.

•

1

Contents

| 1 | AN I<br>COI |               | UCTION TO LATEX AND THE PRINCIPLES OF             | 1        |
|---|-------------|---------------|---|----------|
|   |             | UDA<br>What i | L STABILITT                                       | ار۱<br>۱ |
|   | 1.1         | what i        | S Latex ?   | ····· I  |
|   | 1.2         | Latex S       | Synthesis and Uses                                | Z        |
|   | 1.3         | Histori       | cal Context and Economic Importance               | 8        |
|   | 1.4         | Overvi        | ew of the Film Formation Process                  | 10       |
|   | 1.5         | Enviro        | nmental Legislation                               | 15       |
|   | 1.6         | Releva        | nt Colloid Science                                | 17       |
|   |             | 1.6.1         | Interaction Potentials                            | 17       |
|   |             | 1.6.2         | Fluid Motion                                      | 22       |
|   | Refe        | rences        |   | 24       |
| 2 | EST         | ABLISH        | ED AND EMERGING TECHNIQUES OF STUDYI              | NG       |
|   | LAT         | 'EX FILI      | M FORMATION                                       | 27       |
|   | 2.1         | Techni        | ques to Study Latex in the Presence of Water (Wet |          |
|   |             | and Da        | mp Films)   | 28       |
|   |             | 2.1.1         | Physical Probes of Drying                         | 29       |
|   |             | 2.1.2         | Specialist Electron Microscopies                  |          |
|   |             | 2.1.3         | Scattering Techniques                             |          |
|   |             | 2.1.4         | Profiling Water and Particles with Spectroscopies |          |
|   |             | 2.1.5         | Probe Techniques for the Aqueous Environment      |          |
|   | 2.2         | Techni        | ques to Study Particle Packing and Deformation    |          |
|   |             | in Dry        | Films   | 61       |
|   |             | 2.2.1         | Scanning Probe Microscopies                       | 61       |
|   |             | 2.2.2         | Scanning Near-Field Optical Microscopy (SNOM)     |          |
|   |             |               | and Shear Force Microscopy                        |          |
|   |             | 2.2.3         | Electron Microscopies                             | 71       |
|   | 2.3         | Techni        | ques to Study Film Crosslinking                   |          |
|   |             | 2.3.1         | Ultrasonic Reflection and OCM                     |          |
|   |             | 2.3.2         | Spectroscopic Techniques                          |          |
|   |             |               | I   |          |

