Cryo-SEM Study of Nanostructure Development of Latex Dispersions and Block Copolymer Solutions

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Dedication

To my parents

Mrs. Yiling Feng and Mr. Changcheng Gong
Abstract

High resolution cryogenic scanning electron microscopy (cryo-SEM) was used to study the physics of latex film formation. Fast freezing, controlled freeze-drying and annealing under vacuum, followed by room-temperature and cryogenic SEM demonstrated that van der Waals force alone can compact a latex coating under conditions devoid of surface tension and capillary forces. Rewetting tests of the annealed coatings shed light on distinguishing elastic and viscoelastic deformation.

Key factors affecting the freeze-thaw (F/T) stability of polymer latexes were studied. The nanostructural changes during freeze-thaw cycles were visualized by cryo-SEM. Reducing T_g and modulus of the polymer, latex particle size, amount of protective functional groups, molecular weight and addition of coalescent all lead to reduced F/T stability. Both the freezing and thawing rates have strong impact on F/T stability.

Both functional acid monomer type and degree of neutralization in pre-emulsion greatly influence the ability of the latex and titanium dioxide (TiO_2) particles to interact with each other which prevents TiO_2 particle aggregation. Latexes incorporated with vinylphosphonic or itaconic acid show better TiO_2 efficiency than latexes with acrylic acid or methacrylic acid. For acid monomers with high water solubility, higher degree of neutralization in pre-emulsion yields in general lower TiO_2 efficiency.

Cryo-SEM was employed to further understand the nature of nanostructure deduced by small angle x-ray scattering (SAXS) for poly(butadiene-b-ethylene oxide) diblock copolymers solutions, as a function of copolymer concentration and block copolymer composition. The SAXS measurements and cryo-SEM images reveal a new type of network morphology, comprised of a random arrangement of interconnected cylinders, in addition to the other classical structures.
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Chapter 1: Synopsis

1.1 Introduction to Latex Film Formation

Latex is a stable colloidal dispersion, or suspension, of polymer particles dispersed and suspended in liquid, usually water. The polymer of the particles comprises one or more monomers. The particles range in size from 30 nm to a few microns in diameter. The shape of the latex particles is usually spherical. Most latex materials in use nowadays are synthesized by free radical polymerization, which consists of three major steps: initiation, propagation and termination (Keddie 1997).

Applications of latex polymers continue to mount. Billions of pounds of latexes are synthesized every year in the world and most are dispersed in water. Water-borne latexes are environmentally friendly and widely used in paints, adhesives, binders, carpet backing, paper coatings, textile treatments and so on. The range of applications of water-borne latexes will continue to increase into more and more fields (Steward, Hearn and Wilkinson 2000), such as replacing the solvent-based systems due to the requirement of reducing volatile organic compound (VOC) emissions.

When a latex dispersion is coated on a solid substrate and allowed to dry, a continuous homogeneous film forms under appropriate conditions by the time all the water has evaporated from it. In order to form a continuous film, the mutual repulsion of latex particles in the dispersion must be overcome. This must be achieved in the course of the evaporation of the continuous phase (water). The subject of latex film formation has been studied for more than 50 years. Chapter 2 briefly reviews the current understanding on physics of latex film formation.
Figure 1.1 Three major physical stages in latex film formation: consolidation, compaction and coalescence.

As shown in Figure 1.1, the whole process can be divided into three stages (Ming, Takamura, Davis and Scriven 1995; Ming 1996; Keddie 1997). In Stage One, which is called the consolidation stage, water begins to evaporate from the surface of a layer of dispersion coated on a substrate. Evaporation concentrates the latex solids and brings the latex particles together, *i.e.* it consolidates them. If they are not too sticky to roll or slide into multiple-contact niches, they consolidate into a close-packed structure eventually. In Stage Two, which is called the compaction stage, direct surface tension force, capillary pressure force, and van der Waals force flatten latex particles against one another, thereby shrinking interstices between them (Lin and Meier 1995; Pekurovsky and Scriven 2001). At first the interstices form a connected network, but later the connections break to leave isolated voids, and finally the voids disappear. Whenever the interstices or voids are small enough not to scatter much visible light, coating, or the film becomes transparent. In Stage Three, which is called the coalescence stage, the polymer of each latex particle interdiffuses into neighboring
particles to form a depth equal to an entanglement length or more, thereby a continuous mechanically coherent film.

In order to consolidate, latex particles must overcome forces that stabilize the colloidal dispersion against flocculation and coagulation (Steward, Hearn and Wilkinson 2000). The stabilizing forces in a latex suspension are repulsive electrostatic force and repulsive steric force. The destabilizing forces are van der Waals force, which is generally attractive, and sometimes attractive steric forces. Provided the repulsive forces prevail, they make a suspension stable against flocculation, separate latex particles from one another, and distribute latex particles homogeneously.

As water evaporates from the air-suspension interface, the capillary pressure from surface tension in curved menisci between latex particles in the top surface sucks water from below up to the interface to balance the evaporation at the surface. If viscous resistance to flow is too great, the evaporation cannot be balanced and so the menisci shift to new positions successively deeper in the interstices between particles as long as they remain connected. At the same time the capillary pressure and the direct force of surface tension at contact lines on the top particles, along with attractive van der Waals force between particles tend to overcome the repulsive stabilizing forces and flatten latex particles against each other. The role of capillary forces in flattening latex particles is still disputed in some places (Steward, Hearn and Wilkinson 2000).

1.2 On van der Waals Force of Latex Film Formation

The driving forces that flatten latex particles have been discussed for decades because of their importance to understanding the physics of latex film formation. Several hypotheses have been put forward in which the most-often considered driving forces
of deformation are air-water surface tension, water-polymer and polymer-air interfacial excess free energies, ill-defined osmotic force, vaguely identified surface adhesive forces, and van der Waals attractive force between particle surfaces. How important the van der Waals force is and the way in which it flattens particles seem poorly assessed directly in previous work, excepting in the theoretical modeling by Jagota et al (Jagota et al. 1998). Yet it is unrealistic to omit an always-acting short-range force that is attractive except when the intervening liquid is special (Israelachvili 1991). Consequently, chapter 3 is addressed to the role of van der Waals force in film formation.

The experimental procedure designed to uncover the role of van der Waals force in latex film formation is shown in Figure 1.2. It can be divided into three major steps. In the first step, plunge freezing by hand was used to freeze quickly all the water in the a poly(styrene-butyl acrylate) model latex suspension into crystallites so small as not to affect the particles or their locations, and thereby cryo-immobilize the starting suspension. The suspension had been deposited by a micropipette on precut silicon wafers and drawn down with a wire-wound rod without any pre-drying, i.e. no more than 5 seconds of exposure to room air. In Step Two, freeze-drying under vacuum was used to transform ice directly to water vapor. Thus was avoided the presence of liquid water and attendant of forces of surface tension, both direct at contact lines and indirect through the capillary pressure that results from surface tension in curved menisci, at any time on the way to a bone-dry assemblage of particles held together by adhesion forces at the interparticle contacts. In Step Three, this freeze-dried coating was annealed at different temperatures for a chosen time. Incontestably, attractive van der Waals force acted around the contact’s perimeter, all during the time of annealing, beginning with the interparticle contacts that formed each time that intervening ice was sublimed away and a newly freed particle jumped or fell into adhesive contact with neighbors (Mangipudi 1995; Falsafi 1998). At the end of annealing, a sample was sputter-coated under vacuum with platinum and transferred into the Hitachi
S4700 below-the-lens field emission scanning electron microscope (Hitachi, Pleasanton, CA) to image its microstructure.

Figure 1.2 Experimental procedure designed to reveal the role of van der Waals force in latex film formation.

Cryogenic scanning electron microscopy (cryo-SEM) and room temperature scanning electron microscopy (SEM) images documented, for the first time, van der Waals force alone compacting a completely dry latex coating, beginning with adhesion of neighboring particles as the ice between them sublimes away and their stabilization collapses, and continuing through annealing.
Figure 1.3 SEM images of coatings annealed at different annealing temperatures for three hours show that degree of flattening increase as annealing temperature increases.
Figure 1.3 shows the micrographs of coatings annealed for three hours at 20, 30, 40 and 50°C. Both top and fracture surface micrographs show the degree of particle flattening increase as the annealing temperature increases, especially when the nominal glass transition temperature of the latex is approached.

The effect of annealing time at one temperature, 40°C, was also assessed. Four annealing times were chosen: three, six, twelve, and twenty-four hours. The annealing temperature of 40°C was chosen because it is close enough to the $T_g$, that the latex particles compact completely and begin to coalesce within 24 hours. Figure 1.4 shows the images of the samples annealed at 40°C for three, six, twelve, and twenty-four hours.

Figure 1.4 SEM images of coatings annealed at 40°C for three, six, twelve, and twenty-four hours show that degree of flattening also increase with annealing time.
The dependence of degree of compaction of the consolidated latex particles on annealing temperature and time is indisputable evidence of a viscous-like resistance of the particles to deformation by the loading they suffered. That loading must have been imposed by attractive van der Waals force acting across the annular wedge-shaped clearance around each perimeter of an interparticle contact. Whether the particle flattening in the compacted coatings was elastic or elastoviscous and therefore recoverable, or viscoelastic or elastoviscoplastic and therefore at least partly unrecoverable, was examined by means of rewetting tests of coatings annealed for the same time at various temperatures, as discussed in section 3.4.5 and 3.4.6.

1.3 New Insights into the Freeze-Thaw Stability of Polymer Latexes

Freeze-thaw (F/T) stability of polymer latexes has considerable industrial importance because of the energy and hardware costs that will incur if heated transportations and storages are necessary during winter in cold areas. To be freeze-thaw stable, the polymer suspension must maintain its original properties and absence of coagula after repeated freeze-thaw cycles, which has long been achieved by adding antifreezes, such as glycols, in paint industry (Bosen et al. 1985). However, the new driving force for the coatings industry to develop low-VOC or zero-VOC (Volatile Organic Compounds) waterborne formulations limits the amount of glycols that can be added and it is most probably insufficient to provide freeze-thaw stability.

Chapter 4 clarifies the effects of key factors affecting the freeze-thaw stability of polymer latexes, including glass transition temperature, moduli, molecular weight, particle size, amount of stabilizing functional groups, amount of coalescent, freezing and thawing rates. In contrast to most of the previously published work, model polymer latexes used in this study are well-controlled in particle sizes and compositions.
As illustrated in Figure 1.5 and Figure 1.6, our results show a clear correlation between freeze-thaw stability and glass transition temperature ($T_g$) and modulus of the polymer around 0°C, which is in agreement with some early findings (King and Naidus 1969; Naidus and Hanzes 1969) but not others (Digioia and Nelson 1953; Barb and Mikuchi 1956). The influence of polymer modulus on around 0°C F/T stability can be interpreted using criteria (Mason 1973) established for particle deformation and coalescence in latex film formation.

**Latex Viscosity (cps)**

![Latex Viscosity Graph](image)

Figure 1.5 Influence of polymer Tg on F/T stability of latexes. The polymers are based on MMA/EHA (methyl methacrylate/ 2-ethylhexyl acrylate). The particle sizes of the latexes are all around 190 nm in diameter.

However, high $T_g$ or modulus alone does not guarantee freeze-thaw stability. To achieve freeze-thaw stability, sufficient protective functional groups are also necessary. Reducing particle size and polymer molecular weight and addition of coalescent all lead to reduced freeze-thaw stability.
Figure 1.6 Storage moduli of polymer latex films as a function of temperature: latexes A and B have perfect F/T stability; latexes C and D experience significant viscosity increase over the F/T cycles; latex E completely coagulates during the first F/T cycle. The polymers are based on MMA/BA (methyl methacrylate/ n-butyl acrylate).

In addition to following the viscosity changes during repeated freeze-thaw cycles and analyzing the dynamic mechanical properties of the dried latex films, cryogenic scanning electron microscopy (cryo-SEM) techniques coupled with a high-pressure freezing apparatus is applied, which makes it possible to visualize nano-structural changes and to study the effects of the freezing and thawing processes separately. It was found that both the freezing and thawing rates have strong impact on F/T stability of polymer latexes, which does not support conclusions from early work with regard to the effect of the thawing process (Nakamura and Okada 1976).

The cause of viscosity rise during the freezing and thawing processes in freeze-thaw unstable latexes was also analyzed. The presence of loosely associated particle
aggregates was revealed and such a relatively diffuse aggregate structure is believed to be the cause for the rise in latex viscosity during the freeze-thaw processes in freeze-thaw unstable latexes, as shown in Figure 1.7.

Figure 1.7 Cryo-SEM images of a latex sample before F/T test, on the left, and after 5 F/T cycles, on the right. The viscosity increased 30 times after 5 F/T cycles.

1.4 The Understanding of TiO$_2$ Efficiency in Waterborne Paints through Latex Design

Chapter 5 explores the influence of functional acid monomers incorporated into polymer latex dispersions for their ability to effectively disperse titanium dioxide (TiO$_2$) pigment particles in flat paint applications.

TiO$_2$ is a primary pigment used in paints industry due to its high refractive index ($n_D \approx 2.6$), scattering efficiency, ideal particle size (about 250 nm in diameter) and particle spacing behavior. However, it is difficult to randomly disperse TiO$_2$ particles due to van der Waals colloidal attractive forces. Consequently, TiO$_2$ particles form clusters
which will severely reduce the scattering efficiency of the paint film and increase the roughness or the number of defects of the paint film surface. TiO$_2$ particles that are well dispersed and separated from each other provide respective coatings that have been useful in preparing coatings with improved hiding power and tint strength. In addition, the dispersibility of TiO$_2$ particles throughout the paint ensures that the paint itself becomes a fully integrated composite material which has improved scrub and abrasion resistance. In addition to its contribution to the paint film properties, TiO$_2$ also contributes greatly toward the total cost of the paint. Not surprisingly, it has been a continuing goal of the paint industry to achieve a higher level of TiO$_2$ efficiency, resulting in less TiO$_2$ consumption. With a TiO$_2$ efficient latex binder, not only the amount of the TiO$_2$ pigment can be reduced, but also the amount of the binder which is used in the paint formulation.

The functional acid monomer type (i.e. acrylic acid, methacrylic acid, itaconic acid and vinylphosphonic acid), the partitioning of acid monomer in the polymer or aqueous phase during the emulsion polymerization and the role of the latex polymer particle size were investigated. The model latex dispersions were then formulated into their corresponding flat paints. By using cryogenic scanning electron microscopy, TiO$_2$ efficiency of the paints in the wet state is qualitatively evaluated. Furthermore, these results are correlated with tint strength and scrub resistance of the same paints in the dry state.

Both functional acid monomer type and degree of acid neutralization in pre-emulsion before the emulsion polymerization greatly influence the ability of the latex and TiO$_2$ particles to interact with each other which consequently prevents TiO$_2$ particle aggregation. The chemical nature of the phosphonic acid moiety in vinylphosphonic acid (VPA) and the structural orientation of the two carboxyl groups in itaconic acid (IA), make both monomers suitable for scattering TiO$_2$ particles very effectively. However, functional acid monomers with one carboxylic acid group, such as acrylic
acid (AA) or methacrylic acid (MAA), appear not to disperse the TiO\textsubscript{2} pigments effectively, as seen in Figure 1.8.

![Figure 1.8 Cryo-SEM images show TiO\textsubscript{2} distribution in wet paint samples. TiO\textsubscript{2} particles remain as individual when vinylphosphonic acid or itaconic acid are incorporated, while form clusters when methacrylic acid or acrylic acid is used.](image)

In the example using itaconic acid, the increase of its degree of neutralization in the pre-emulsion before emulsion polymerization takes place greatly influences the TiO\textsubscript{2} efficiency of the latex. The trend observed in Figure 1.9 is that higher degree of neutralization leads to better TiO\textsubscript{2} efficiency. The reverse is seen when vinylphosphonic acid is used as the functional acid monomer: the lower the degree of acid neutralization yields latexes with improved TiO\textsubscript{2} efficiency.

![Figure 1.9 Higher degree of neutralization in the pre-emulsion leads to better TiO\textsubscript{2} efficiency when itaconic acid monomer is incorporated.](image)
The effect of particle size was examined and the general trend shows that as particle size decreases the TiO₂ efficiency of the latex increases. This is also the general trend observed in the decrease of the scrub resistance property of the paint film as latex particle size increases.

Finally, the sole interaction of these tailored latexes with TiO₂ pigment particles is investigated through cryo-SEM to gain a comparative insight into how the way these particles orient themselves with one another depends on the functional acid monomer employed. As Figure 1.10 makes plain, latexes particles incorporated with VPA and IA groups interact with TiO₂ particles very well. They surround and attach to TiO₂ particles and form a steric barrier to prevent TiO₂ particles forming clusters.

![Figure 1.10](image.png)

Figure 1.10 High resolution cryo-SEM images show the sole interaction of latex particles with TiO₂ pigment particles.

### 1.5 Disordered Network Nanostructure of PEO-PB Diblock Copolymer Solutions

In Chapter 6, cryogenic scanning electron microscopy was employed to further understand the nature of nanostructure deduced by small angle x-ray scattering for poly(butadiene-\textit{b}-ethylene oxide) (PEO-PB) diblock copolymers solutions, as a function of copolymer concentration (wt % copolymer in water) and block copolymer composition (weight fraction of PEO block).
Five different diblock copolymers were synthesized with a core molecular weight of 9200 g/mol ($N_{PB} = 170$) and PEO weight fractions ranging from 0.3 to 0.49. They were then hydrated to 25 different diblock copolymer solutions for cryo-SEM study. Cryo-SEM images visualized the random network morphology (denoted $N$), formed from interconnected struts with predominately cylindrical symmetry, situated at concentrations and compositions between those associated with hexagonal and lamellar phases, disappears as the molecular weight is reduced.

