use in the manufacture of natural rubber objects. (iStockPhoto)

The market for emulsion polymers is large and growing, with worldwide sales in 2007 of 17.9 billion US dollars. The vast range of industries that use polymeric coatings makes the economic influence of the coatings industries particularly immense. For example, the paper industry creates 91 million tonnes of paper in the EU annually, using coatings to provide a brilliant white shine. The annual market for paper coatings in the EU is 800 million Euros (Urban and Takamura 2002). Adhesives and sealants are used in more than 100 end-use product markets, and they had a demand of four million tonnes in the European region in 2008. A growth of 2.5% is predicted between 2008 and 2011. Of the entire European market for adhesives, valued at 11.3 billion Euros (15.8 billion US dollars), a share of 37 % was held by water-based adhesives, which are made from latex (von Dungen 2009). The water-based sector is growing at the expense of other manufacturing processes that emit organic solvents.

In 2008, there were 135 billion latex gloves manufactured and the growth rate is around 10% per annum (Tan 2008). In response to the allergic reaction of some people to natural latex, the US market for nitrile latex gloves increased from 18.6% in 2006 to 26.8% in 2007, with the market share of natural rubber falling from 48% to 41% (Tan 2008). The biggest exporter of rubber gloves is Malaysia. In 2007, the total number of exported pairs of gloves was 41.7 billion pairs with a sale value of 5.9 billion Malaysian dollars (1.72 billion US dollars). This corresponds to approximately one percent of the Malaysian GDP (Department of Statistics 2008). For textiles, the annual consumption in 2001 was 160,000 dry

tonnes of polymer, and for carpet backings it was 500,000 dry tonnes of latex in 1999 (Urban and Takamura 2002).

Latex is most associated with water-based paints used to paint the inside and outside of buildings and houses, referred to as 'architectural paints'. It is predicted that – as a result of tough environmental legislation – 88% of all architectural paints sold in Europe in the year 2011 will be water-based, using latex polymers as their binder. Globally, 73% of the market share of architectural paints is predicted to be water-based in that same year. The production of all architectural paints is predicted to reach 21 million metric tonnes in 2011 and to have a value of 47 billion US dollars. Despite a harsh economic climate, an annual global growth rate of nearly 4% is predicted for 2006–2011 (European Coatings Journal 2008).

1.4   Overview of the Film Formation Process

The process of transforming a stable dispersion of colloidal polymer particles into a continuous film is called 'latex film formation'. It involves many steps that span from a dilute through to a concentrated dispersion, into a packed array of particles, and eventually into a continuous polymer film. From a modelling perspective (and for drawing cartoons!), it is conventional to split the process into three sequential steps (drying, particle deformation, and diffusion). But, as will be discussed in later chapters, the steps can overlap in time. There is a large literature examining the mechanism of film formation with many excellent reviews and commentaries (Steward et al. 2000, Winnik 1997, Dobler and Holl 1996, Winnik 1997b, Keddie 1997).

Crucially, the film formation process, sketched in Fig. 1.8, has a pronounced influence on the final film properties. A recurring theme in this book is how the process and properties are interrelated. When a stable dispersion (state 1) is deposited on a surface and subject to evaporation, the particles consolidate into some form of close packing (state 2). The latex dispersion typically does not dry in a uniform manner across the film. As Fig. 1.9 illustrates, the edges often dry first. In this illustration, light scattering by the particles in water makes the wet regions turbid. There is a possibility of colloidal crystallisation (i.e. the formation of an ordered array of particles) if the drying is slow enough. More likely, the particles will collect in the form of a random close-packing with a volume fraction in the region of 0.64 for mono-sized particles (Russel 1990, Routh and Russel 1998, 2001). This means that the spherical particles occupy 64% of the space and the remainder is occupied by water. An image of an array of particles in close packing is shown in Fig. 1.10a. Here, the individual particles make the topography appear like a mountain range with the peak-to-valley distance corresponding to the particle radius. The drying step is considered in detail in Chapter 3.