|   | 2.4               | Techni   | iques to Study Interdiffusion and Coalescence      | 74  |
|---|-------------------|----------|--|-----|
|   |                   | 2.4.1    | Small Angle Neutron Scattering (SANS)              | 75  |
|   |                   | 2.4.2    | Fluorescence Resonance Energy Transfer (FRET)      | 76  |
|   |                   | 2.4.3    | Transmission Spectrophotometry                     | 83  |
|   | 2.5               | Conclu   | uding Remarks                                      |     |
|   | Refe              | rences   |  |     |
| 3 | DRY               | ING OF   | LATEX FILMS  | 95  |
| 0 | 3.1               | Humid    | lity and Evaporation                               |     |
|   |                   | 3.1.1    | Background   |     |
|   | 3.2               | Evapor   | ration Rate from Pure Water                        |     |
|   | 3.3               | Evapor   | ration Rate from Latex Dispersions                 |     |
|   | 3.4               | Vertica  | al Drving Profiles                                 |     |
|   |                   | 3.4.1    | Scaling Argument                                   | 101 |
|   |                   | 3.4.2    | Governing Equations                                | 102 |
|   |                   | 3.4.3    | Experimental Studies                               | 104 |
|   |                   | 3.4.4    | Consequence of Inhomogeneous Vertical Drying:      |     |
|   |                   |          | Skin Formation                                     | 107 |
|   | 3.5               | Horizo   | ontal Packing and Drying Fronts                    | 107 |
|   |                   | 3.5.1    | Model for Horizontal Drying Fronts                 |     |
|   |                   | 3.5.2    | Lapping Time and Open Time                         |     |
|   | 3.6               | Colloic  | dal Stability                                      | 114 |
|   | 3.7 Film Cracking |          | 116  |     |
|   |                   | 3.7.1    | Do the Cracks Follow the Drying Front or Propagate |     |
|   |                   |          | Quickly Over the Entire Film?                      | 116 |
|   |                   | 3.7.2    | What Sets the Crack Spacing?                       | 117 |
|   | Refer             | rences   |  | 117 |
| 4 | PAR               | TICLE    | DEFORMATION  | 121 |
| • | 4 1               | Introdu  | iction   | 121 |
|   | 4 2               | Driving  | y Forces for Particle Deformation                  | 122 |
|   | 1.2               | 421      | Wet Sintering                                      | 123 |
|   |                   | 4.2.2    | Dry Sintering                                      | 123 |
|   |                   | 4.2.3    | Capillary Deformation                              | 124 |
|   |                   | 4.2.4    | Capillary Rings                                    | 126 |
|   |                   | 4.2.5    | Sheetz Deformation                                 | 126 |
|   | 4.3               | Particle | e Deformations                                     |     |
|   |                   | 4.3.1    | Hertz Theory – Elastic Spheres with an             |     |
|   |                   |          | Applied Load                                       | 127 |
|   |                   | 4.3.2    | JKR Theory – Elastic Spheres with an               |     |
|   |                   |          | Applied Load and Surface Tension                   |     |
|   |                   | 4.3.3    | Frenkel Theory – Viscous Spheres with Surface      |     |
|   |                   |          | Tension  | 128 |
|   |                   | 4.3.4    | Viscoelastic Particles                             |     |

|   | 4.4   | The Pro  | oblem with Particle-Particle Approach            |     |
|---|-------|--|--|-----|
|   |       | 4.4.1  | Routh and Russel Film Deformation Model          |     |
|   | 4.5   | Deform   | nation Maps                                      |     |
|   |       | 4.5.1  | Wet Sintering                                    |     |
|   |       | 4.5.2  | Capillary Deformation                            | 133 |
|   |       | 4.5.3  | Dry Sintering                                    | 133 |
|   |       | 4.5.4  | Receding Water Front                             | 133 |
|   |       | 4.5.5  | Use of the Deformation Maps                      | 134 |
|   | 4.6   | Dimens   | sional Argument for Figure 4.6                   | 135 |
|   |       | 4.6.1  | Wet Sintering                                    | 135 |
|   |       | 4.6.2  | Capillary Deformation                            | 135 |
|   |       | 4.6.3  | Dry Sintering                                    | 136 |
|   |       | 4.6.4  | Sheetz Deformation                               | 136 |
|   | 4.7   | Effect of  | of Temperature                                   | 137 |
|   | 4.8   | Effect of  | of Particle Size                                 | 139 |
|   | 4.9   | Experir  | mental Evidence for Deformation Mechanisms       | 140 |
|   |       | 4.9.1  | Inferring Deformation Mechanisms from Water      |     |
|   |       |  | Distributions                                    | 140 |
|   |       | 4.9.2  | Determination of Deformation Mechanisms Using    |     |
|   |       |  | an MFFT Bar and Optical Techniques               | 143 |
|   |       | 4.9.3  | Microscopy of Particle Deformation               | 143 |
|   |       | 4.9.4  | Scattering Techniques                            | 146 |
|   |       | 4.9.5  | Detection of Skin Formation                      | 146 |
|   | Refer | ences  |  | 146 |
|   |       | _  |  |     |
| 5 | MOL   | ECULA  | R DIFFUSION ACROSS PARTICLE                      |     |
|   | BOU   | NDARIE   | £8   |     |
|   | 5.1   | Essenti  | al Polymer Physics                               |     |
|   |       | 5.1.1  | Interface Width at Polymer-Polymer Interfaces    |     |
|   |       | 5.1.2  | Polymer Reptation                                |     |
|   | 5.2   | Develo   | pment of Mechanical Strength and Toughness       | 158 |
|   |       | 5.2.1  | Dependence on the Density of Chains Crossing     |     |
|   |       |  | the Interface                                    |     |
|   |       | 5.2.2  | Dependence on Interdiffusion Distance, $\Lambda$ | 162 |
|   | 5.3   | Factors  | that Influence Diffusivity                       | 164 |
|   |       | 5.3.1  | Molecular Weight and Chain Branching             | 164 |
|   |       | 5.3.2  | Temperature Dependence                           | 165 |
|   |       | 5.3.3  | Influence of Hard Particles                      |     |
|   |       | 5.3.4  | Latex Particle Size                              | 172 |
|   |       | 5.3.5  | Particle Structure and Hydrophilic Membranes     | 172 |
|   | 5.4   | Faster I   | Diffusion with Coalescing Aids                   | 174 |
|   | 5.5   | Simultaneous Crosslinking and Diffusion: Competing |  |     |
|   | D. C  | Enects   |  | 1/5 |
|   | Reter | ences  |  | 1/9 |