Further study by cryo-SEM shows results in accordance to SAXS measurements in most cases. The cryo-SEM results of samples chosen near phase boundaries between bilayer ($B$), network ($N$) and lamellar ($L$) phases generally show co-existence of two or three phases. Cryo-SEM images of samples chosen from the two phase ($N + L$) region show only lamellar structure, which conflicts the SAXS measurement. This could indicate that one or both technique may contain artifacts during the sample preparation, or the certain structure is beyond the imaging capability of the scanning electron microscope.
Chapter 2

Introduction to Latex Film Formation

2.1 Introduction

Latexes are stable colloidal dispersions of solid fine polymer particles dispersed and suspended in an aqueous solution. Latex is a misnomer because it is synthetic polymer that may look just like natural latex but has a completely different chemical makeup and different properties, while the natural latex product comes originally from the Brazilian rubber tree. Yet it has become an accepted name. The latex particles are composed of polymers of one or more kinds of monomers, including styrene, butadiene, vinyl acetate, acrylic esters, vinyl chloride and copolymers of any of these (Snuparek 1996). The particle size of latex ranges from 30 nm to a few microns in diameter. They are referred as “microspheres”, much larger than the water molecules but still small enough to undergo Brownian motion. Usually the polymer particles are in spherical shape. Although natural latex materials can be found in natural rubber and vegetable gums, most latex materials nowadays are artificially synthesized by free radical polymerization, which consists of three major steps: initiation, propagation and termination (Keddie 1997). When a latex, \textit{i.e.} a colloidal polymer dispersion, is applied to a solid substrate and allowed to dry in the air, the particles may coalesce with each other and form a continuous film, which is called a latex coating. Whether the particles do this depends on the drying temperature and other conditions, such as the glass transition temperature of the polymer latex.
Latexes have been widely used as industrial applications in the five decades since they were introduced. Billions of pounds of synthetic latexes are produced every year because latexes are environmentally friendly. These latexes have two major kinds of applications: bulk polymer production and direct use to form films (Dobler and Holl 1996). In the first application, polymers, such as styrene-butadiene rubber are synthesized by emulsion polymerization and elimination of water. In the latter case, dried latex films after evaporation of water are widely used in the fields of paints, papers, coatings, adhesives, textiles, carpet backing, binders, pharmaceuticals, membranes for separation, embedding media for whole-cell bioreactors and other products. It appears that the range of applications of latex polymers will continue to increase into more and more fields (Steward, Hearn and Wilkinson 2000). For example, the water-based systems are currently replacing the solvent-based systems not only because the requirement of reducing volatile organic compound (VOC) emissions but also because water is much cheaper than organic solvent. And crystals of ordered packed polymer latex formed into porous coatings are being synthesized to work as starting materials for photonic crystals (Zeng et al. 2002), which can block a certain energy of photons (Zakhidov et al. 1998).

2.2 Latex Film Formation by Stages

When a latex dispersion is cast, or coated, on a solid substrate and subsequently allowed to dry, a continuous homogeneous film forms under appropriate conditions by the time all the water has evaporated from it. This dynamic process is called “latex film formation” (Keddie 1997). In order to form a continuous film, the mutual repulsion of latex particles in the dispersion must be overcome. This must be achieved in the course of the evaporation of the continuous phase (water) (Keddie 1997; Steward, Hearn and
The subject of latex film formation has been studied for more than 50 years (Winnik 1997) and several basic models of the mechanisms of latex film formation have emerged.

Current understanding of latex film formation commonly consists of three major physical processes, or stages: (1) evaporation of water and particle ordering — the consolidation stage; (2) particle deformation and elimination of pore spaces — the compaction stage; (3) interdiffusion of polymers across flattened surface between particles — the coalescence stage (Ming, Takamura, Davis and Scriven 1995; Ming 1996; Keddie 1997).

### 2.2.1 Consolidation Stage

Evaporation of solvent, usually water, begins spontaneously from the surface after latex dispersions are coated onto a substrate in the air. At first, the evaporation concentrates the latex particles near the air-dispersion interface and latex particles are destabilized with respect to flocculation or coagulation, which eventually allows consolidation (Ma 2002). As drying proceeds, more and more latex particles become consolidated at the air-dispersion interface. Curved menisci develop between these latex particles and they lower the hydrodynamic pressure underneath. The rate of evaporation of water remains almost constant as these menisci work as small pumps to suck the water from underneath to the air-dispersion interface. Atmospheric pressure presses down and capillary pressure reduces liquid pressure underneath. Capillary pressure, together with the local surface tension in the top layer, exerts a downward force on the packing of latex particles. The hydrodynamic pressure is lowest right under the air-dispersion interface and rises toward atmospheric deeper in the coating. The increasing gradient drives liquid upward and
presses latex particles against those above them to move downward. Eventually, a consolidation front appears from the air-dispersion interface and moves downward. After the consolidation front reaches the substrate, a translucent coating results with residual water left in the pore spaces between consolidated latex particles.

The properties of latex particles and the rate of evaporation of water are important to the consolidation stage. Latex particles with high modulus and constant evaporation rate can make the compaction stage and air invasion begin only after the consolidation front reaches the substrate (Arlinghaus 2004). When latex particles have low modulus and/or the evaporation rate is relatively high, latex particles can be deformed downward from top before the consolidation front reaches the substrate, which means the compaction stage may overlap with the consolidation stage on the top of the latex coating. With even lower modulus, latex particles may coalesce after deformation or not, which means the coalescence stage may overlap with consolidation stage, with or without compaction stage. These phenomena are called transport skinning and mechanical skinning respectively (Ge 2005). Skinning is important because it can influence the property of latex film a lot by affecting the drying rate.

Some ordering in the packing of consolidated latex particles can often be seen if the particles are all within a few percent of one another in diameter. The degree of ordering is determined by the rate of latex particles arriving at the consolidation front, the strength of the attractive and repulsive forces and the Brownian motion (Ma 2002). Slower rate of particles’ arrival, stronger repulsion compared to attraction and more diffusion by Brownian motion compared to the liquid drag, promote particles ordering (Sutanto, Ma, Davis and Scriven 2001). The symmetry of packing may be different: perfect close
packing, defective close packing and random close packing. “Hexagonal packing” and “square packing” are the most commonly seen ordered packing.

2.2.2 Compaction Stage

As drying proceeds, more water is lost and the curvature of the menisci increases. Air invades into the pore spaces created by consolidation after a Haines Jump is completed. Some residual water between latex particles in the pore spaces forms pendular rings. The consolidated latex particles deform more rapidly by flattening under the action of capillary forces in the pendular rings together with van der Waals attraction force, although deformation begins even before air invasion by capillary pressure in the top menisci: the compaction stage begins. Because the curvature of the pendular rings varies from top down, compaction also varies, which indicates the existence of a compaction gradient. If the polymer of each particle does not interdiffuse and interpenetrate into adjacent particles, or if the entanglement length of the polymer chains is less than the radius of gyration of the polymer, the flattened particles can be regarded as elastically deformed and the compacted coating should be able to redisperse when rehydrated. As the pore spaces shrink between particles, a transparent or clear film results when the size of the pore spaces are appreciably smaller than the wavelength of visible light (400 nm to 700 nm), so that little light is scattered (Keddie, Meredith, Jones and Donald 1995). The coating can then be called fully compacted.

As reviewed in section 2.2.1, the compaction stage can overlap with the consolidation stage and/or the coalescence stage, depending on the modulus of the latex particles and the rate of evaporation of water. The mechanism of the compaction stage can vary with
the properties of the latex particles.

Several sintering hypotheses arose since Dillon, Matheson and Bradford proposed the dry sintering hypothesis in 1951 (Dillon, Matheson and Bradford 1951). In 1953, Henson, Taber and Bradford proposed the wet sintering hypothesis and soon supplanted dry sintering model (Henson, Taber and Bradford 1953), and subsequently Vanderhoff, Tarkowski, Jenkins and Bradford (1966). Five years later, in 1956, Brown brought up his hypothesis of capillary force compaction of latex particles and identified the moist compaction stage in the pendular state (Brown 1956). Another important hypothesis is that which Sheetz proposed in 1965. In it he identified for the first time the wet compaction stage (Sheetz 1965). Some of these hypotheses are discussed in section 2.3.

2.2.3 Coalescence Stage

The coalescence stage of latex film formation corresponds to the disappearance of the interfaces between latex particles as their polymer molecules interdiffuse. Ordinarily, by the onset of coalescence, the stabilizer layer between compacted particles has ruptured, enabling the polymer chains to diffuse across the boundaries between particles (Lebow 1997). After enough interdiffusion, i.e. on the order of the chain entanglement length, the latex particles have not only lost their boundaries but also irreversibly fused together. Then the coalescence stage is complete.
2.3. Latex Particle Deformation and Driving Forces

The driving forces responsible for latex particle deformation have been discussed for decades because it is the most important part of the mechanism of latex film formation. Several hypotheses about driving forces have been proposed. The most-often considered driving forces of deformation are air-water surface tension, water-polymer, and polymer-air interfacial excess free energy or so called “interfacial tensions”, osmotic force and surface adhesive forces, and attractive van der Waals force between particle surfaces. The importance of van der Waals force and the way it deforms particles are not well described, notwithstanding the papers discussed in this chapter. To investigate the mechanism of latex particle deformation and roles of the driving forces in latex film formation, several important relative hypotheses are discussed in this section for better understanding.

2.3.1 Dry Sintering Hypothesis

The dry sintering hypothesis was proposed by Dillon, Matheson and Bradford in 1951 (Dillon et al. 1951). They proposed that the water evaporated completely at first, after latex suspension was coated on a substrate. And then, the totally dried latex particles sintered or coalesced, and formed a continuous film.

They imagined that the deformation of particles was driven by a so-called particle-air interfacial tension, as though the solid particles were liquid. This interfacial tension was estimated at 30 mN/m. The particles would be under a pressure $P$ (relative to ambient) given by Young-Laplace equation:
The $\gamma_{PA}$ is the particle-air interfacial tension and $R$ is the radius of the particles. On the basis of a rough model of the accompanying viscous flow of the hypothesized liquid particle, the extent of coalescence would be given by Frenkel’s (1943) formula:

$$P = \frac{2\gamma_{PA}}{R}$$

Here, $\theta$ is the half angle of the contact zone, $t$ is elapsed time and $\eta$ is the viscosity of the latex.

Dillon et al. (1951) did not recognize the role of water in the latex film formation and took latex particles as viscous liquid droplets, which can sinter together. They also overlooked the interparticle van der Waals attractive force which draws the particle surfaces together around the particle-particle contacts. The relationship between the crack-closing mechanism and hypotheses of sintering was analyzed by Jagoda, Argento and Mazur (1998). They examined the viscoelastic model of growth of adhesive contacts for a sphere on a rigid plane. Using the JKR (Johnson-Kendall-Roberts) model restricted their attention to sintering by viscoelastic deformation and they divided the whole process into two parts: initial elastic adhesion and viscous sintering. Later Lin, Hui and Jagota (2001) extended this topic into what they called viscoelastic adhesive contact between two
spherical, linearly viscoelastic “Maxwell” particles. But they still dealt only with the viscoelastic model and didn’t pay any attention to the other possibilities. This topic was further developed by Thurn (2002) and Thurn and Cook (2003).

2.3.2 Wet Sintering Hypothesis

In 1953, Henson, Taber and Bradford of the Dow Chemical Company proposed the wet sintering hypothesis, which soon supplanted dry sintering. Henson et al., and subsequently Vanderhoff, Tarkowski, Jenkins and Bradford (1966), proposed that as water evaporated, latex particles assemble into a packing by overcoming the repulsive forces between them and the interparticle pore spaces were filled with water. Driven by the polymer-water interfacial tension, latex particles sinter by viscous flow. After the particles are deformed from spheres into polyhedral, the stabilizers give away to let polymer cores make contact. Henson, Taber and Bradford are the first to propose that polymer-water interfacial tension rounds the water-filled pore spaces between particles into spheres and correctly recognized that water played a role in the compaction of particles. But they also persisted that latex particles were like viscous drops, whose surfaces can sustain tension, just like Dillon et al.(1951). Vanderhoff et al. proposed that the water-air surface tension force compacted latex particles at first and the particle-water surface tension drove wet sintering and finish the film formation after the layer of stabilizer ruptured.

Dobler et al. (1992) plotted the limiting temperature and relative humidity conditions for coalescence of a series of latexes with different surface compositions and found that those conditions were just the same, regardless of polymeric compositions and the
absence or presence of added surfactant. This finding they took as indications that capillary forces alone cannot coalesce latex particles (Dobler et al. 1992 and 1996). But they didn’t pay attention to van der Waals attraction force either and they turned to support Sheetz’s (1965) hypothesis, which is described in Section 2.3.4.

2.3.3. Capillary Forces Hypothesis

The dry sintering and wet sintering hypotheses of latex fusion as being due to purely viscous flow is at variance with physics and proved inadequate to explain the mechanism of latex film formation. Brown (1956) developed his own hypothetical mechanism of film formation after stating several criticisms of the dry sintering mechanism: experimentally, it has been demonstrated that film formation occurs simultaneously with water evaporation, and is complete when evaporation is complete; it has also been observed that the rate of water evaporation influences the degree of coalescence a lot; if the film formation proceeds below a certain critical value of temperature, an incompletely fused film results; lightly crosslinked latex may form continuous film with low mechanical strength, and this means that the hypothesis of purely viscous flow is incorrect because mutual penetration, i.e. interdiffusion in the course of sintering by viscous flow should be hindered by crosslinking.

Brown’s hypothesis is known as the capillary forces hypothesis. He argued that capillary forces are the main driving forces of particle deformation. As water evaporates from bulk, the solids concentration increases and the particles pack in an ordered packing, which is known as consolidation stage nowadays. As the menisci form around the contacts of latex particles in what is now known as the moist stage, several forces act on particles to either
promote deformation or hinder it.

Brown imagined: (1) a force somehow created by the curvature of polymer surface, \( F_s \); (2) capillary force, \( i.e. \) the capillary pressure of water-air surface tension in curved water-air menisci, presumably times some projected area of those menisci, \( F_c \); (3) van der Waals force, \( F_v \); (4) gravity force, \( F_g \); (5) mechanical resistance force from particles, \( F_r \); (6) Coulomb repulsive force, \( F_e \), arising from charge on the particle surfaces. Brown neglected the force created by the curvature of polymer surface \( F_s \), van der Waals force \( F_v \) and gravity force \( F_g \) at first, supposing that they are usually smaller than \( F_c \). Then he posited a purely elastic resistance force, that is, he took the polymer particles to be solid, deformable only elastically and not at all viscously. And he neglected the Coulomb repulsive force \( F_e \) also. Resorting to (1) the Young-Laplace equation of capillary pressure (and continuing to overlook the force of surface tension at contact lines on particles) and (2) Hertz’s formula for flattening of elastic spheres in contact and loaded by a force, Brown concocted a criterion that film formation occurs when:

\[
G_t < \frac{35\gamma}{R}
\]

He took \( G_t \) to be the time-dependent elastic shear modulus of polymer, but overlooked any viscous contribution to a particle’s resistance to elastic deformation.

Brown’s hypothesis has massive limitations. Some scientists later improved it incrementally. Mason (1973) corrected Brown’s erroneous assumption of capillary pressure constant through drying; Eckersley and Rudin (1990), pointed out that Brown
and Mason considered only elastic deformation of particles, whereas deformation might be viscoelastic, like bulk polymer that lacks cross-linking. They also argued that capillary forces alone are not sufficient to deform polymer particles. What they proposed is that capillary forces account for some viscoelastic deformation of particles, and that this is accompanied by viscous flow that is driven by liquid-like “interfacial tension”, of solid particles. In contrast, Lin and Meier (1995) argued that capillary pressure is the dominant driving force in film formation, on the basis of scanning probe microscopy of the corrugation height on top surfaces of coatings as evidence of particle deformation, and comparisons of the time required by the initially corrugated surface to reach the same degree of smoothness under dry and wet conditions.

Against the hypothesis that capillary forces are the primary driving force of particle deformation, Sperry et al. (1994) measured the minimum film formation temperature (MFFT) of latexes drying under gas at different humidities. They found about the same MFFT for pre-dried and wet samples of hydrophobic latex, and argued that capillary forces therefore didn’t play a major role in the particle deformation. A big limitation of their work is they reported no effect to evaluate the forces they believed do cause compaction upon water loss in hydrophobic latex, namely a so-called “polymer-air interfacial tension” as well as van der Waals attraction force between particles. In order to determine the limits of the “dry-sintering regime”, Routh and Russel (1999) modeled latex particles as viscoelastic drops. Carra et al. (2002) claimed that the deformation of the top dried layer of latex particles were driven by the polymer-air interfacial tension as the water-air interface receded into the film during film formation.

All these views are based on Brown’s model, or support it. But it is unrealistic to omit the
role of van der Waals attraction force in latex film formation. Eckersley (1990) deduced that capillary forces may not be sufficient to account for particles’ deformation, but instead of paying attention to van der Waals attraction force, which can deform particles, she focused on viscous flow, which can only slow the rate of deformation of particles when they are being deformed by other forces. Moreover, leveling of the top surface of a coating, which SPM users took to be an indication of coalescence, appears to be poorly correlated with what is happening inside the coating. A better idea is to use cryogenic Scanning Electron Microscopy to look into the interior of the coating rather than to look only at the top surface, as Ge (2004) has done recently.

Considering a coating of monodispersed latex spheres that (1) have consolidated into an ordered packing, (2) behave purely elastically according to Hertz’s model as they flatten against one another, and (3) deform as flattening spheres of constant volume according to Frenkiel’s approximation, Pekurovsky and Scriven demonstrated that capillary forces alone can deform latex particles and compact latex coatings (Pekurovsky and Scriven 2001, Pekurovsky 2006).

2.3.4 Sheetz’s Hypothesis

Sheetz (1965) first hypothesized the wet compaction stage that precedes the pendular state that was identified by Brown (1956). His calculation supported his hypothesis that the evaporation of water supplies the energy which is converted to useful film-forming work by the change of the Gibbs free energy of evaporation. This free energy change is sufficient to coalesce latex particles.
According to Sheetz’s theory, the latex particles flocculate as water evaporates, which means the particles crowded into a secondary minimum in their interparticle potential and remain slightly separated. After all the particles are consolidated in a packing, the water-air interface recedes into the top layer of the latex particles and curves with lower pressure in the water. The water-air surface tension around the contact lines of menisci deforms the top layer of particles. Water flows towards the surface, where it evaporates, through the pore spaces. At the same time, water also diffuses through the latex particles and reaches the surface, which is much slower. But when the top layer of pore spaces close, the water can only escape by diffusion through the top layer of latex particles, which is a view of transport skinning (Ge 2004). Sheetz explained the compaction mechanism that the pressure beneath the skin was reduced by the continuing diffusion of water through the skin to the air, which seems confusing as the curved menisci no longer exist in the packing. He claimed that “the compressive pressure generated thereby completes the compaction process to give a polymer film with essentially no void spaces present”.