Polymer-in-water dispersion
State 1
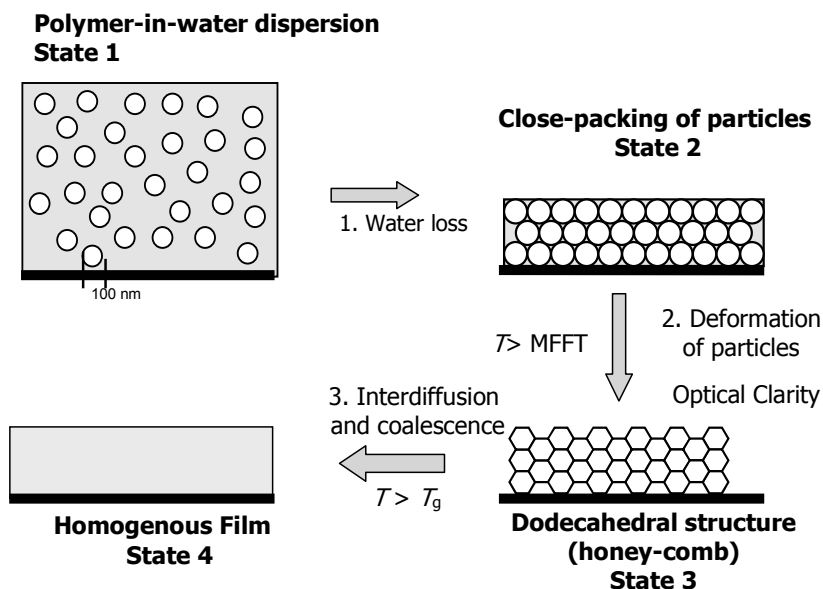
Fig. 1.8 Schematic of the process of film formation: a colloidal dispersion's transition into a continuous polymer film. (Drawing courtesy of Jacky Mallégol, University of Surrey)

Fig. 1.9 Drying of 200 nm polystyrene particles in water. The particles pack and consolidate at the edge, and these packed particle fronts propagate laterally across the film toward the centre. (Photographs courtesy of Wai Peng Lee)

When the particles come into close contact, they will deform from their spherical shape to fill the void space around them. As the individual particles are deformed, they can remain as distinct objects (state 3 in Fig. 1.8). With the loss of the interparticle voids, the particle layer becomes optically transparent, because light is no longer scattered by heterogeneities in the refractive index. The onset of transparency is sometimes used to define the point of film formation.
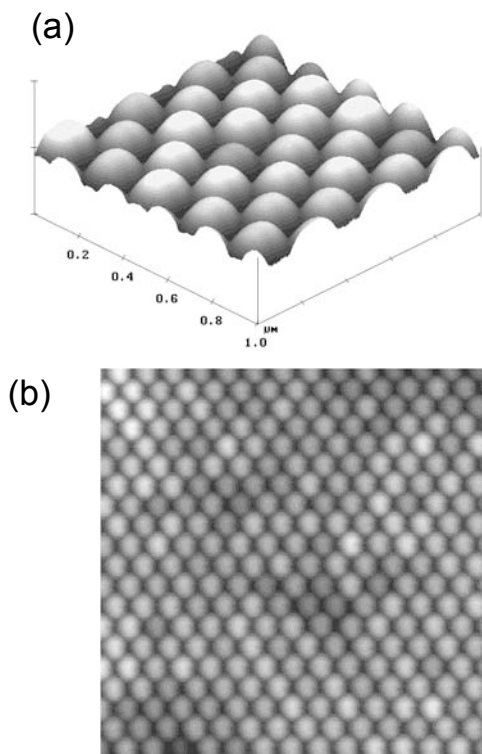
Fig. 1.10 a AFM topographical image of a latex film surface in a three dimensional view. The film was cast at room temperature, and since the polymer's glass transition temperature is about 20 °C, the particles do not flatten much. Scan area is 1 μm x 1 μm. **b** When viewed from above, the high degree of order in the particle packing in a hexagonal array can be seen. (Images courtesy of J. Mallégol, University of Surrey)

An atomic force microscope (AFM) image of deformed particles is shown in Fig. 1.11a. The particles are no longer spherical, and only small voids are seen at the particle boundaries. There are numerous possible driving forces for the particle deformation, which are discussed at length in Chapter 4 (Brown 1956, Henson et al. 1953, Vanderhoff et al. 1966, Sheetz 1965, Routh and Russel 1999, Dobler and Holl 1996). The resistance to deformation comes from the particles themselves, and hence the temperature, relative to the glass transition temperature, is a crucial parameter in determining the extent of particle deformation.