| 6 | SUR  | FACTA       | NT DISTRIBUTION IN LATEX FILMS                           | 185 |
|---|--|-------------|--|-----|
|   | 6.1  | Introdu     | action   | 185 |
|   |  | 6.1.1       | Where Can Surfactant Go in a Dried Film?                 | 186 |
|   |  | 6.1.2       | Effect of Non-Uniform Surfactant Distributions           | 188 |
|   |  | 6.1.3       | Mechanisms of Surfactant Transport                       | 191 |
|   | 6.2  | Adsorp      | otion Isotherms  | 192 |
|   | 6.3  | Model       | ling of Surfactant Distribution during the Drying Stage  | 194 |
|   | 6.4  | Effect      | of Surfactant's Vertical Distribution on Film Topography | 199 |
|   | 6.5 Experimental Evidence for Surfactant Locations |             | mental Evidence for Surfactant Locations                 | 201 |
|   |  | 6.5.1       | Interfaces with Air and Substrates                       | 201 |
|   |  | 6.5.2       | Surfactant in the Bulk of the Film                       | 202 |
|   |  | 6.5.3       | Depth Profiling and Mapping                              | 202 |
|   | 6.6  | Reactiv     | ve Surfactants   | 204 |
|   |  | 6.6.1       | Reactive Surfactant Chemistry                            | 205 |
|   |  | 6.6.2       | Effect of Surfmers on Film Properties                    | 205 |
|   | 6.7  | Summa       | ary  | 207 |
|   | Refe   | rences      | -  | 207 |
|   |  |             |  |     |
| 7 | NAN  | <b>OCOM</b> | POSITE LATEX FILMS AND CONTROL OF                        |     |
|   | THE  | IR PRO      | PERTIES  | 213 |
|   | 7.1  | Introdu     | action   | 213 |
|   |  | 7.1.1       | Properties of Nanocomposites                             | 214 |
|   |  | 7.1.2       | Applications of Colloidal Nanocomposites                 | 216 |
|   | 7.2  | Types       | of Hybrid Particles                                      | 217 |
|   |  | 7.2.1       | Polymer-Polymer Hybrid Particles                         | 217 |
|   |  | 7.2.2       | Inorganic and Polymer Nanocomposite Particles            | 219 |
|   |  | 7.2.3       | 'Self-Assembly' of Nanocomposite Particles by            |     |
|   |  |             | Precipitation or Flocculation of Pre-Formed              |     |
|   |  |             | Nanoparticles  | 223 |
|   | 7.3  | Colloid     | al Particle Deposition and Assembly Methods              | 225 |
|   |  | 7.3.1       | Deposition Methods                                       | 227 |
|   |  | 7.3.2       | Vertical Deposition                                      | 229 |
|   |  | 7.3.3       | Surface Pattern-Assisted Deposition                      | 230 |
|   |  | 7.3.4       | Long-Range Order from Self-Assembled Core-               |     |
|   |  |             | Shell Particles  | 232 |
|   | 7.4  | Colloid     | al Nanocomposites from Particle Blends                   | 233 |
|   |  | 7.4.1       | Advantages of Particle Blends                            | 233 |
|   |  | 7.4.2       | Dispersion of Nanoparticles                              | 233 |
|   |  | 7.4.3       | Long-Range Order in Particle Blends                      | 235 |
|   | 7.5  | Three I     | Lessons about the Properties of Waterborne               |     |
|   |  | Nanoco      | omposite Films   | 238 |
|   |  | 7.5.1       | Lesson One   | 238 |
|   |  | 7.5.2       | Lesson Two   | 244 |
|   |  | 7.5.3       | Lesson Three   | 245 |
|   |  |             |  | -   |