2.4 Characterization Techniques

The best way to study the mechanism of latex film formation is to visualize the microstructure evolution as the coating dries from a suspension to form a thin film. However, the drying process is difficult to visualize due to the limitation of the current characterization techniques. Conventional Optical Microscopy has limited resolution which is not sufficient to image the submicron latex particles. Furthermore, the Brownian motion moves the latex particles in the suspension and the volatility of the aqueous solvent, water in most cases, makes it difficult to image the drying process with the
conventional Electron Microscopy, such as a room temperature Scanning Electron Microscopy (SEM), which requires high vacuum.

Keddie (1997) and Steward et al. (2000) documented the current visualization techniques that have been previously used to study latex film formation in their review papers. The leading techniques employed in this thesis are Scanning Electron Microscopy and cryogenic Scanning Electron Microscopy (cryo-SEM). To properly use them, it is important to understand the fundamentals of these techniques, which are briefly reviewed in the following sections.

2.4.1 Scanning Electron Microscopy

Scanning Electron Microscopy is the most frequently used technique to visualize material structure from hundreds of microns down to several nanometers scale. It has been widely used to characterize the microstructure of dried latex films, dried film containing latex and inorganic components, such as titanium dioxide (TiO₂) particles, and coatings of latex particles with very high glass transition temperature. The room temperature SEM has certain limitation though. The high vacuum requirement makes it an improper method to study the dynamic process of latex film formation, as the volatile solvent in the latex suspension will not survive.

To image a specimen with an SEM, the electron gun in the microscopy emits electrons and focused them into a fine electron beam. The electron beam then scans the specimen surface and interacts with the atoms on the surface. Radiation products, such as secondary electrons, backscattered electrons, and X-rays, are generated by the interaction.
Collected by different electron detectors separately, secondary and backscattered electrons form secondary electron (SE) and backscattered electron (BSE) images. Secondary electron images provide topographic contrast on the specimen surface and backscattered electron images can differentiate compositional contrast in the specimen.

Due to the poor electrical conductivity in the non-conductive specimen, such as polymer latex coatings, electrons remain in the specimen if they cannot pass through after the electron beam strikes the specimen. These electrons accumulate at the specimen surface and become charge. When the electron beam scans the specimen surface, these accumulated electrons interact with the beam and may cause distortion in the images. This artifact is called charging. Charging artifacts are detrimental to the SEM imaging but can be prevented. It is very common that a thin layer of metal coating, such as platinum, is used to serve as a conductive layer that helps prevent electrons accumulating on the specimen surface. Another difficulty in visualizing soft polymer materials is the radiation damage of specimen by the high energy electron beam, and it can be reduced by using lower accelerating voltages, i.e. lower energy electron beams.

### 2.4.2 Cryogenic Scanning Electron Microscopy

As described in the previous section, the conventional SEM technique is not suitable to visualize the dynamic process of latex film formation because the volatile solvent, i.e. water, in the latex suspension cannot survive the high vacuum in the SEM chamber. In the early 1980s, cryogenic Scanning Electron Microscopy (cryo-SEM) was developed to study the latex film formation by the Coating Process Fundamental Program (CPFP) of the Department of Chemical Engineering and Materials Science at the University of
Cryo-SEM has many advantages over the conventional SEM and has become the most powerful tool to visualize the microstructure evolution of drying latex coatings. First of all, cryo-immobilization of suspension samples makes it possible for them to survive the high vacuum. It also freezes the Brownian motion of the polymer particles. Most important of all, it can capture the dynamic drying process of the latex film formation. Imaging samples that are cryo-immobilized after drying for successively longer time can reveal the changes of the microstructure of the drying coating. This technique provides the solution of imaging the whole timeline of the latex film formation, from the suspension state to a final dried thin film. Moreover, sample preparation is relatively easy and flexible. Samples can be cryo-immobilized by High Pressure Freezing (HPF) or plunge freezing by hand. Furthermore, Field Emission Scanning Electron Microscopy (FESEM) brings high resolution to image the detailed information at nanometer scales.

Two Field Emission Scanning Electron Microscopes were used in the research projects in the following chapters of this thesis, a Hitachi S900 in-the-lens FESEM (Nissei Sangyo America, Ltd., Rolling Meadows, IL), and a Hitachi S4700 below-the-lens FESEM (Nissei Sangyo America, Ltd., Rolling Meadows, IL). Both microscopes are equipped with cryo-stages for imaging frozen samples at cryogenic temperature. The freezing techniques, sample preparation procedures and cryogenic systems for these microscopes are quite different though. The detailed sample preparation procedures will be discussed in the experiment sections in each of the following chapters. A brief overview is reviewed in this section.
Thick, water-rich samples, such as latex suspensions or polymer solutions, are usually cryo-immobilized by High Pressure Freezing by a Bal-Tec HPM 010 high pressure freezing machine (Goldstein et al. 1992). As illustrated in Figure 2.1, a droplet of liquid sample is sandwiched between two brass or aluminum discs each with a cylinder-shaped indentation, usually 3 mm in diameter and 100 μm to 200 μm in depth. The space between both dishes should be filled with samples to avoid any air bubble being trapped when they are put together. The assemblage is then loaded into a Bal-Tec HPM 010 high pressure freezer and is frozen at 2100 bar within 7 to 8 millisecond. High pressure freezing is critically important for minimizing disturbance by large ice crystals to the original morphology of an aqueous sample. At 2100 bar, the high pressure lowers the water's melting temperature and supercooling temperature for homogenous ice nucleation, while it increases the viscosity of the water by 1500 times that under atmospheric conditions at the same time so that freezing water has a better chance to reach the glass transition temperature and be vitrified before ice nucleates and ice crystals grow. After the high pressure freezing, the assemblage is unloaded from the Bal-Tec high pressure freezer and transferred to a liquid nitrogen container for cryo-fracture. The fractured frozen samples are then pre-treated, i.e. sublimated and sputter-coated in a Gatan 626 cryo-transfer holder (Gatan, Pleasanton, CA), with a Balzers MED 010 cryogenic sample preparation apparatus (Balzers Union, Balzers, Liechtenstein). The Hitachi S900 microscope fits for imaging latex suspensions or polymer solutions, while not for time-sectioning samples due to the limitation of the size of the specimen holders.

To capture the dynamic changes of microstructure, time-sectioning samples are prepared. As illustrated in Figure 2.2, a latex dispersion is applied by a wire-wound rod to a 7 mm by 5 mm silicon chip substrate; then the coating is plunged into liquid ethane slush by
hand after it is allowed to dry under certain conditions for a certain time period. By using the plunge freezing method, a high cooling rate is required to prevent ice crystals growth that may disrupt the microstructure appreciably. Liquid ethane slush provides mean cooling rates as high as $1.5 \times 10^4$ K/s (Goldstein et al. 1992) and is chosen as the cryogen for this method. Plunge freezing can handle a relatively larger sample size than High Pressure Freezing. However, it is only for thin, water-lean samples, and those that contain a nucleation suppressant. The plunge frozen samples are then transferred to an Emitech K1250 cryo-system for further treatment and imaged by the Hitachi S4700 microscope.

Figure 2.1 Sample preparation procedure of High Pressure Freezing by Bal-Tec HPM 010 high pressure freezer. This process is commonly used to study the microstructure of thick, water-rich samples, such as latex suspensions or polymer solutions.
Chapter 2 Introduction to Latex Film Formation

Figure 2.2 Sample preparation procedure of plunge freezing into liquid ethane slush by hand. This process is used to study the dynamic drying process of the latex film formation.

After the cryo-immobilization, the frozen samples are fractured at cryogenic temperature to expose the interior detail of the coatings. Samples frozen by High Pressure Freezing are fractured by inserting tip of a cold knife in between the rims of the two brass discs in a liquid nitrogen bath. Samples frozen by plunge freezing into liquid ethane slush are fractured in the Emitech K1250 cryo-system. They are first transferred to a specially designed cryogenic sample holder (Ma 2002) in a liquid nitrogen bath and then to the Emitech K1250 cryo-system by using an Emitech cryogenic transfer unit. The Emitech K1250 system is pre-cooled by a liquid nitrogen Dewar to about –170 °C. The samples
are then fractured by pushing a cold rod against the exposed part of the standing sample, as illustrated in Figure 2.3.

Freeze-drying, i.e. sublimation, is usually carried out to produce more topographic contrast by removing some of the frozen solvent after the samples are fractured to expose the interior of the samples. Freeze-drying is usually done by raising the temperature of the samples so that the equilibrium vapor pressure of the frozen solvent at the higher temperature will be higher than the partial vapor pressure in the vacuum chamber. At higher temperature the coating can freeze-dry much faster than at a lower temperature. But when temperature is high enough, water vapor may recrystallize on the cold coating surface and form relatively large ice crystals, and these might damage the
microstructure in the samples. Theoretical estimates indicate that the ice recrystallization becomes significant only when the freeze-drying temperature is higher than – 90°C (Lindroth et al. 1991). The significant effect of temperature on the freeze-drying rate is illustrated in Figure 2.4.

![Figure 2.4](image.png)

Figure 2.4 Predicted temperature dependence of rate of freeze-drying by effusion from a planar ice surface in the range below – 90°C (Ma 2002).

As discussed in the previous section, charging artifacts can be detrimental to the imaging process. Depend on the chemical composition and physical structure of the frozen samples, a thin layer of metal coating, usually platinum, becomes necessary in many cases to avoid the charging problem. However, the metal coating could cover up some fine details on the sample surface if its thickness is comparable to the size of these fine structures. Therefore, the metal coating thickness should be balanced between achieving higher resolution and revealing more detailed structures. Another approach is to use an electron beam with lower energy, i.e. using a lower accelerating voltage, so that less
charge could accumulate during scanning.

Cryogenic Scanning Electron Microscopy technique is a powerful tool to visualize not only the dynamic drying process of latex film formation, but also microstructure of many other aqueous systems, such as paints and di-block copolymer solutions. Chapter 5 and Chapter 6 will elaborate these applications. Figure 2.5 shows the microstructure of mixture of a latex dispersion and titanium dioxide (TiO₂) slurry. At high magnification, the interaction between individual TiO₂ and latex particles is clearly revealed. Figure 2.6 shows the nanostructure of a poly (butadiene-b-ethylene oxide) diblock copolymer solution. At a given polymer concentration and weight fraction of the PEO block, a random disordered wormlike micelle structure is revealed by cryo-SEM.

2.5 Closure

Current understanding of latex film formation consists of consolidation, compaction and coalescence stages is reviewed. The main driving forces in latex film formation are capillary pressure force, air-water surface tension force and van der Waals force. Hypotheses of latex particle deformation in latex film formation are briefly reviewed. The high resolution cryogenic Scanning Electron Microscopy technique is a powerful tool to visualize the microstructure development not only in latex film formation, but also in other aqueous systems, such as paint and block copolymer solutions. The basics of the cryo-SEM technique are briefly summarized.
Figure 2.5 High magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which itaconic acid monomers were incorporated. TiO$_2$ particles were surrounded by latex particles. These latex particles work as a polymeric barrier to prevent the TiO$_2$ to form clusters.
Figure 2.6 Cryo-SEM image of a PEO-PB diblock copolymer solution, showing a disordered wormlike micelle structure. Some branching and nodules can be observed in the image.
Chapter 3

On van der Waals Force of Latex Film Formation

3.1 Introduction

The forces that drive the compressive deformation of flattening latex particles have been discussed for decades because of their importance to understanding the physics of latex film formation. Several hypotheses have been put forward in which the most-often considered driving forces of deformation are air-water surface tension, water-polymer and polymer-air interfacial excess free energies (often referred to as surface or interfacial “tensions”), ill-defined osmotic force, vaguely identified surface adhesive forces, and van der Waals attractive force between particle surfaces. How important the van der Waals force is and the way in which it flattens particles — if indeed it can — seem poorly assessed directly in previous work, excepting in the theoretical modeling by Jagota et al (Jagota et al. 1998). Yet it is unrealistic to omit an always-acting short-range force that is attractive except when the intervening liquid is special (Israelachvili 1991). Consequently, this chapter is addressed to the role of van der Waals force in film formation.

A poly(styrene-butyl acrylate) model latex was coated as an aqueous suspension, quickly frozen, then freeze-dried and annealed under well-controlled bone-dry, i.e. water-free, conditions that totally excluded capillary pressure (also called Laplace pressure) force and direct surface tension force during film formation. Successions of annealing temperatures and times were chosen to follow on the freeze-drying. Cryo-SEM and room temperature SEM images documented, for the first time, van der Waals force alone compacting a completely dry latex coating, beginning with adhesion of neighboring
particles as the ice between them sublimes away and their stabilization collapses, and continuing through annealing. Whether the particle flattening in the compacted coatings was elastic or elastoviscous and therefore recoverable, or viscoelastic or elastoviscoplastic and therefore at least partly unrecoverable, was examined by means of rewetting tests of coatings annealed for the same time at various temperatures.

3.2 Compaction Driven by van der Waals Force

Experimental investigation of the role of van der Waals force of attraction in particle deformation is a blank area notwithstanding the ubiquity of van der Waals forces and the evidence that they are indeed important in latex compaction. In this chapter, what has been called dry sintering (see Section 2.3.1) is used to examine their roles under bone-dry, i.e. totally dry, condition. The roles of van der Waals force in film formation in the totally wet condition, the moist condition and the condition of a coating that is partly wet and partly moist need to be examined too, but are not discussed in this chapter.

When two particles are close to each other, i.e. within approximately a few nanometers, they experience a mutual force, which is called the van der Waals force. Van der Waals attractive force is one of the three most important forces that act in latex suspensions and govern their stability to flocculation and coagulation. Yet most researchers of latex film formation have neglected it, notable exceptions are Jagota et al.

The van der Waals force originates in the fluctuations in the charge distributions of two atoms, in particular in the dipole moments of those distributions and their interactions. In 1937, London derived an equation that related van der Waals force to the polarizability of atoms, as it contributes to the interaction of the dipole moment of one and the induced
dipole part of the others (London 1937). Although there are two other contributions from
the Kessom and the Debye interactions, the London force is usually the strongest and
always present. Also in 1937, Hamaker derived a macroscopic approximation of van der
Waals force. With modifications to take care of retardation of the interaction when
particles are at a longer distance, the van der Waals attraction force $F_{VDW}$ between two
homogeneous spheres with identical radius in vacuum can be approximated by:

$$F_{VDW} = -\frac{A}{6R} \left[ -\frac{4s}{(s^2 - 4)^2} - \frac{4}{s^3} + \frac{8}{s(s^2 - 4)} \right]$$

A is the Hamaker constant, R is the radius of the sphere and s is the distance between the
centers of spheres measured in units of their radius.

The minimum distance that two point particles can approach is about 0.2 nm, according
to both Israelachvili (1991) and Hiemenz (1986). So in the latex film formation, the van
der Waals force is always an attractive force to bring latex particles together and flatten
against each other.

Sperry et al. (1994) made a series of experiments in which they used what they called
pre-dried film a coating. The coating was dried in room air at room air atmosphere, which
was below the Minimum Film Formation Temperature (MFFT). Consequently in the
pre-drying process capillary forces were surely present in the wet state, and in the moist
state. Though Sperry et al. assent that no deformation occurred during the drying process,
this cannot be determined without high magnification imaging, which they did not report.
A good way to improve on Sperry et al.’s approach is to use freeze-drying instead.

Freeze-drying can make a bone-dry coating without water-air menisci and pendular rings ever being present, so that no capillary forces can have been present. This is because freeze-drying sublimes ice directly into water vapor in the gas phase without the ice transforming to liquid water. Freeze-drying was done at very low temperature of \(-86^\circ C\) in this thesis. Figure 3.1 illustrates the difference of forces acting in two different models: capillary force model and bone-dry model achieved by freeze-drying.

![Diagram of forces](image)

Figure 3.1 Van der Waals force alone can compact latex particles. On the left, according to Brown’s capillary hypothesis, capillary forces flatten latex particles against one another elastically. On the right, there are no capillary forces and van der Waals force is the only force to deform the particles against one another. In both cases the degree of flattening is just that to make the elastic reaction force balance the compacting force.

Freeze-drying is the key to the new experiment to make a bone-dry coating that has never experienced capillary force. Followed by annealing at a chosen temperature for a chosen
time and by high-magnification imaging, freeze-drying makes it possible to see unequivocally whether van der Waals force can compact latex particles alone or not.

To anneal at a higher temperature than the freeze-drying temperature is to reduce the modulus of the latex particles, which can enhance the compaction, i.e. the degree of flattening of contacts. Slight flattening can often be detected by careful examination at high magnification after freeze-drying is complete; moreover, the freeze-dried compact retains its integrity when it is freeze-fractured from this examination.

The annealing temperature can be higher or lower than the glass transition temperature of latex. In annealing below \( T_g \), the latex particles remain stiff and their polymer chains have little mobility so that they can interdiffuse only on time scales of days, months, or years. Adhesion, with obvious flattening or without, is then overwhelming evidence of van der Waals attraction force alone compacting latex particles. In annealing above \( T_g \), the polymer chains of the latex particles are mobile and interdiffusion far more rapidly, so it may be more complicated to distinguish what is role of the van der Waals force. But to coalesce, latex particles must be close enough and the contact area should be as large as possible, which could also demonstrate the “crack closure” by van der Waals force. To examine the relationship of annealing temperature and time, annealing temperature above \( T_g \) is processed and the result shows a high degree of compaction with coalescence after a short annealing time.