If mono-sized particles are packed into a face-centred cubic array, each particle (in the bulk of the film) will be in direct contact with twelve nearest neighbours. When the contact regions between the particles flatten, the particles will each create a twelve-sided geometric figure called a 'rhombic dodecahedron', drawn in Fig. 1.11b. In a face-centred cubic crystal, each particle has six neighbours

hexagonally arranged around it in the (111) plane (Fig. 1.11a). If a thick film of deformed particles is sliced along a (111) plane, the particle cross-sections will be hexagonal. The array will take on an appearance similar to natural honeycomb (Fig. 1.11c), such as is shown schematically in State 3 in Fig. 1.8.
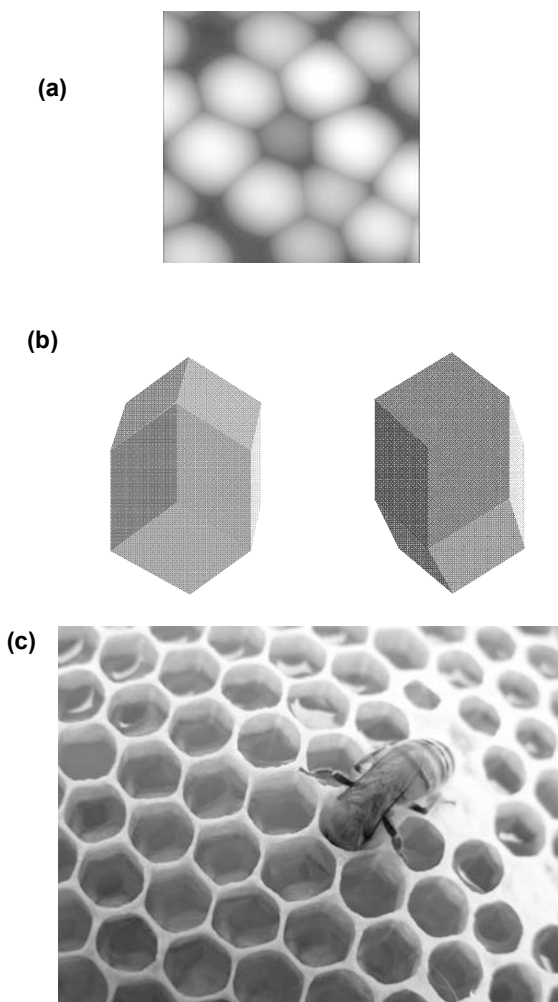
Fig. 1.11 a Example of flattening at particle/particle boundaries. Particle identity is still retained. Size of AFM image is 1.5 μm along each side. Image courtesy of A. Tzitzinou (University of Surrey). **b** Two different views of a rhombic dodecahedron. There are six rhomboids on the vertical faces. There are six square faces, three each on the top and bottom. **c** A cross-section slice of the dodecahedral structure in a film shows a hexagonal array, which is reminiscent of natural honeycomb. (iStockPhoto)

If the particles are too hard, then they will not be able to deform. The film will be cloudy and cracked, as seen in Fig. 1.12a. It will be brittle and possibly powdery. The polymer can be softened by heating to temperatures above its T_g. Then, the film will be less brittle and will achieve optical transparency (Fig. 1.12b). The lowest temperature at which optical transparency may be achieved is referred to as the 'minimum film formation temperature' or MFFT. It is an important characteristic of latex formulation because it determines the conditions under which the latex can be successfully applied. If hard particles are blended with softer particles, film formation may still occur (Fig. 1.12c). The softer particles will create the film, and the harder particles will be dispersed throughout it.

Fig. 1.12 a Latex $T_g \approx 80°C$; Film cast at room temperature; Film is opaque and has regular cracking patterns. **b** Latex $T_g \approx 80°C$; Film formation at 150°C for 10 min.; Film is cracked but is now translucent, but note the haziness. **c** A blend of latex particles with $T_g \approx 80°C$ (as in (a) and (b)) and $T_g \approx -50°C$; Film formation at room temperature (21°C). Film is smooth and transparent. (Photographs courtesy of Tao Wang, University of Surrey)

When the particles are deformed, their surfaces come into close contact over large areas. At temperatures above the polymer's T_g, the molecular chains within the particles will move across the boundaries between particles. This diffusion blurs the boundaries between individual particles and leads to a continuous film with increased mechanical strength (State 4 in Fig. 1.8). The process by which long polymer chains diffuse in a molten material is called 'reptation'. It has been shown that full mechanical strength is obtained once reptation has progressed by the distance comparable to the polymer's radius of gyration (Prager and Tirrell 1981, Richard and Maquet 1992). The diffusion process is considered in detail in Chapter 5.