| 8 | FUTURE DIRECTIONS AND CHALLENGES |  |  |
|---|----------------------------------|--|--|
|   | 8.1                              | Film Formation from Anisotropic Particles          |  |
|   | 8.2                              | Assembly of Particles over Large Length Scales     |  |
|   | 8.3                              | Technique Development                              |  |
|   | 8.4                              | Nanocomposite Structure and Property Correlations  |  |
|   | 8.5                              | Interdiffusion of Polymers in Multiphase Particles |  |
|   | 8.6                              | Templating Film Topography                         |  |
|   | 8.7                              | Resolving the Film Formation Dilemma               |  |
|   | Refe                             | rences   |  |
|   |                                  |  |  |

## APPENDICES

.

| A | Derivation of Creeping Flow and the Result for Low |  |     |  |
|---|--|--|-----|--|
|   | Reyi   | nolds Number Flow Around a Sphere            |     |  |
|   | A.1  | Derivation of Creeping Flow                  |     |  |
|   | A.2  | Scaling of the Navier-Stokes Equation        |     |  |
|   | A.3  | Stokes Flow                                  |     |  |
|   | A.4  | Sedimentation                                | 277 |  |
| B | GAF  | RField Profiling Techniques and Experimental |     |  |
|   | Para   | ameters                                      |     |  |
|   | Refe   | rences                                       |     |  |
| С | Terr   | ninology of Humidity and an Expression for   |     |  |
|   | Evaporation Rate                                   |  |     |  |
|   | C.1  | Humidity                                     |     |  |
|   | C.2  | Relative Humidity                            |     |  |
|   | C.3  | Dry Bulb Temperature                         |     |  |
|   | C.4  | Wet Bulb Temperature                         |     |  |
|   | C.5  | Specific Volume                              |     |  |
|   | C.6  | Enthalpy of Air                              |     |  |
|   | C.7  | Psychrometric Chart                          |     |  |
|   | C.8  | Dew Point                                    |     |  |
|   | C.9  | Relating Humidity to Partial Pressure        |     |  |
|   | Example 1  |  |     |  |
|   | Example 2  |  |     |  |
|   | Exar   | nple 3                                       |     |  |
|   | Exar   | nple 4                                       |     |  |
|   | Exar   | nple 5                                       |     |  |
|   | C.10   | Evaporation Rate                             |     |  |
|   | Refe   | rences                                       |     |  |

| Frac   |  |  |
|--------|--|--|
| D.1    | Fracture Toughness, K <sub>IC</sub>                |  |
| D.2    | Plastic Zone Size at the Crack Tip, r <sub>v</sub> |  |
| D.3    | Critical Energy Release Rate, G                    |  |
| D.4    | Fracture Strength                                  |  |
| D.5    | Fracture Energy                                    |  |
| Refe   | rences   |  |
| 100101 |  |  |

| INDEX | )1 |
|-------|----|
|-------|----|