3.3 Experiments

A series of experiments was designed to investigate the role of van der Waals force in latex film formation under bone-dry condition. Four different annealing temperatures
were chosen to investigate the role of annealing temperature in deformation of latex particles. They were 20°C, 30°C, 40°C and 50°C. Four different annealing times were chosen to investigate the role of annealing time in deformation of latex particles. They were three hours, six hours, twelve hours and twenty-four hours at 40°C. Both room temperature scanning electron microscopy (SEM) and cryogenic scanning electron microscopy (cryo-SEM) were used for imaging, together with scanning probe microscopy (SPM).

The experimental procedure designed to uncover the role of van der Waals force in latex film formation is shown in Figure 3.2. It can be divided into three major steps. In the first step, plunge freezing by hand was used to freeze quickly all the aqueous solution in the sample into crystallites so small as not to affect the particles or their locations, and to thereby cryo-immobilize the starting latex suspension. In Step Two, freeze-drying under vacuum in the chamber was used to transform ice directly to water vapor. Thus was avoided the presence of liquid water and attendant forces of surface tension, both the direct force at contact lines and the indirect force through the capillary pressure (Laplace pressure) that results from surface tension in curved menisci, at any time on the way to a bone-dry assemblage of particles held together by adhesion forces at the interparticle contacts. In Step Three, this freeze-dried coating was annealed in the vacuum at one or another temperature for a chosen time. Incontestably, attractive van der Waals force acted across the flattening contact and across a narrow annular wedge around each contact’s perimeter, all during the time of annealing, beginning with the interparticle contacts that formed each time that intervening ice was sublimed away and a newly freed particle jumped or fell into adhesive contact with neighbors (cf. the experiments in other polymer system by Mangipudi (1995, 1998) and Falsafi (1997, 1998). At the end of the chosen time of annealing, a sample was sputter-coated under vacuum with platinum and
transferred into the microscope to image its nanostructure. The procedures before and after annealing were different for different imaging purposes, however.

Figure 3.2 Experiment to expose the role of van der Waals attractive force in latex film formation. Parallel samples were imaged after one, two or all three steps.
Table 3.1 Details of the samples whose images are used here to illustrate how nanostructure evolves with freeze-drying and annealing.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample thickness $\mu$m</th>
<th>Freeze-drying time minutes</th>
<th>Annealing temperature $^\circ$C</th>
<th>Annealing time hours</th>
<th>Top (T) or Fracture (F) surface image</th>
<th>Cryogenic or Room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS1</td>
<td>150</td>
<td>5</td>
<td>N/A</td>
<td>N/A</td>
<td>Top</td>
<td>Cryo</td>
</tr>
<tr>
<td>FD1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fracture</td>
<td></td>
</tr>
<tr>
<td>FD2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Top</td>
<td></td>
</tr>
<tr>
<td>VF1</td>
<td>10</td>
<td>180</td>
<td>20</td>
<td>3</td>
<td>Top</td>
<td>RT</td>
</tr>
<tr>
<td>VF2</td>
<td></td>
<td></td>
<td>30</td>
<td>3</td>
<td>Fracture</td>
<td>Cryo</td>
</tr>
<tr>
<td>VF3</td>
<td></td>
<td></td>
<td>40</td>
<td></td>
<td>Top</td>
<td>RT</td>
</tr>
<tr>
<td>VF4</td>
<td></td>
<td></td>
<td>50</td>
<td>6</td>
<td>Fracture</td>
<td>Cryo</td>
</tr>
<tr>
<td>VF5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Top</td>
<td>Cryo</td>
</tr>
<tr>
<td>VF6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fracture</td>
<td></td>
</tr>
<tr>
<td>VF7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fracture</td>
<td></td>
</tr>
</tbody>
</table>

a) All samples were incidentally pre-dried no more than 5 sec before freezing

b) All freeze-drying was carried out at $-86^\circ$C at about $1 \times 10^{-5}$ Pa

c) All samples were sputter-coated at $1 \times 10^{-3}$ Pa with platinum to a nominal layer thickness of about 5 nm; the temperature was near that of imaging.
3.3.1 Model Latex

The model latex in the experiment, designated ML233, was synthesized by free radical polymerization in the BASF Charlotte Technical Center, Charlotte, NC. Its composition was 61% styrene, 37% butyl acrylate and 2% acrylic acid, together with 1% sodium dodecylsulfate (SDS) as surfactant. ML233 was stabilized by acrylic acid and by SDS reversibly adsorbed from the “serum”, i.e. the aqueous suspending solution. The solids weight percent of ML233 was 40.0% and pH value was 8.3. Its glass transition temperature was measured by DSC with a value of 45°C as the mid-point by BASF. Its minimum film formation temperature was 40°C, which was measured by Rhopoint 90 MFFT Bar. The number average particle size was 205 nm and the volume average size was 218 nm.

The details of the preparation of samples used in this chapter to illustrate the outcomes of the experiments are recorded in Table 3.1.

3.3.2 Sample Generation

For research on the role of van der Waals force in latex film formation, precut silicon wafers of 5 mm x 7 mm (Ted Pella Inc., Redding, CA) were selected as the substrate because of silicon’s conductivity and good brittle fracture behavior. The silicon wafers were pre-scratched on the polished side along <100> direction for easier freeze-fracture in the later experiment. After the silicon wafer was laid flatly on the operation desk with the polished surface facing up, 2 or 3 small drops of latex suspension were deposited on it from a 10 ml pipette and spread in the 5 mm direction. Then a rod of diameter 4 mm and length 6 cm and wound with wire was drawn behind the liquid across the 7mm length.
(Figure 3.3). When the drawdown was finished, the wire marks in the coating leveled within seconds, because of the low viscosity of the suspension, and the target coating thickness was less than $10 \, \mu\text{m}$ in most of the experiments. The reason for choosing such thin coatings is discussed in section 3.4.2. Without any further time for drying, the leveled sample was frozen by hand plunge freezing, as described in Section 3.3.3.

Figure 3.3 Latex coating was applied on a precut silicon wafer by a wire-wound rod.

Thicker coatings of $150 \, \mu\text{m}$ of ML233 were applied to the silicon wafers by the same wire-wound rod spaced by two steel support rails (Figure 3.4). As soon as the coating was completed, the whole piece of coating and substrate and was plunged into liquid ethane and transferred to the Emitech K1250 cryo-system (Emitech, Kent, UK) under the protection of liquid nitrogen. The piece was fractured in the liquid nitrogen. The fractured specimen was withdrawn and its fracture surface was sputter-coated with a nominal thickness of 5 nm of platinum. Cryo-SEM images were made of the cross-section —
sometimes slightly tilted so that the top surface and fracture surface of the coating show obliquely — under the low temperature of – 170°C on the Hitachi S4700 FESEM (Hitachi, Pleasanton, CA).

Figure 3.4 Thicker coating thickness can be achieved by adding two steel rails to support the wire-wound rod during drawdown.

3.3.3 Cryo-immobilizing

Plunge Freezing was selected as the cryo-immobilizing method. Liquid ethane was chosen as the cryogen basically because of the large gap between its melting temperature and boiling temperature, which allows the high heat transfer rate of deeply subcooled nucleate boiling (as compared to film boiling).

As shown in Figure 3.5, a liquid ethane bath was prepared for plunge freezing. First of all,
boiling liquid nitrogen was used to cool down the small cylindrical copper cup (2 cm in diameter and 2 cm deep) for holding liquid ethane. Ethane gas was blown from a tank of compressed gas into the cooled cup. As the gaseous ethane made direct contact with the cold metal, it condensed to liquid virtually immediately. As the container filled with liquid ethane, the liquid ethane adjacent to the copper wall began to freeze because of the colder temperature of liquid nitrogen boiling at atmospheric pressure.

Figure 3.5 Samples of coated substrate were plunged into liquid ethane, at its freezing point in a cup surrounded by a bath of boiling liquid nitrogen.

Before the coating was ready to plunge, an aluminum metal rod with a diameter of 6 mm, which has a good thermal conductivity, was used to disturb and melt enough of the solid ethane to make a suitable mixture — a slush — of liquid and solid ethane. Then when the coating sample was ready, the whole piece was plunged into the ethane slush, tangentially
to the coating surface to achieve the fastest cooling rate, but at some risk of shearing by
the liquid affecting the coatings surface: no evidence of this was found in this research.
The total processing time from start of coating to entry into the ethane slush was about 10
seconds and any drying during that time is negligible according to observations by naked
eye and in the Hitachi S4700 cryo-SEM.

3.3.4 Freeze-drying

After plunge freezing, frozen ML233 coatings were transferred under liquid nitrogen in
the bath to a sample holder specially designed for the next step — freeze-drying

A frame with four windows of the same size as the silicon wafers’ was fabricated to hold
four frozen coatings at the same time for replication and efficiency purposes. This frame
was placed on a flat surface on the sample holder and a clamp was applied above the
frame to ensure that samples and frame were fixed on the sample holder, as shown in
Figure 3.6. A cryo-transfer unit was used to transfer the loaded sample holder to the
sample preparation apparatus — Emitech K1250 cryo-system — and to avoid moisture
contamination from room air. The Emitech K1250 cryo-system had been pre-cooled to a
temperature that was below –170°C before this sample transfer.
Figure 3.6 Frame and sample holder used for freeze-drying. Four samples can be put into the frame on the holder at the same time for freeze-drying and subsequent annealing.

After transferring the sample holder from liquid nitrogen to the Emitech K1250 system, the whole system was allowed to sit for 10 to 15 minutes to reach equilibrium before the temperature was raised. After the temperature reading on the Emitech K1250 system, which showed the temperature of the sample holder, remained steady at –170°C or below, a heating current was applied by turning on the Emitech heater’s controller. The temperature then rose continuously until it reached the set-point on the temperature controller. In the series of experiments reported here, the set-point of the freeze-drying temperature was chosen to be –86°C.

Choosing freeze-drying temperature is important because it directly influences freeze-drying rate. At higher temperature the coating can freeze-dry much faster than at a lower temperature. But when temperature is high enough, water vapor may recrystallize on the cold coating surface and form relatively large ice crystals, and these might damage
the nanostructure in the samples. Theoretical estimates indicate that the ice recrystallization becomes significant only when the freeze-drying temperature is higher than \(-90^\circ C\) (Lindroth et al. 1991). Consequently former Ph.D students Yue Ma and Haiyan Ge in the Department of Chemical Engineering & Materials Science at the University of Minnesota used \(-96^\circ C\) as the freeze-drying temperature, that is, the temperature at which they sublimated ice from fracture surface of frozen aqueous latex suspensions and coatings in order to develop topographic contrast for cryo-SEM imaging. As shown in Figure 3.7, temperature has a significant effect on the freeze-drying rate.

![Figure 3.7 Predicted temperature dependence of rate of freeze-drying by effusion from a planar ice surface in the range below \(-90^\circ C\).](image)

To achieve even higher freeze-drying rate without ice recrystallization, experiments were carried out to compare our system at two different sublimating temperatures, \(-96^\circ C\) and \(-86^\circ C\). The results were surprising in that no ice recrystallization was observed in the Hitachi S4700 FESEM, after the samples was freeze-dried for three hours at \(-86^\circ C\), which has the same nanostructure as the sample that was freeze-dried at \(-96^\circ C\). One
possible reason is the imperfect thermal contact between the samples and sample holder, which makes the actual temperature on the samples is lower than – 86°C, and different properties between pure ice and blend of latex and ice. As the result, – 86°C was chosen as the freeze-drying temperature to achieve higher rate.

After the temperature reading of the Emitech system unit reached and remained steady at – 86°C for 10 minutes, freeze-drying was begun. The pressure in the Emitech K1250 cryo-chamber was $1 \times 10^{-4}$ mbar and remained steady throughout the three hours of freeze-drying. During the three hours of freeze-drying, temperature was well maintained at – 86°C by the Omron temperature controller (Omron, Kyoto, Japan). In this experiment, the freeze-drying time was set to three hours, which proved to be longer than what is needed to freeze dry the whole latex coating. This is because freeze-drying is the key step, which freeze-dries the coating to bone-dry condition. If any ice is left in the latex coating, it could become water again during the annealing process and capillary forces would then be acting.

### 3.3.5 Annealing

After the three hours of freeze-drying, the temperature of the freeze-dried sample was raised to a certain annealing temperature directly from – 86°C. This was done with the same temperature controller in the Emitech system so that the annealing could be done without moving the samples. After heated for about 20 minutes, the temperature of the sample and sample holder could be raised to desired annealing temperature. Annealing is the stage in which latex particles flattened against each other.
Four different temperatures were chosen to anneal the bone-dry latex coating: 20°C, 30°C, 40°C and 50°C. These temperatures were chosen to cover the range from room temperature to a temperature that was higher than the glass transition temperature of the model latex. Three hours was chosen as the standard annealing time. Another series of experiments at different annealing times at 40°C annealing temperature was designed to investigate the effect of annealing time. Four annealing times were chosen: three hours, six hours, twelve hours and twenty-four hours. Because all the ice had already been removed by sublimation before annealing began, the latex particles annealed in a bone-dry condition and presumably the only force that could act during the process was the van der Waals force.

### 3.3.6 Acquisition of SEM Images

The annealed samples were imaged in several ways. Imaging the top surface of the coating required no further treatment of annealed samples. They were coated with a thin layer of platinum, usually 5 nm thick nominally, in Emitech K1250 cryo-system, and transferred to the Hitachi S4700 below-the-lens Field Emission SEM for examination at a low acceleration voltage of 3.0 KV. Imaging the interior nanostructure of the coating was accomplished by cooling and transferring the sample to another sample holder, No.2, which was specially designed for the freeze-fracture purpose. Once fractured, deposition of a 5 nm thick platinum layer was required as a further treatment of the exposed fracture surface before transferring to Hitachi S4700 SEM.

Liquid nitrogen boiling at atmospheric pressure was used as a cryogen to cool the Emitech K1250 cryo-system after annealing. The cooling rate was low; usually taking about 40 minutes to cool the whole system from the annealing temperature back to –
170°C. To ensure no frost from moisture contamination, samples were transferred either under vacuum or under liquid nitrogen in the bath. After the Emitech K1250 cryo-system had been completely cooled to – 170°C and the temperature reading was steady, a cup of liquid nitrogen was prepared in a separate vacuum chamber of the Emitech K1250 cryo-system and used to make nitrogen slush in which the sample holder was transferred back to the liquid nitrogen bath. As the pump began to evacuate the chamber the pressure fell rapidly and the cup of liquid nitrogen boiled. After the pressure dropped under a certain value, the liquid nitrogen began to solidify. At this time, evacuation was stopped to maintain some liquid phase nitrogen, which is necessary for transferring. The sample holder was again transferred by a cryo-transfer unit sealed under vacuum to protect the sample from moisture and consequent front. The cryo-transfer unit was connected to the vacuum chamber, where nitrogen slush was present. As the nitrogen slush was being prepared and the chamber was under vacuum, the valve on the transfer unit could be opened and the sample holder could be plunged into nitrogen slush under vacuum. Once the sample holder was in the nitrogen slush, the chamber was vented and the cup was taken out of it. Then the sample holder was transferred from the nitrogen slush to a liquid nitrogen bath and samples were unloaded from the frame.

Sample holder No.2, as shown in Figure 3.8, was specially designed with channels that can hold the samples vertically. The samples were sandwiched by small aluminum blocks that can provide mechanical stability and prevent damage by direct contact of the side screw to the samples. After the mounting of samples was completed, the sample holder was covered by a copper lid, which could protect samples from moisture outside. Again the cryo-transfer unit was used to transfer the sample holder to the Emitech K1250 cryo-system for freeze-fracture and platinum coating.
Figure 3.8 Sample holder No.2 used for examine fracture surface of the coating (Ma, 2002)

The whole Emitech K1250 cryo-system remained at a low temperature of \(-170^\circ C\) during the freeze-fracture and platinum coating process. After it was transferred into the Emitech K1250 cryo-system, the copper lid was removed under vacuum by a manipulator mounted on the side wall of Emitech K1250 system. By the same manipulator, samples were fractured to expose cross-sections of the coating. After being coated with platinum under an argon atmosphere to raise their surface conductivity, samples were transferred to the Hitachi S4700 Field Emission SEM with the same cryo-transfer unit, which was also maintained at vacuum, for imaging at low temperature. During the entire process of fracturing, sublimating, coating and imaging, the sample was kept below \(-170^\circ C\).
3.3.7 Rewetting Tests

The rewetting test was designed to probe whether a coating had coalesced to a degree that prevented particles from separating when they were exposed to water at room temperature. Of course, the particles of a well coalesced sample cannot separate from contact because they are welded together by interdiffusion of their polymer molecules. Tests were carried out on samples that had been annealed for three hours at different temperatures; namely 20°C, 30°C, 40°C and 50°C; a sample that had been annealed for twenty-four hours at 40°C was tested too.

Each of these samples after annealing was taken out from vacuum and immersed into deionized (DI) water at room temperature for twenty-four hours to ensure enough time for latex particles in the top surface to round up and separate. DI water was used to avoid any complication from ions in the water. After twenty-four hours of rewetting, the whole sample coating plus substrate, was taken out of the DI water with a pair of tweezers. It was then blotted with tissues to suck off the residual water on its surface. The rewetted sample was frozen by hand plunge freezing in liquid ethane.

To image the top surface of a frozen rewetted sample, it was sublimed for 5 to 10 minutes and coated with 5 nm of Platinum. To compare it with samples merely annealed for twenty-four hours at 40°C, and not rewetted, a fracture surface was needed. Again, the specially designed sample holder No.2 was used and the fracture procedure described above was followed.
3.4 Results and Discussions

3.4.1 Nanostructure Development of Model Latex by SEM

As a prelude to interpreting images of nanostructure development with time and temperature of annealing, it is appropriate to document the nanostructure of frozen coatings of suspension that were neither freeze-dried nor annealed, and of frozen coatings that were partially and fully freeze-dried, without annealing. Figure 3.9 and 3.10 show top and fracture surfaces, respectively, of a frozen suspension, Sample FS1, after only 5 minutes of freeze-drying at – 86°C to enhance the topographic contrast; freeze-drying of this extent is commonly referred to as “sublimation” or “etching” of a frozen sample. It’s notable that some pullout features appear in Figure 3.10. The plastic deformation forming pullouts is documented and analyzed elsewhere (Ge et al. 2006). Here these features indicate strong adhesion between the particles and the ice to which their opposite sides adhered on the two sides of the fracture as it opened. Figure 3.11 and Figure 3.12 show top and fracture surfaces, respectively, of fully freeze-dried Sample FD2, after three hours of freeze-drying; there was no annealing in the bone-dry condition.

These images were all at a temperature lower than – 170°C. What is remarkable is that features that seem to be bits of “junk” can be seen in Figure 3.9. They are most likely water-soluble surfactant, unreacted monomers, oligomers, and possibly polymer from the “serum”, i.e. the suspending liquid of the model latex suspension. They were presumably stranded by subliming ice but had not collapsed in the 5 minutes of sublimation time, whereas in Figure 3.11, some “junk” remains visible in the top surface, presumably because it is incompletely collapsed.
Figure 3.9 Cryo-SEM image of the top surface of Sample FS1 that was frozen without drying; it was then sublimated, i.e. freeze-dried, for 5 minutes at –86°C to increase topography contrast. Deposits of — presumably phase-separated soluble components of the aqueous phase — “Junk” can be seen between the latex particles, which themselves are separated and spherical.

Figure 3.10 Cryo-SEM image of a fracture surface of Sample FS1 that has not been freeze-dried. Fracture surface shows a continuous ice matrix and parts of fractured particles held by the ice. Most of them plastically deformed into pullouts.
Figure 3.11 Cryo-SEM image of the top surface of Sample FD2 that was frozen without drying and after three hours of freeze-drying at – 86°C. The latex particles plainly remained distinct and unflattened. “Junk” can still be seen between many of these latex particles at the top surface.

Figure 3.12 Cryo-SEM image shows a fracture surface of Sample FD2 that was frozen without drying after three hours of freeze-drying at – 86°C, but not annealed. Most of the particles evidently adhere to one another strongly enough to remain adhered by van der Waals force (and possibly others) during and after cryo-fracture. Slightly flattening against particles can be seen; so can incipient pullouts on some particles.
3.4.2 Freeze-drying Front

The experimental procedures of freeze-drying are discussed in Section 3.3.4. The present section discusses the freeze-drying front, which was accidentally discovered in the course of testing the effect of freeze-drying on a thick latex coating — Sample FD1 — about 150 \( \mu m \) thick, the originally chosen coating thickness. As Figure 3.13 makes plain, a sharply defined freeze-drying front is about 25 particles diameters below the top surface after three hours of freeze-drying at \(-86^\circ C\). The coating in this sample was 150 \( \mu m \) thick and would have been totally freeze-dried had the rate been the theoretically calculated unhindered rate of effusion of sublimating pure ice at \(-86^\circ C\); that rate is about 30 nm/second (Ma 2002).

The rate of sublimating pure ice, \( r \), can be estimated from kinetic theory and expressed as:

\[
r = k(P_s - P_c)\sqrt{\frac{M}{2\pi RT}}
\]

where \( k \) is the coefficient of evaporation, \( P_s \) is the saturated vapor pressure of pure ice, \( P_c \) is the pressure at the condensing surface, \( M \) is the molecular weight of water vapor, \( R \) is the gas constant, and \( T \) is the temperature of ice (Dolan 1998).

Obviously the sublimation was not unhindered. There must have been substantial resistance to diffusion and flow of water vapor through the compacting ice-free pore space. Incidentally, the image strongly suggests that the particles in the top six or eight
layers were more compacted than those deeper down, which had been freed of ice between them for progressively shorter times.

Figure 3.13 Cryo-SEM image of a fracture surface of Sample FD1 showing the freeze-drying front. Above the front is the freeze-dried region and below it is the unfreeze-dried region, which is same as in the frozen suspension. Here the ice free region after three hours of freeze-drying at –86°C is approximately 25 particles diameters thick.

Figure 3.14 shows a place near the center of the same freeze-drying front at higher magnification. Above the front, the latex particles appear to be bone-dry. No ice is evident on them where the interparticle contacts can be seen edge on. Some particles appear to be slightly flattened, as expected of contact adhesion (Mangipudi 1995, Falsafi 1998). Below the freeze-drying front, the latex particles are still surrounded by bulk ice, and look exactly like those in the originally frozen latex coating before freeze-drying, as shown in Figure 3.10.
Figure 3.14 Higher magnification cryo-SEM image of the fracture surface in Figure 3.13. Above the freeze-drying front is the freeze-dried region, where the fracture ran between particles, whose contacts were not strong enough to deform the particles noticeably at the former contacts. Below the front is the unfreeze-dried region, where the fracture ran through latex particles, surely because of the strength of their stronger adhesion to the ice, that surrounded them and to the strength of the ice in which they were embedded.

The latex particles evidently consolidated as the freeze-drying front descended. In the fracture surface and behind, the particles remained in contact after freeze-fracture, which is undeniable evidence of van der Waals attraction force and perhaps additional surface forces holding them together, because there is no sign of their being welded by coalescence. As particles were set free from the bulk ice by freeze-drying, they may have fallen together by gravity, but they must have been drawn into contact — slightly
flattened contact — by van der Waals force between them. This must have taken some time because the uppermost layers seem more compacted, *i.e.* the contacts are more flattened, than those layers closer to the front. Furthermore, were they being consolidated by the force of gravity, the weight of those above would be greatest just above the front; but that is where they are least consolidated. Certainly were the distance between two particles to become close enough, they would jump into contact with each other by strong short-range van der Waals attraction force, which is short-range and stronger, the closer the approach (Jagota 1998, Israelachvili 1991, Mangipudi 1995, Falsafi 1998).

There appears to be three possible reasons for the freeze-drying rate being lower than the rate calculated from the rate of unhindered effusion of sublimating ice into vacuum as indicated by the progress of the freeze-drying front. Besides resistance to effusion of water vapor by the consolidated and compacting packing of freeze-dried latex particles above the front, they are poor thermal contact between the sample and the sample holder, and appreciable water vapor partial pressure in the vacuum chamber.

The possibility of poor thermal contact appears the least likely in this experiment. The reason to consider this possibility is that the temperature reading of the controller was actually the temperature of the sample holder. As shown in Figure 3.6, the samples were put into windows in the frame on the sample holder. Hence if there was a bad thermal contact between sample and sample holder, the temperature reading would not be the actual temperature of the sample. However, after the three hours of freeze-drying, sample and sample holder must have reached equilibrium. Furthermore, compared with the results of another two control groups, which has the sample clamped directly to the sample holder, the freeze-drying front always existed and the thicknesses of freeze-dried coatings were almost the same. Thus the rate of descent of the freeze-drying front was
The possibility of appreciable water vapor partial pressure in the vacuum chamber seems reasonable and could be important. As the freeze-drying continued, water vapor in the vacuum chamber kept climbing and it would finally reach to saturate because of the insufficient pumping speed of the turbo molecular pump in the back. Once the water vapor partial pressure became saturated, the freeze-drying would get into equilibrium with the pumping speed of water vapor, which would definitely make the freeze-drying rate drop a lot. Because the freeze-drying rate was not following the theoretical value any more, the coating couldn’t be totally freeze-dried within the calculated time and a freeze-drying front clearly show the extent of freeze-drying. This possibility could be totally eliminated by adding additional cold trapping capacity into the vacuum chamber, which can trap water vapor and turn it back into solid phase by its colder temperature.

There still could be another possibility that when the ice around latex particles was freeze-dried away, the distance between individual particles became much shorter, or to say, latex particles began to contact with each other by the action of both gravity force and van der Waals attraction force. As an important parameter, the mean free path of particles in the gas phase can be simply expressed as (Atkins 1994):

\[ \lambda = \frac{k_B T}{1.414 P \sigma} \]

where \( \lambda \) is the mean free path; \( k_B \) is the Boltzmann constant; \( T \) is the temperature; \( P \) is the pressure and \( \sigma \) is the collision cross section.

As the barrier of the consolidated packing of latex particles formed above the
freeze-drying front, $\lambda$ of water molecules decreased as $\sigma$ decreased, i.e. collisions increased. This suggests fewer molecules can effuse and more molecules may strike a particle surface before it can escape. Although those that strike a particle surface may escape on the next leg of their path — but may rattle around a while, thereby higher pressure is built in the pore spaces. The deeper the ice front, the much less likely a subliming molecule can effuse. Escape through the pore network becomes diffusion, which is enormously slower than effusion. This directly slows down the freeze-drying rate. This factor might not be able to be eliminated in the experiment.

In order to have the freeze-drying front reach the coating’s substrate and make a latex coating really bone-dry in less freeze-drying time, the coating has to be very thin. To take into account of the original volume size of freeze-dried coating with ice, a coating that has a thickness of less than $10 \ \mu m$ was chosen for three hours of freeze-drying. Figure 3.11 and Figure 3.12 show the bone-dry latex coating after three hours freeze-drying with an original coating thickness of $10 \ \mu m$ observed under S4700 cryo-SEM. The sample preparation procedure is described in Section 3.3.2 and is also shown as in Figure 3.3.

### 3.4.3 Nanostructure Development over Annealing Temperature

Four different annealing temperatures were chosen to investigate the effect of annealing temperature on deformation of latex particles, i.e. their flattening against each others. They were 20°C, 30°C, 40°C and 50°C.

Annealing the coating at 20°C for three hours changed the nanostructure very little from its original freeze-dried state. Figure 3.15 is a room temperature SEM image of the top
surface of Sample VF1 after three hours of annealing at 20°C which followed the three hours of freeze-drying at –86°C. Unless other noted, the annealing process was begun after three hours of freeze-drying. Figure 3.16 is a cryo-SEM image that shows the fracture surface of Sample VF1 after three hours of annealing at 20°C. The procedure of re-freezing the sample for freeze-fracture after it has been annealed is described in Section 3.3.6 above.

Figure 3.15 Room temperature SEM image of the top surface of Sample VF1 after three hours of annealing at 20°C. Some flattening at many particle-particle contacts is evident but the degree of flattening is limited.

As Figure 3.15 portrays, many adjacent latex particles were in contact — adhesive contact, no doubt — but their flattening against each other was quite limited. The particles are obviously distinct from one another: they have not begun to coalesce. Comparison with Figure 3.16 shows that the latex particles were still only slightly
flattened against each other after three hours of annealing at 20°C under the sole action of van der Waals force that must have brought them into contact as the ice sublimed away. Evidently the elastic modulus of latex particles was still high enough to resist further elastic deformation by van der Waals force, and the viscosity-like modulus of elastoviscous or viscoelastic response was high enough to prevent appreciable creep under the van der Waals force.

Figure 3.16 Cryo-SEM image of the fracture surface of Sample VF1 that was frozen without drying after three hours of freeze-drying at – 86°C and three hours of annealing at 20°C, a temperature below both the nominal T_g of 45°C and MFFT of 40°C. The flattening of many particles against their neighbors is obvious, although the degree of compaction of the assemblage is limited, particularly four and more layers beneath the top surface.
As the annealing temperature was raised to 30°C, three hours of annealing did change the nanostructure a little more than the annealing at 20°C. Figure 3.17 is a room temperature SEM image of the top surface of Sample VF2 after three hours of annealing at 30°C. Figure 3.18 is a cryo-SEM image that shows the fracture surface of Sample VF2 after three hours of annealing at 30°C.

Figure 3.17 Room temperature SEM image of the top surface of Sample VF2 after three hours of annealing at 30°C. The flattening at particle-particle contacts is still limited, but appears to be more than in the case of the coating annealed at 20°C.

The deformation of latex particles against each other was still limited, but detectably more than in the case of annealing at 20°C. The difference in the top surfaces of the coatings in Figure 3.15 to Figure 3.17 is notable. Obviously the elastic modulus of the latex particles was still high enough to resist further elastic deformation by van der Waals force, and the viscosity-like modulus of elastoviscous or viscoelastic response was also
still high enough to prevent appreciable creep under the van der Waals force. However, at the higher annealing temperatures, the moduli were lower than during annealing at 20°C; yet this change of moduli was enough to increase the degree of deformation.

Figure 3.18 Cryo-SEM image of the fracture surface of VF2 that was frozen after three hours of freeze-drying at – 86°C, and three hours of annealing at 30°C, a temperature below both the nominal $T_g$ of 45°C and the MFFT of 40°C. The flattening of many particles against their neighbors is quite obvious. The degree of compaction of the assemblage is plainly greater than that of the coating similarly prepared but annealed at 20°C.

When the annealing temperature was raised to 40°C, the annealing in three hours changed the nanostructure a lot more than when the annealing temperature was 20°C or 30°C. Figure 3.19 is a room temperature SEM image of the top surface of Sample VF3 after
three hours of annealing at 40°C; Figure 3.20 is a cryo-SEM image of a fracture surface of Sample VF3 annealed three hours at 40°C.

Figure 3.19 Room temperature SEM image of the top surface of Sample VF3 after three hours of freeze-drying at –86°C and three hours of annealing at 40°C, which is the nominal MFFT and below the nominal T_g of 45°C. Plainly the latex particles in the top surface are well ordered and the degree of flattening is more advanced.

The flattening of latex particles against each other after three hours of annealing at 40°C was also much more advanced than when the annealing temperature was 20°C or 30°C. As Figure 3.19 makes plain, latex particles were well flattened against each other and formed a hexagonal packing. Moreover as Figure 3.20 shows the latex particles were heavily flattened and the contacts between particles appear to be closing as a crack would. However no top-down ordering of a hexagonal packing was detected.
Figure 3.20 Cryo-SEM image of the fracture surface of Sample VF3 that was frozen after three hours of freeze-drying at –86°C and three hours of annealing at 40°C, which is the nominal MFFT and is below the nominal $T_g$ of 45°C. Most of the particles are substantially flattened against their neighbors and therefore the degree of compaction is much greater than that of the coatings annealed at 20°C and 30°C.

The reason that degree of compaction of latex particles rose must have been the raising of the annealing temperature. Van der Waals force is independent of annealing temperature and time. The nominal Minimum Film Formation Temperature of this model latex is, as noted above, 40°C, which is quite near its glass transition temperature of 45°C. Presumably both the elastic modulus and “viscous” modulus of the latex particles fell more rapidly as the transition region was approached (Lagakos, Jarzynski, Cole and Bucaro 1986; Ferry 1980; Perepechko 1981), which made it much easier for van der Waals force to flatten latex particles.
Fig 3.21 Cryo-SEM image of fracture surface of a latex coating of ML233 dried at 40°C for 20 minutes on the Rhopoint 90 MFFT Bar, where the visual appearance was of the late Compaction Stage of latex film formation.

The cryo-SEM images of a compacted latex coating of ML233 dried at 40°C on a Rhopoint Minimum Film Formation Temperature Bar (RhoPoint Instrumentation Inc., East Sussex, UK), as shown in Figure 3.21 and Figure 3.22, reveal a degree of compaction quite similar to that of the sample annealed at 40°C. However, this comparison raises the issue of ordering of latex particles. Apart from that, the comparison indicates that at the temperature of 40°C, van der Waals attraction force can alone flatten latex particles under bone-dry condition.
Fig 3.22 Cryo-SEM image of fracture surface at 30° tilt, showing nanostructure of a latex coating of ML233 dried at 40°C for 20 minutes on Rhopoint 90 MFFT Bar, where the visual appearance was of the late Compaction Stage of latex film formation.

At an annealing temperature of 50°C, three hours of annealing changed the nanostructure even more than of the coatings annealed at 20°C, 30°C and 40°C. Figure 3.23 is a room temperature SEM image of a top surface of Sample VF4 after three hours of annealing at 50°C; Figure 3.24, of the fracture surface of Sample VF4 after three hours of annealing at 50°C.

Figure 3.23 shows a view of the top surface in which the latex particles appear to be coalesced. However, some of the boundaries between individual particles appear blurry. Nevertheless Figure 3.23 and Figure 3.24 together make clear that the latex particles were very nearly if not totally compacted after three hours of annealing at 50°C. In Figure 3.24,
there are some pullout features that bridge several adjoining latex particles, which is an indication that they had begun coalescing by interdiffusion during the annealing at 50°C. How much the nanostructure changed during shorter time intervals of annealing would require getting images closer together in time at 50°C. In other words, better time resolution, or finer time sectioning, is desirable.

Figure 3.23 Room temperature SEM image of the top surface of Sample VF4 after three hours of freeze-drying at –86°C and three hours of annealing at 50°C, a temperature above the nominal $T_g$ of 45°C. The boundaries between latex particles are no longer distinct, which indicates that adjacent particles have coalesced by interdiffusion, i.e. they have welded together.

The nanostructure developed after three hours annealing at 50°C can be easily explained. The annealing temperature of 50°C is higher than the glass transition temperature of this
model latex, which is 45°C as measured by Differential Scanning Calorimeter (DSC). The latex particles became soft and the modulus became low at such a high temperature. The molecular level picture is that polymer chains became more mobile at temperatures above the glass transition temperature and began to diffuse into other adjoining latex particles and there to entangle with other active polymer chains. This picture accords with the coalescence of latex particles. Nevertheless the degree of coalescence was still limited, because the boundaries between individual particles could still be resolved, which might be because of the relatively short annealing time.

Figure 3.24 Cryo-SEM image of the fracture surface of Sample VF4 that was frozen without drying after three hours of freeze-drying at –86°C and three hours of annealing at 50°C, a temperature above the nominal T_g of 45°C. The latex particles appear to be nearly totally compacted; few pore spaces are evident and those are compensatively tiny. Pullout features are present everywhere and indicate strong adhesion force between adjoining particles, which still retain their identity.
Scanning probe microscopy (SPM) images were made with Nanoscope III Multimode SPM by Digital Instrument (Veeco Instruments, Woodbury, NY). Figures 3.25, 3.26, 3.27 and 3.28 are tapping mode SPM images of the top surfaces of latex coatings that were annealed for three hours at 20°C, 30°C, 40°C and 50°C, respectively. Comparing either 2D or 3D SPM images of latex samples annealed at different temperatures makes it plain that the degree of deformation rose as the annealing temperature was increased. Although the latex particles in the 2D images of latex coating annealed at 20°C and 30°C looked more deformed than what can be seen in the SEM images, combined with the 3D images, latex particles were not well compacted and deformed until the annealing temperature was raised to 40°C. In the SPM image of the coating annealed for three hours at 50°C, interference as by possible tip contamination was observed. Nevertheless it is still obvious that the boundaries between latex particles were more distinct from the image of fracture surface.

The evidence shows that the nanostructure development of latex coating is a function of annealing temperature. As the annealing temperature is raised, the moduli of latex particles, both elastic and “viscous”, falls and their resistance against deformation by van der Waals force diminishes. The degree of compaction is also a function of annealing temperature. As the annealing temperature was raised, the degree of compaction increased. At the nominal MFFT of 40°C of this model latex, well compacted and/or heavily flattened latex particles were captured by both room temperature and cryo-SEM. Both 2D and 3D tapping mode SPM images also show the same tendency of nanostructure development and degree of compaction, in accord with cryo-SEM images.
Figure 3.25 SPM images of the top surface of Sample VF1 after three hours of annealing at 20°C.
Figure 3.26 SPM images of the top surface of Sample VF2 after three hours of annealing at 30°C.
Figure 3.27 SPM images of the top surface of Sample VF3 after three hours of annealing at 40°C.
Figure 3.28 SPM images of the top surface of Sample VF4 after three hours of annealing at 50°C.
As shown in Figure 3.29, in the low temperature Region 1, polymer is hard like a Hookean solid and its Young’s modulus $E$ varies slowly with temperature. In the transition Region 2, $E$ falls rapidly as temperature rises. This accounts for the rapid decline of the elastic part of the moduli of latex particles as the glass transition temperature was approached, as manifested by the degree of compaction by annealing at $20^\circ\text{C}$ and $30^\circ\text{C}$ being slight and about the same, whereas it was great when the annealing temperature was $40^\circ\text{C}$ and $50^\circ\text{C}$, near and above the nominal $T_g$ of $45^\circ\text{C}$, respectively.

Figure 3.29 Temperature dependence of Young’s modulus of a representative amorphous polymer ($T_1<T_2$) (Lagakos, Jarzynski, Cole and Bucaro 1986; Ferry 1980; Perepechko 1981). What is most important is that Young’s modulus increases rapidly across the transition region, i.e. the value of Young’s modulus of glassy, or “plastic” polymers is two orders of magnitude greater than that of rubbery polymer.
3.4.4 Nanostructure Development over Annealing Time

To investigate how particles deformed with time, four different annealing times were chosen: three, six, twelve and twenty-four hours. They were all at the same annealing temperature of 40°C, chosen because it is close to the glass transition temperature, so that compaction advances in twenty-four hours and coalescence begins. In this section, cryo-SEM images of fracture surfaces of the samples are discussed along with SPM images of a sample annealed twenty-four hours. A rewetting test was done on the same selected sample, as described in Section 3.3.7.

Annealing the coating at 40°C for three hours altered the nanostructure a lot from its initial freeze-dried state shown in Figure 3.20 and discussed in Section 3.4.3. Well compacted hexagonal packing of latex particles were observed by cryo-SEM on the top surface of the annealed coating. In Figure 3.20, the degree of compaction is greatly advanced beyond what is seen in the images in Figure 3.16 and Figure 3.18 from the coating annealed at 20°C and 30°C.

Doubling the annealing time to six hours at 40°C produced the nanostructure altered further from that after three hours of annealing. Figure 3.30 shows a fracture surface of Sample VF5 annealed six hours at 40°C. It’s quite obvious that the latex particles flattened more. Beyond that, pullout features show up in the fracture surface and some bridge a couple of particles. These pullouts indicate that enough coalescence occurred during the annealing to generate sufficiently strong adhesion of the latex particles, that many of them that remain in the fracture surface were plastically drawn by the fracture before breaking from their counterparts in the complementary fracture surface. The bridging of some of the pullouts also indicates some degree of coalescence (Ge 2004).
Figure 3.30 Cryo-SEM image of the fracture surface of Sample VF5 that was frozen without drying after three hours of freeze-drying at –86°C, and six hours of annealing at 40°C, the nominal MFFT. Latex particles were well flattened against each other. The Bridging of pullouts indicated coalescence between those adjoining particles. Pore spaces shrank but still visible.

Doubling the annealing time again to twelve hours at 40°C produced still more change. In Figure 3.31, again a cryo-SEM image of the fracture surface of Sample VF6, the particles still retain their individuality yet are even more deformed, i.e. flattened against one another. The pullout features are more prominent in Figure 3.31 and some of them bridge bunches of latex particles, indicating that coalescence occurred between these latex particles during annealing and progressed further than it had in six hours. The pore spaces between latex particles were also diminished compared to those after three and six hours of annealing.
Figure 3.31 Cryo-SEM image of the fracture surface of Sample VF6 that was frozen without drying after three hours of freeze-drying at –86°C, and twelve hours annealing at 40°C, the nominal MFFT. Particles were more flattened. More bridged pullout features were captured and indicated greater degree of coalescence. Pore spaces shrank more but still visible.

When the annealing time was doubled yet again to twenty-four hours at 40°C, the nanostructure became even more different from that after only three hours at 40°C; it became quite similar, however, to that after annealing for just three hours at the higher temperature of 50°C. Figure 3.32 is a cryo-SEM image of the fracture surface of Sample VF7 annealed for twenty-four hours at 40°C. The latex particles are almost totally compacted. And although most of them can still be individually identified, the boundaries between some are blurred and it is difficult to make out every latex particle. Again, some pullouts are bridged between particles. Between some of those particles are pockets lined
Chapter 3  

On van der Waals Force of Latex Film Formation  

by flattened faces of what must be now-polyhedral particles. From those pockets must have been plucked particles by the complementary fracture surface, the fracture passing locally through planes between particles on which adhesion was not strong enough to cause pullouts. This cryo-SEM image is quite similar to that in Figure 3.24, which is the fracture surface of Sample VF4 annealed for three hours at 50°C.

Figure 3.32 Cryo-SEM image of the fracture surface of Sample VF7 that was frozen without drying after three hours of freeze-drying at – 86°C, and twenty-four hours annealing at 40°C, the nominal MFFT. Particles were more flattened. More pullout features and bridging of them were captured, which indicated greater degree of coalescence. Pore spaces shrank more and are almost undetectable.

Tapping mode SPM was used again to image the top surface of Sample VF7 annealed twenty-four hours at 40°C and then cooled to room temperature. Figure 3.33 is the image. Comparing it with Figure 3.28 reveals that the boundaries between the latex particles on
the top surface were still distinct after twenty-four hours annealing at 40°C, but not after only three hours of annealing at a higher temperature of 50°C. Thus it appears that the degree of coalescence of the coating after twenty-four hours of annealing at 40°C was less than after three hours of annealing at 50°C. In this respect, changing annealing temperature by 10°C in the MFFT — $T_g$ range has much greater effect than changing the annealing time by hours. But the nanostructure development is plainly a function of both temperature and time of annealing. Above the glass transition temperature the time-temperature superposition probably applies; whether it does in the range of temperatures chosen here has not been investigated.

3.4.5 Relationship between Annealing Temperature and Time

As described by room temperature SEM and cryo-SEM images of both top surface and fracture surface of coatings after annealing, it is evident that the compaction and early coalescence stages of latex film formation in bone-dry condition devoid of capillary forces are driven by the action of the van der Waals force, which itself is independent of temperature. As noted just above, the degree of compaction could be the same after a relatively long annealing at 40°C and after a much short annealing time at 50°C — although the degree of coalescence, another matter, could be a lot less at the lower temperature.
Figure 3.33 SPM images of the top surface of Sample VF7 annealed twenty-four hours at 40°C.
The role of time that is demonstrated by the foregoing results is clear evidence of viscous-like resistance of the latex particles to deformation by the loads imposed by the attractive van der Waals force that must act around the perimeters of particle-particle contacts, as diagrammed in Figure 3.34. Moreover, the sharpness of the wedge’s corner suggests that elastic response is strong on scales no less than about 10 nm. These forces are the so-called crack-closing forces discussed above at Section 3.2. The viscous-like resistance can arise in three ways, as also shown in Figure 3.35:

1. Viscoelastic deformation, \textit{i.e.} change of elastic stress-free state by the imposed elastic stress at a rate that depends on the “loss modulus” or “viscoelastic viscosity”, as in the classical viscoelastic model of uncrosslinked rubbery polymer. When the imposed stress is released, the particles take the shape dictated by their new elastic stress-free state. That shape is necessarily different from their original spherical shape.

2. Elastoviscoelastic deformation, \textit{i.e.} deformation in which the elastic stress-free state does not change, so that when the imposed stress is removed, the particles take their original spherical shape. In this case, the “storage modulus” or “elastoviscoelastic modulus”, as well as the deformation, changes at a rate that depends the “elastoviscous viscosity”, as in the standard model of elastoviscous solids. In the closely related elastoviscous deformation, the “storage modulus” does not change.

3. Elastoviscoplastic deformation, \textit{i.e.} deformation in which the elastic stress-free state does not change until the load exceeds the yield stress and then changes on a rate that depends on the “post-yield viscosity”, as in established models of plastic yielding of various solids including glassy polymer.
Figure 3.34 Diagram of attractive van der Waals force acting across the annular wedge-shaped clearance around the perimeter of interparticle contact. The van der Waals force, plus perhaps other short-range adhesion forces, must also act across the contact area within the wedge-shaped annulus.

Figure 3.35 Diagrams of four common models: Elastoviscoelastic — “Standard model”; Elastoviscous — “Voigt model”; Viscoelastic — “Maxwell model” and Elastoviscoplastic.
The three mechanisms can be simply distinguished if the latex particles can be separated and thereby unloaded. Only those whose deformation in the compacted coating was elastoviscoelastic regain their spherical shape. To distinguish between viscoelastic deformation, the first mechanism, and elastoviscoplastic deformation it is necessary to separate and thereby unload the particles at successive degrees of compaction. If at low degrees they regain their original spherical shape, whereas at higher degrees they retain progressively more of their flattening, the mechanism is elastoviscoplastic. If no such threshold of permanent deformation can be detected, the mechanism can be declared to be viscoelastic, which is the limit of elastoviscoplastic when the yield stress falls to zero.

For the viscoelastic mechanism there is a well-known time-temperature superposition approximation when the deformation is sufficiently small. It is the WLF (Williams-Landel-Ferry) equations (Ferry 1980):

\[
\log a_t = -\frac{C_1^0 (T - T_0)}{C_2^0 + T - T_0}
\]

An equivalent form of WLF expression is:

\[
a_t = \exp\left[\frac{1}{\beta(T - T_x)} - \frac{1}{\beta(T_0 - T_x)}\right]
\]

The variable \( a_t \) brings the time dependence into the relationship as a frequency scale shift factor. Constants \( C_1^0 \) and \( C_2^0 \) will be different for different materials, and will be defined at the reference temperature \( T_0 \). These two constants are usually determined
empirically. $\beta$ is related to the thermal expansion coefficient of the fractional free volume and $T_\infty$ is the temperature where free volume would go to zero in the absence of $T_g$.

It seems that the others mechanisms are not recognized in the literature on latex film formation. For example, in 1998, Jagoda, Argento and Mazur examined the viscoelastic model of growth of adhesive contacts for a sphere on a rigid plane (Jagota et al. 1998). They restricted their attention to sintering by viscoelastic deformation and divided the whole process into two parts: initial elastic adhesion and viscous sintering. The initial elastic contact and early stage of time-dependent contact growth were in a zipping model of “contact closure” that was dominated by direct attraction force, i.e. van der Waals attraction force. The later stage was by stretching of contact, like a “neck growing”, by the curvature-based tractions. Later Lin, Hui and Jagota (2001) extended this topic into what they called viscoelastic adhesive contact between two spherical, linearly viscoelastic “Maxwell” particles. But they dealt only with the viscoelastic model and didn’t pay any attention to the other three important models: elastoviscoelastic, elastoviscous and elastoviscoplastic, which are shown and illustrated in Figure 3.35.

Yaqing Ming (1996) discovered that in some cases, at least, the deformed particles of compacted coatings can be separated, and thereby unloaded, by immersing them in water. Presumably this is possible only if the strength of adhesion between particles can be overcome by diffusion of water into the interparticle contacts, perhaps assisted by swelling of hydrophilic groups there (as may remain from colloidal stabilizer present on the particle surfaces in suspension). A related, less definitive rewetting test is described in Section 3.3.7 and results from it are discussed next.
3.4.6 Implication for Mechanism of Compaction and Coalescence

Rewetting tests were done by dipping the annealed latex coatings into deionized water for 24 hours at room temperature: compare Table 3.2. Figures 3.36, 3.37, 3.38 and 3.39 are cryo-SEM images of top surfaces of rewetted latex coatings that had been annealed for three hours at 20°C, 30°C, 40°C and 50°C, respectively, prior to rewetting.

Figure 3.36 Cryo-SEM image of the top surface of Sample RW1 that had been annealed at 20°C for three hours. The latex particles in the top surface rounded up and separated, after twenty-four hours of rewetting in deionized water at room temperature. The implication is that the flattening of latex particles against each other was elastic and reversible. A lot of “junk” appeared after rewetting on the top surface; presumably it consists of swellable residues that had been collapsed and trapped by the freeze-drying.
Table 3.2 Details of the samples whose images are used here to illustrate change in nanostructure after rewetting.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Freeze-drying, annealing &amp; rewetting information</th>
<th>Image information</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample information</td>
<td></td>
</tr>
<tr>
<td>RW1 (VF1)</td>
<td>20 °C, 3 hours</td>
<td>Cryogenic images</td>
</tr>
<tr>
<td>RW2 (VF2)</td>
<td>30 °C, 3 hours</td>
<td></td>
</tr>
<tr>
<td>RW3 (VF3)</td>
<td>40 °C, 20 minutes</td>
<td>Cryogenic images</td>
</tr>
<tr>
<td>RW4 (VF4)</td>
<td>50 °C, 24 minutes</td>
<td></td>
</tr>
<tr>
<td>RW5 (VF7)</td>
<td>40 °C, 24 minutes, 5 minutes</td>
<td></td>
</tr>
</tbody>
</table>

a) All these samples were freeze-dried at – 86°C for three hours prior to rewetting.

b) All these sample were rewetted by 24 hours of immersion in deionized water at room temperature.

c) All samples were sputter-coated at $1 \times 10^{-3}$ Pa with platinum to a nominal layer thickness of about 5 nm; the temperature was about – 120°C.
On the top surfaces of Sample RW1 and RW2 that had been annealed at 20°C and 30°C for three hours, the particles that were previously partly flattened separated and rounded back into spherical shape, as shown in Figure 3.36 and Figure 3.37. These two images demonstrate that the flattening was reversible, *i.e.* elastic. So it is obvious that deformation by van der Waals force alone was either elastoviscoelastic, or elastoviscous, or short-time viscoelastic, *i.e.* so short as to be virtually elastic.

Figure 3.37 Cryo-SEM image of the top surface of Sample RW2 that had been annealed at 30°C for three hours. The latex particles in the top surface rounded up and separated after twenty-four hours of rewetting in deionized water at room temperature. The implication is that the flattening of latex particles was elastic and reversible. A lot of “junk” appeared after rewetting on the top surface; presumably it consists of swellable residues that had been collapsed and trapped by the freeze-drying before annealing.
On the top surface of Sample RW3 that has been annealed at 40°C for three hours, some particles separated and rounded up but the others remained in contact and partly flattened against each other, as shown in Figure 3.38. If all the particles deformed the same mechanism, then the flattening was elastic and it was the adhesion between some particles that prevented them from separating and rounding up. Alternatively, the separated particles deformed elastically but the adhering ones were flattened permanently, i.e. their stress-free state had changed and their deformation was either viscoelastic or elastoviscoplastic.

Figure 3.38 Cryo-SEM image of the top surface of Sample RW3 that had been annealed at 40°C for three hours. Some latex particles in the top surface rounded up but others remained in contact and flattened after twenty-four hours of rewetting in deionized water at room temperature. The pore spaces between latex particles obviously expanded during rewetting, which implies swelling of the coating and bulging outward of its surface region. No “junk” is visible, presumably because something happened during annealing.
On the top surface of Sample RW4 had been annealed at above $T_g$, 50°C, for three hours, the particles neither separated nor rounded out, as shown in Figure 3.39. In fact, individual particles cannot be discerned at all. Comparing Figure 3.39 with Figure 3.24 reveals that boundaries between particles disappeared only on the top surface and not in the interior during annealing — evidence that a “skin” had formed in the surface zone. If the flattening was elastic or elastoviscoelastic, adhesion and coalescence prevented particles in the top surface from separating. Alternatively, if the flattening was permanent because the stress-free state had already changed, latex particles were either viscoelastically or elastoviscoplasticly deformed.

Figure 3.39 Cryo-SEM image of the top surface of Sample RW4 that had been annealed at 50°C for three hours. No latex particle in the top surface rounded up or separated after twenty-four hours of rewetting in deionized water at room temperature. No individual particles can be discerned and almost certainly coalescence did occur during annealing at 50°C.
On the fracture surface of a rewetted coating that had been annealed at the lower temperature of 40°C for twenty-four hours, many of the latex particles remained distinguishable but neither separated nor rounded up, as shown in Figure 3.40. If the flattening was elastic and partial coalescence prevented particles from separating, the deformation was viscoelastic. If the flattening was permanent because the stress-free state changed, the deformation was either viscoelastic or elastoviscoplastic.

Figure 3.40 Cryo-SEM image of the fracture surface of Sample RW5 that had been annealed at 40°C for twenty-four hours. No latex particle in the fracture surface rounded up or separated after twenty-four hours of rewetting in deionized water at room temperature. Boundaries between latex particles still remained distinct and bridged pullout features can be seen.

These results of the rewetting test are informative. But they need to be augmented by tests by total immersion like those of Yaqing Ming and additional tests in which the
immersed coating is subjected to varying degrees of sonication to see if adhesion and the beginnings of coalescence can be overcome and apparently coalesced coatings can be redispersed.

Further experiments are desirable to distinguish among the mechanisms of deformation. Tensile testing of modulus and strength of a coating can help distinguish if there was interdiffusion and interpenetration between particles in contact, or they were merely strongly adhering by van der Waals and other short range forces. Whatever the mechanisms of compaction and coalescence, it is evident that van der Waals force is the force that drives the compaction of the freeze-dried latex coatings.

And there is challenge to understand the fine features in Figure 3.9 again in Figure 3.36 and Figure 3.37, which might be “junk” from the serum as discussed. What is puzzling is this kind of feature is absent from Figure 3.38, which is of Sample RW3 annealed at a higher temperature, 40°C. Questions are where the “junk” went during freeze-drying and annealing, and how it reappears — or does not — A mystery!

3.5 Closure

Fast freezing, controlled freeze-drying and annealing under vacuum, followed by room temperature and cryogenic Scanning Electron Microscopy, complemented by room temperature tapping mode Scanning Probe Microscopy, proved to be a potent combination for investigating the role of van der Waals force in latex film formation under bone-dry condition. Both Scanning Electron Microscopy and Scanning Probe Microscopy images demonstrated that van der Waals attraction force alone can indeed compact a latex coating under conditions devoid of surface tension and capillary forces.
That means that capillary forces, which occur only at liquid surfaces in wet and moist coatings, are not necessary for latex film formation. When they are present they surely can promote the speed of film formation, however.

The data are still insufficient to test quantitatively the conventional time-temperature superposition rule from linear viscoelasticity. Rewetting tests of the coatings annealed for the same time at different temperatures can distinguish elastic and inelastic, \textit{i.e.} viscoelastic deformation; they can also shed light on the fate of grafted colloidal stabilizer and soluble constituents of the original suspending liquid.
Chapter 4

New Insights into the Freeze-Thaw Stability of Polymer Latexes

4.1 Introduction

Freeze-thaw (F/T) stability of polymer latexes and waterborne coating formulations is of considerable industrial importance because of the need to store and transport these products within cold areas during winter, and because of the energy and hardware costs that will otherwise incur if heated transportations and storages are necessary. The requirement of being freeze-thaw stable is that the suspension of polymer particles in water maintains its original properties, such as rheology and absence of coagula, after repeated freeze-thaw cycles. For example, F/T stability of latex paints has long been achieved by addition of antifreezes such as glycols (Bosen et al. 1985). However, environmental concerns and legislative measures have in recent years created a new driving force for the coatings industry to develop low-VOC or zero-VOC (Volatile Organic Compounds) waterborne formulations. In a lower-VOC formulation, the total volatile organic compounds cannot exceed 50 g/L. Then the amount of glycols that can be added into the formulations has to be substantially reduced and is most probably no longer sufficient to impart F/T stability by depressing the freezing point of the aqueous medium and/or by altering the pattern of ice crystal formation. It is a challenging goal that the next-generation polymer latexes need to be improved in such a way that they are not only freeze-thaw stable themselves but are also capable of providing freeze-thaw stability to the coatings formulations which are based on them.
Despite its importance, fundamental aspects of freeze-thaw stability have not been studied extensively and are not well-understood yet. Perhaps because of the lack of adequate experimental and analytical techniques, it has not been possible to elucidate micro-structural changes occurring during the F/T processes. Blackley (1997) gives a comprehensive review of colloidal destabilization of latexes by freezing. The freezing process starts with the reduction of temperature which leads to the appearance of a third phase: pure ice. The formation of ice crystals progressively increases polymer particle concentration in unfrozen water and frequency of encounters between particles. Eventually polymer particles are forced into contact with each other under the high pressures from the growing ice crystals, resulting in rapid particle aggregation and interparticle coalescence. In the case of F/T instability, it has not been possible to conclude whether coagulation takes place during freezing or during thawing, because one can judge the freeze-thaw stability only after thawing process is completed. For this reason, freeze-thaw stability covers both the freezing and thawing processes without pinpointing the precise stage in which colloidal destabilization actually occurred. Although Blackley discussed several factors expected to affect inter-particle coalescence during freezing and thawing, no technique was available to demonstrate that interparticle coalescence was really involved.

The influence of polymer hardness or glass transition temperature (Tg) on latex freeze-thaw stability is also inconclusive, if not contradictory, in published work. While there does not appear to be a correlation between F/T stability and the Tg of the copolymer latexes studied by Digioia and Nelson (1953) and Barb and Mikucki (1956), results from King and Naidus (1969) and Naidus and Hanzes (1969) point to an unambiguous interdependency between the two properties: the harder polymers require
less protective groups to achieve F/T stability than the soft ones, and vice versa. There has not been much work on the effect of polymer molecular weight on F/T stability. Barb and Mikucki’s investigation (1956) indicates that within the range studied (60K to 4M Daltons), molecular weight does not appear to affect F/T stability. The only published work that we know of, which studied the effects of freezing and thawing separately, was carried out by Nakamura and Okada (1976), who came to the conclusion that coagulation does not occur in the process of thawing. However, their study was based on chloramphenicol suspensions used in the pharmaceutical industry. The particle sizes ranged from about 800 nm to 70 microns in diameter and are thus much larger than those of the polymer latex particles typically used in the coatings industry.

The objective of the study in this chapter is to clarify and better understand the effects of key factors affecting the F/T stability of polymer latexes. The following factors were investigated: glass transition temperature, moduli, molecular weight, particle size, amount of stabilizing functional groups, amount of coalescent, freezing and thawing rates. In contrast to most of the previously published work, we prepared model polymer latexes with well-controlled particle sizes and compositions. In addition to following the viscosity changes during repeated freeze-thaw cycles, we apply advanced cryogenic scanning electron microscopy (cryo-SEM) techniques coupled with a high-pressure freezing apparatus, which allows us to visualize micro-structural changes and to study the effects of the freezing and thawing processes separately. The relationships between F/T stability and polymer and colloidal characteristics were analyzed, and we also tried to gain information on the cause of viscosity rise during the freezing and thawing processes in an freeze-thaw unstable latex.
4.2 Experiments

4.2.1 Latex Synthesis

The acrylic polymer latexes were synthesized by a seeded semi-continuous emulsion polymerization process under monomer-starved conditions. The seeded process affords easy control of particle size while the slower-than-polymerization feed rates for the monomers avoid composition drift in the copolymers formed throughout the polymerization process. Two surfactants, a sulfated fatty alcohol ethoxylate with $C_{12-14}$ hydrophobes and 30 EO units and sodium dodecyl sulfate (SDS), were used. Two pairs of monomers were used in making up the backbones of the model copolymer latexes: methyl methacrylate and n-butyl acrylate (MMA/BA), and MMA and 2-ethylhexyl acrylate (MMA/EHA). By maintaining the seed level and varying the ratio of the two monomers in each pair, the glass transition temperature of the polymer latex can be easily manipulated while the particle size stays the same. Functional co-monomers, such as acrylic acid (AA), methacrylic acid (MAA) and acrylamide (AM), were also incorporated either alone or in combination for further enhancing the latex stability. The latexes were neutralized with ammonia to pH value of 8 to 9 at the end of the synthesis. The copolymer compositions along with basic physical properties are listed in the following sections where they are studied. The particle sizes were determined using photon correlation spectroscopy and glass transition temperatures by differential scanning calorimetry (DSC) at 20 °C/min. The number average particle size and midpoint temperature in the glass transition region are reported.
4.2.2 Freeze-Thaw Stability Test

The freeze-thaw stability of polymer latexes was evaluated based on ASTM standard test method D2243-95. Typically, a pint of latex or paint (in a one-pint plastic can) is stored at 0 °F (-18 °C) for about 17 hours and then removed and allowed to thaw for 7 hours undisturbed at ambient temperatures. This completes one freeze-thaw cycle. The thawed latex is then gently stirred by hand with a tongue depressor before measurement of the Brookfield viscosity (spindle #2 at 50 RPM). The thawed sample is also subjected to cryogenic scanning electron microscopy examination after being fast frozen at high pressure, as described below.

4.2.3 High Pressure Freezing, Fracture, Surface Treatment and Cryo-SEM

The detailed sample preparation procedure has been described elsewhere (Huang et al. 1999; Sutanto et al. 2000). A droplet of polymer dispersion is sandwiched between two brass discs each with a cylinder-shaped indentation. The assemblage is then quickly frozen in a Bal-Tec HPM 010 high pressure freezing machine at 2100 bar. High pressure freezing is critically important for minimizing disturbance by large ice crystals to the original morphology of an aqueous sample. It works as follows: high pressure lowers the temperature range of supercooled water from 233–273 K at atmospheric pressure to 183–251 K at 2100 bar so that freezing water has a better chance to reach the glass transition temperature and be vitrified before ice crystals grow, as illustrated in Figure 4.1. The frozen sandwich is then fractured in liquid nitrogen. One side of the fractured sample is mounted on a cryo-transfer stage and metal-coated. The metal-coated fracture surface sits on the cold stage and is examined in the in-lens Hitachi S900 field emission scanning
electron microscope. Both secondary electron (SE) and backscattered electron (BSE) images are recorded. The former provides better topographical contrast while the latter is more preferred for maximum contrast between organic and inorganic phases. Unless otherwise specified, the electron micrographs shown in this chapter are SE images.

Figure 4.1 Phase diagram of supercooled water under high pressure: high pressure lowers the temperature range of supercooled water from 233–273 K at atmospheric pressure to 183–251 K at 2100 bar, which makes it easier for the freezing water to reach the glass transition temperature and be vitrified before ice crystals grow.
4.3 Results and Discussion

4.3.1 Glass Transition Temperature and Freeze-Thaw Stability

As reviewed in the introduction, there are contradictory reports in the literature with regard to the effect of glass transition temperature on latex freeze-thaw stability. The copolymer latexes studied by Digioia and Nelson (1953) and Barb and Mikucki (1956) did not appear to have a correlation between the glass transition temperature and F/T stability. While results from King and Naidus (1969) and Naidus and Hanzes (1969) clearly show that F/T stability depends on the polymer Tg: the harder polymers require less protective groups to achieve same F/T stability than the soft ones, and vice versa.

To better understand the influence of Tg on the F/T stability, we prepared eight MMA/EHA copolymer latexes using the same amounts of seed (target particle diameter 190 nm), surfactants and acrylic acid, but different ratios of the two main monomers. By changing the ratios of the two monomers, we prepared polymers with a Tg range covering about 45 °C (from –11 to 33 °C). The solids contents of the latexes are all around 50%. The viscosities of the original latexes as well as those after each F/T cycle were measured using a Brookfield viscometer (#2 spindle at 50 RPM), and are represented in Figure 4.2.

Figure 4.2 illustrates that below 23 °C, as Tg continues to decrease, there is more and more viscosity increase for the latex over the F/T test cycles. The rise of latex viscosity during F/T cycles is a clear indication of F/T instability of the polymer latex particles. The reason behind such a viscosity increase will be discussed later in conjunction with
the cryogenic microscopic observations. When Tg is at and below 0 °C, the polymer latexes can no longer survive five F/T cycles: they failed through total coagulation before completion of the test cycles. The transition from F/T stability to F/T instability occurs over the Tg range of 15 - 0 °C. In summary, the higher-Tg latexes experience less viscosity increase over the F/T cycles than lower-Tg ones and therefore have better F/T stability. Our results thus support the findings by King and Naidus (1969) and Naidus and Hanzes (1969).

**Latex Viscosity (cps)**

![Graph showing the influence of polymer Tg on F/T stability of latexes](image)

**Tg of Polymer (°C)**

Figure 4.2 Influence of polymer Tg on F/T stability of latexes. The polymers are based on MMA/EHA (methyl methacrylate/ 2-ethylhexyl acrylate). With all other parameters maintained constant, different Tg’s are achieved by varying the ratio of MMA to EHA. The particle sizes of the latexes are all around 190 nm in diameter.
4.3.2 Particle Size and Freeze-Thaw Stability

Another principal latex property that could affect freeze-thaw stability is latex particle size. To better evaluate the effect of particle size, we prepared three series of nine latexes, with glass transition temperatures at −11, 0 and 33 °C, and target particle sizes at 90 nm, 190 nm and 360 nm, using the same basic recipe as that described in the preceding section 4.3.1. In each series, the same Tg was obtained by maintaining the MMA/EHA ratio constant while varying the level of seed to achieve three different particle sizes. All latexes are stabilized by the same amounts of surfactants and acrylic acid. The solids contents of the latexes are again all around 50%. The viscosities of the original latexes as well as those after each F/T cycle are reported in Figure 4.3.

The results in Figure 4.3 show a clear correlation between particle size and F/T stability. At the same Tg, the smaller the particle size, the worse the F/T stability. The phenomenon can be explained by the fact that at the same solids content, a smaller-sized latex has a larger surface area that needs to be protected than a larger-sized one. In another way, it can also be explained as the interparticle contact areas will be larger as the particle size increases, which could provide a stronger repulsive effect on the contacting polymer particles. This particle size dependency of F/T stability is in agreement with the findings of Nakamura and Okada (1976), although their study was based on suspensions of much larger non-polymeric particles with sizes ranging from about 800 nm to 70 microns. With variations in both particle size and Tg, data in Figure 4.3 also confirm the effect of Tg on F/T stability.
Figure 4.3 Influence of polymer particle size as well as Tg on F/T stability of latexes. The polymers are based on MMA/EHA. For each Tg (−11, 0 or 33 °C), three target particle sizes are investigated: 90 nm, 190 nm and 360 nm.
4.3.3 Dynamic Mechanical Properties and Freeze-Thaw Stability

A series of five latexes were prepared to better understand this correlation. Here instead of the copolymer composition based on MMA/EHA, a different pair of acrylic monomers that are also commonly used in the coatings industry were utilized: methyl methacrylate and n-butyl acrylate (MMA/BA). For latex stabilization, polymerizable functional monomers acrylamide (AM) and methacrylic acid (MAA), at 2% of each, were incorporated, in addition to the two surfactants, sulfated fatty alcohol ethoxylate with C_{12-14} hydrophobes and 30 EO units and sodium dodecyl sulfate (SDS), at 1% of each based on total polymer weight. The solids contents of the latexes are about 40%. The latexes were neutralized with ammonia to pH values around 8.5. Table 4.1 summarizes the basic characteristics and the freeze-thaw stabilities of the five latexes.

Table 4.1  Characteristics of Latex Samples Used in Dynamic Mechanical Studies

<table>
<thead>
<tr>
<th>Composition*</th>
<th>Particle Diameter (nm)</th>
<th>Tg (°C)</th>
<th>F/T stability (5 Cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. 45 BA/51 MMA/2 MAA/2 AM</td>
<td>143</td>
<td>29</td>
<td>Stable</td>
</tr>
<tr>
<td>B. 50 BA/46 MMA/2 MAA/2 AM</td>
<td>145</td>
<td>24</td>
<td>Stable</td>
</tr>
<tr>
<td>C. 55 BA/41 MMA/2 MAA/2 AM</td>
<td>146</td>
<td>14</td>
<td>Viscosity increased 2 times</td>
</tr>
<tr>
<td>D. 60 BA/36 MMA/2 MAA/2 AM</td>
<td>146</td>
<td>6</td>
<td>Viscosity increased 30 times</td>
</tr>
<tr>
<td>E. 80 BA/16 MMA/2 MAA/2 AM</td>
<td>149</td>
<td>-18</td>
<td>Coagulated in first cycle</td>
</tr>
</tbody>
</table>

* MMA = Methyl Methacrylate; BA = n-Butyl Acrylate; MAA = Methacrylic Acid; AM = Acrylamide

Despite significant differences in stabilization and polymer backbone structure than the EHA/MMA model latexes, data in Table 4.1 based on BA/MMA/MAA/AM essentially
lead to the same conclusion: freeze-thaw stability of polymer latexes depends on glass transition temperature and suffers drastically once the Tg is reduced to a certain range, from 14 to 6 °C, in the current series. As for the case of the EHA/MMA latexes, this transition also occurred approximately in the similar range (15 - 0 °C). To understand why F/T stability is lost when Tg is reduced to the 15-0 °C range, we measured the dynamic mechanical properties of these five latex films (dried at ambient conditions for about 24 hours). The storage moduli as a function of temperature are displayed in Figure 4.4.

Latexes A and B do not experience any viscosity change after five F/T cycles. Starting from sample C, however, there is substantial viscosity increase (Viscosity increased 2 times). After five F/T cycles, the viscosity of latex D has increased by a factor of 30. Latex E even coagulated during the first F/T cycle. After carefully evaluation of the data plotted in Figure 4.4, we consider that the modulus of the polymer around 0 °C could be a key parameter in determining the F/T stability of the latex, as that is the temperature at which ice crystals form and grow until the whole aqueous latex is frozen. A higher modulus around 0 °C would provide more resistance to particle deformation and coalescence, and therefore more F/T stability. We mention “around 0 °C” because the actual freezing point of the latex suspensions might be suppressed by the presence of impurities such as electrolytes in the aqueous phase. Latexes C, D and E have gradually decreasing moduli around 0 °C and progressively worsening their F/T stabilities.

The importance of polymer modulus in resisting particle deformation and coalescence has been recognized in early work on latex film formation. Refining the analysis of Brown (1956), Mason (1973) developed new criteria for particle deformation due to the capillary pressure when the shear modulus $G$ of the polymer obeys the inequality:

$$G \leq 266 \sigma / R$$
where $\sigma$ is the air-water interfacial tension and $R$ is the latex sphere radius, capillary pressure can cause particle deformation. With $\sigma = 72$ dynes/cm and $R = 75$ nm, we obtain $G \leq 2.6 \times 10^8$ Pa for our latex systems. Thus according to Mason’s equation, when the shear modulus of our latex polymer is less than $2.6 \times 10^8$ Pa, the latex particles will not be able to resist deformation and coalescence may take place.

![Graph](image)

Figure 4.4 Storage moduli of polymer latex films as a function of temperature. The polymers are based on MMA/BA and their characteristics summarized in Table 4.1. Note that latexes A and B have perfect F/T stability. From latexes C through E, F/T stability increasingly worsens: latexes C and D experience significant viscosity increase over the F/T cycles; latex E completely coagulates during the first F/T cycle.
In Figure 4.5, we plot the viscosity increase (ratio of latex viscosity after 5 F/T cycles, $\eta_{FT}$, to the initial viscosity, $\eta_0$) as a function of the storage modulus of latex films at 0 °C based on data from Table 4.1 and Figure 4.4. It can be seen that the transition from F/T stability to instability indeed takes place when the modulus is reduced to less than about $2.5 \times 10^8$ Pa, which is in excellent agreement with Mason’s prediction for particle deformation and coalescence. Phenomenologically this also makes sense because, when the modulus is significantly reduced, the polymer becomes more “sticky” and polymer chains have increased mobility, allowing for easier coalescence and interparticle diffusion when the polymer particles are forced into contact with each other under the enormous pressures from the ice crystals.

**Viscosity Increase ($\eta_{FT}/\eta_0$)**

![Graph showing viscosity increase vs. storage modulus](image)

**Storage Modulus $G'$ at 0 °C**

Figure 4.5 Viscosity increase (ratio of latex viscosity after 5 F/T cycles, $\eta_{FT}$, to the initial viscosity, $\eta_0$) as a function of the storage modulus at 0 °C of latex films from Table 4.1 and Figure 4.4. Note that latex E ($G' = 4 \times 10^5$ at 0 °C) completely coagulated during the first F/T cycle and thus has theoretically an infinite viscosity increase.
4.3.4 Coalescent and Freeze-Thaw Stability

Coalescent is commonly used in formulating latex paints, although their usage will decrease due to the low-VOC requirement. To assess the impact of a coalescent on freeze-thaw stability, we used Latex A from Table 4.1 and post-added two different levels of TPM (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate with a trade name of Texanol from Eastman Chemical Company) to this latex. Films were dried for one day before glass transition temperature and dynamic mechanical measurements (Figure 4.6) were carried out. Data in Table 4.2 indicates that the addition of coalescing agent reduces Tg and freeze-thaw stability of the latex. In a similar trend as in Figure 4.4, the loss of F/T stability with addition of coalescent is a direct result of the reduction of the polymers moduli especially around 0 °C, as illustrated in Figure 4.6.

<table>
<thead>
<tr>
<th>Coalescent Level (wt.% on polymer)</th>
<th>Tg (°C)</th>
<th>F/T Stability (5 Cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>29</td>
<td>Stable</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>Coagulated in third cycle</td>
</tr>
<tr>
<td>30</td>
<td>-17</td>
<td>Coagulated in first cycle</td>
</tr>
</tbody>
</table>

* Latex A: 45 BA/51 MMA/2 MAA/2 AM with 143 nm in diameter.
Figure 4.6 Storage moduli of polymer latex films as a function of temperature. As summarized in Table 4.2, latex A has perfect F/T stability; at 10% coalescent (based on polymer weight), the latex coagulated during the third F/T cycle; at 30% coalescent, the latex coagulated during the first F/T cycle. Latex A from Table 4.1 is used for post-addition of two different levels of TPM.
**4.3.5 Molecular Weight and Freeze-Thaw Stability**

A series of four latexes, based on the same basic recipe as that for the samples in Table 4.1, were prepared to understand the correlation between molecular weight and freeze-thaw stability. A chain transfer agent, tert-dodecyl mercaptan (TDM), was incorporated at three different levels into the monomer feed to reduce the polymer molecular weight. Table 4.3 summarizes the basic characteristics and F/T stabilities of these 4 latexes.

<table>
<thead>
<tr>
<th>TDM** (wt.% on polymer)</th>
<th>Tg (°C)</th>
<th>Mn</th>
<th>Mw</th>
<th>F/T Stability (5 Cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18</td>
<td>57300</td>
<td>193400</td>
<td>Stable</td>
</tr>
<tr>
<td>0.2</td>
<td>16</td>
<td>47800</td>
<td>140000</td>
<td>Viscosity Increased 3 times</td>
</tr>
<tr>
<td>0.5</td>
<td>14</td>
<td>25000</td>
<td>88200</td>
<td>Viscosity Increased 4 times</td>
</tr>
<tr>
<td>1.0</td>
<td>13</td>
<td>16400</td>
<td>46200</td>
<td>Viscosity Increased 17 times</td>
</tr>
</tbody>
</table>

* Polymer composition: 52.5 BA/43.5 MMA/2 MAA/2 AM with 150 nm target particle diameter; ** TDM = tert-dodecyl mercaptan.

As can be seen in Table 4.3, reduction of polymer molecular weight has a detrimental effect on latex F/T stability. Although not totally coagulated, the latexes with higher
levels of TDM experience more pronounced viscosity rises over the F/T cycles. Inspecting the dynamic mechanical curves in Figure 4.7, we can notice the substantial reduction of the polymers moduli due to TDM in the temperature range from about 0 °C to 30 °C. Around 0 °C, however, the modulus reduction is measurable but not drastic. This explains the viscosity rise instead of total coagulation, of the molecular weight-reduced latexes. Our results here suggest that molecular weight does affect latex F/T stability. Although the reduced molecular weight doesn’t kill the freeze-thaw stability, the viscosity increase is still noticeable. This contradicts the findings of Barb and Mikucki (1956).

Figure 4.7 Storage moduli of polymer latex films as a function of temperature. As reported in Table 4.3, the latex without any chain transfer agent has perfect F/T stability. With increasing level of the chain transfer agent, however, the latexes experience more pronounced viscosity rises over the F/T cycles.
4.3.6 Functional Groups and Freeze-Thaw Stability

The work by King and Naidus (1969) and Naidus and Hanzes (1969) have revealed that carboxylic acid groups are a key factor in imparting freeze-thaw stability to latex particles. To verify this effect, we synthesized 2 more latexes based on Latex A from Table 4.1 with reduced amounts of methacrylic acid and acrylamide. The significance of the data, which are summarized in Table 4.4, is not only that fewer stabilizing groups lead to reduced F/T stability, which is expected, but also the implication that hardness (glass transition temperature, or modulus of the polymer) is not a sufficient condition for F/T stability. In other words, high Tg or high modulus alone cannot guarantee F/T stability.

<table>
<thead>
<tr>
<th>Polymer Composition*</th>
<th>Particle Diameter (nm)</th>
<th>Tg (°C)</th>
<th>F/T stability (5 Cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 BA/51 MMA/2 MAA/2 AM</td>
<td>144</td>
<td>29</td>
<td>Stable</td>
</tr>
<tr>
<td>45 BA/53 MMA/1 MAA/1 AM</td>
<td>145</td>
<td>30</td>
<td>Stable</td>
</tr>
<tr>
<td>45 BA/55 MMA/0 MAA/0 AM</td>
<td>143</td>
<td>25</td>
<td>Coagulated in first cycle</td>
</tr>
</tbody>
</table>

* MMA = Methyl Methacrylate; BA = n-Butyl Acrylate; MAA = Methacrylic Acid; AM = Acrylamide.

All three latexes are also stabilized by two surfactants, sulfated fatty alcohol ethoxylate with $C_{12-14}$ hydrophobes and 30 EO units and sodium dodecyl sulfate (SDS), at 1% of each based on total polymer weight.
4.3.7 Cryogenic SEM Observation of Freeze-Thaw Stability

In a previous publication (Zhao et al. 2006), we examined the structures of coagulated latexes after regular freeze-thaw cycles, as well as latex paints using the high-pressure freezing technique and cryogenic scanning electron microscopy. Coalescence of polymer particles and segregation of pigment particles were revealed. Here we focus on the causes for the viscosity increase of the latexes, which are stable enough to avoid severe coagulation, during the F/T cycles.

The viscosity of Latex D increased by 30 (Table 4.1) after five F/T cycles. This latex was examined before any F/T cycle and after five. The scanning electron micrographs of these samples are shown in Figure 4.8. Comparing the two micrographs in Figure 4.8, we can see the presence of loosely associated particle aggregates in Latex D after five F/T cycles. Such a relatively diffuse aggregate structure, which presumably is caused by the high pressures from the ice crystals during the freezing process, has been known to increase drastically the latex viscosity (Bicerano, Douglas and Brune 1999). The reason for this loose aggregation occurring instead of total coagula forming is probably that the latex particles, when forced into contact, fall into the secondary minimum instead of the primary minimum of their interaction potential, as illustrated in figure 4.9. The secondary minimum is at relatively large distance and the depth is proportional to the particles size of the polymer latexes. The flocculation results upon collision of the latex particles, which adhere without coalescing. The loosely flocculated aggregates explain the viscosity increase and, yet, are redispersible.
Figure 4.8 Cryo-SEM images of Latex D before F/T test, on the left, and Latex D after 5 F/T cycles, on the right. The viscosity of Latex D increased by a factor of 30 after 5 F/T cycles. Refer to Table 4.1 for more sample details. The latexes were diluted to a solids content of 5% before cryo-SEM investigation.
Figure 4.9 Diagram of the electrostatic repulsion vs. dispersion-force attraction in the suspension. Particles of latex D fall into the secondary minimum instead of the primary minimum after repeated freeze-thaw cycles, resulting a viscosity increase, while not a total coagula.
4.3.8 Freezing and Thawing Rates on Freeze-Thaw Stability

As noted in the introduction, by investigating freezing and thawing separately, Nakamura and Okada (1976) came to the conclusion that fast freezing is less detrimental to freeze-thaw stability and that coagulation does not occur in the process of thawing. Equipped with the cryogenic scanning electron microscopy technique and by changing dramatically the freezing rates, we examined a latex sample based on MMA/BA, which did not have any F/T stability by the standard ASTM D2243-95 test (slow freezing and thawing). The results are shown in Figure 4.10. In Figure 4.10a, the polymer particles survived the fast freezing process in liquid ethane (boiling point of –88 °C) and maintained individual particle identities. Additionally, the same latex sample was fast frozen under high pressure in liquid nitrogen (-196 °C). As in Figure 4.10a, there was no sign of particle instability. These two experiments show that an extremely fast freezing process does not cause particle coagulation. This can be explained by a “spacer” effect created by small ice crystals formed almost simultaneously between polymer particles when the sample is subjected to fast freezing process. When the same latex sample was first fast frozen under high pressure in liquid nitrogen and then thawed slowly overnight, polymer particles were coagulated as seen in Figure 4.10b. This experiment indicates that slow thawing is the cause for coagulation/instability in this experiment, which contradicts the results of Nakamura and Okada (1976). Coagulation during thawing can be explained as follows: thawing does not occur homogeneously and simultaneously, considering the heat-transfer requirement (which may result in temperature gradient) and compositional heterogeneity within the frozen
sample. Some areas melt first while other areas still remain frozen and therefore exert pressures, which could cause coalescence of the particles that are being thawed.

Figure 4.10c shows that slow freezing also causes particle coagulation. As expected, a combination of slow freezing and thawing would be even worse for polymer particle stability. This is indeed the case as shown in Figure 4.10d. These results show that particle coagulation can be induced in both the freezing and thawing processes and that a slower freezing and thawing process is more detrimental to the freeze-thaw stability of the polymer latex.
Figure 4.10 Images of the same latex after being frozen and/or thawed at different rates. 
a: the latex was fast frozen in liquid ethane (bp –88 °C). b: the latex was first fast frozen 
under high pressure in liquid nitrogen (bp –196 °C) and then thawed slowly overnight. c: 
the latex was slowly frozen in a freezer at –18 °C. d: the latex was slowly frozen in a 
freezer at –18 °C and then slowly thawed overnight.
4.4 Closure

Key factors affecting the F/T stability of polymer latexes were studied in this chapter, which included polymer Tg, moduli, molecular weight, particle size, amount of stabilizing functional groups, amount of coalescent, freezing and thawing rates. In addition to following viscosity changes during F/T cycles and analyzing the dynamic mechanical properties of the dried latex films, we applied an advanced analytical technique — cryogenic scanning electron microscopy — coupled with a high-pressure freezing apparatus, to visualize the micro-structural changes occurring during freeze-thaw cycles. The combination of the analytical techniques also allowed us to study the effects of the freezing and thawing processes separately. It was found that both the freezing and thawing rates have strong impact on F/T stability of polymer latexes, which does not support conclusions from early work with regard to the effect of the thawing process (Nakamura and Okada 1976). Our results also show a clear correlation between F/T stability and Tg and modulus of the polymer, which is in agreement with some early findings (King and Naidus 1969; Naidus and Hanzes 1969) but not others (Digoia and Nelson 1953; Barb and Mikuchi 1956). The influence of polymer modulus on F/T stability can be interpreted using criteria (Mason 1973) established for particle deformation and coalescence in latex film formation. However, high Tg or modulus alone does not guarantee F/T stability. To achieve F/T stability, sufficient protective functional groups are also necessary. Reducing particle size and polymer molecular weight and addition of coalescent all lead to reduced F/T stability. The presence of loosely associated particle aggregates was revealed and such a relatively diffuse aggregate structure is believed to be the cause for the rise in latex viscosity during the F/T processes in an F/T-unstable latex.
Chapter 5

The Understanding of TiO$_2$ Efficiency in Waterborne Paints through Latex Design

5.1 Introduction

This chapter explores the influence of functional acid monomers incorporated into polymer latex dispersions for their ability to effectively disperse titanium dioxide (TiO$_2$) pigment particles in flat paint applications. The functional acid monomer type (i.e. acrylic acid, methacrylic acid, itaconic acid and vinylphosphonic acid), the partitioning of acid monomer in the polymer or aqueous phase during the emulsion polymerization and the role of the latex polymer particle size were investigated. The model latex dispersions were then formulated into their corresponding flat paints. By using cryogenic scanning electron microscopy (cryo-SEM), it is possible to qualitatively observe the TiO$_2$ efficiency of the paints in the wet state. Furthermore, these results can be correlated with measurable performance properties (i.e. tint strength and scrub resistance) of the same paints in the dry state. Finally, the sole interaction of these tailored latexes with TiO$_2$ pigment particles is investigated through cryo-SEM to gain a comparative insight into how the way these particles orient themselves with one another depends on the functional acid monomer employed.

As environmental regulations for formulating architectural coatings become ever more stringent, the role of the polymeric latex toward bringing out the utmost in performance properties has never been greater. In particular the South Coast Air Quality Management District (SCAQMD) legislation, which will be become law in mid 2008, will offer new
challenges and opportunities to architectural coatings manufacturers in providing latex dispersion products which are volatile organic compounds (VOC) compliant at 50 g/L or less. As a result, such properties as freeze-thaw resistance, scrub resistance, and substrate adhesion, which in the past were mainly imparted by the high levels of VOC components in the paint formulation, are now optimized through developing technologies that are centered around the nature of the latex design.

At the same time, there is an increasing demand to model the latex to be more compatible with the other raw materials in the paint formulation. As costs rise for the paint manufacturers, the need to minimize the amount of the costlier raw materials gains a growing importance. Figure 5.1 shows a rough cost breakdown for a gallon of paint in high, semi-gloss, and flat sheens. It is plainly evident in Figure 5.1 that the TiO$_2$ component contributes greatly toward the total cost of the paint, independent of the paint sheen. With this in mind one could easily envision the cost savings that could be generated through developing a TiO$_2$ efficient binder, especially in instances of the lower sheens. With a TiO$_2$ efficient latex binder, not only the amount of the TiO$_2$ pigment can be reduced, but also the amount of the binder which is used in the paint formulation. Not surprisingly, it has been a continuing goal of the paint industry to achieve a higher level of TiO$_2$ efficiency, resulting in less TiO$_2$ consumption. This chapter explores the role of latex design toward optimizing the property of TiO$_2$ efficiency in flat sheen paints and shows the consequences of TiO$_2$ efficiency toward the physical performance improvements of the dried paint film. Specifically, the role of functional acid monomers is examined to further elucidate their interaction with TiO$_2$ particles.
Figure 5.1 Raw material cost assessment of different paint sheens. In instance of flat sheen, the TiO₂ pigment contributes 48% of the total cost. TiO₂ contributes 38% and 34% of the total cost for the semi-gloss and high gloss paint respectively.
TiO$_2$ is a primary pigment used in paints due to its high refractive index ($n_D \cong 2.6$), scattering efficiency, ideal particle size (about 250 nm in diameter) and particle spacing behavior. However, TiO$_2$ particles tend to be difficult to randomly disperse due to van der Waals colloidal attractive forces. Consequently, clusters of TiO$_2$ particles are formed which detrimentally influence the characteristics of the paint film in its dried state. These clusters severely reduce the scattering efficiency of the paint film and increase the roughness or the number of defects of the paint film surface. TiO$_2$ particles that are well dispersed and separated from each other provide respective coatings that have been useful in preparing coatings with improved hiding power and tint strength. In addition, the dispersibility of TiO$_2$ particles throughout the paint ensures that the paint itself becomes a fully integrated composite material which has improved scrub and abrasion resistance.

TiO$_2$ is typically sold as a dried powder and milling is often required prior to formulating the pigment into the paint. However, agglomeration, flocculation, and settling of the particles can still occur even after milling. Nowadays, TiO$_2$ pigments are also available in a concentrated slurry form using polyelectrolyte dispersants and surfactants. These auxiliary components usually contain anionically charged polycarboxylate or polyphosphate moieties which directly interact with the positively charged TiO$_2$ particle surface and disrupt interparticle aggregation. Although these slurries are effective in breaking up TiO$_2$ agglomeration, they still do not provide the optimum performance in pigment efficiency. By designing the latex dispersions with anionically charged functional acid groups, which can interact directly with the pigment particle, an additional steric barrier can be created that can further prevent pigment agglomeration.
This chapter is continuing in part the previous work that we have conducted concerning the use of cryogenic scanning electron microscopy to elucidate the behavior of the model latexes themselves and their respective paints in the wet state. This qualitative analytical method has in the past given key insight into better understanding and improving freeze/thaw behavior of latex dispersions, as discussed in chapter 4, and the assessment of the TiO$_2$ efficiency in paints (Zhao et al. 2006; Tiarks et al. 2002; Zhao et al. 2001; Zhao et al. 2001). In this chapter we evaluate the TiO$_2$ efficiency of several latex prototypes where the both the type of the functional acid monomer is varied along with the degree of its partitioning throughout the polymer and aqueous phases of the polymer latex dispersion. Through cryo-SEM we are able to survey the sole interaction of TiO$_2$ particles with latex particles in the wet state of their mixtures and in the formulated paints.

### 5.2 Experiments

#### 5.2.1 Latex Synthesis

The model latexes used in this study were synthesized in BASF Charlotte Technical Center in North Carolina, USA. The acrylic polymer latexes were synthesized by a seeded semi-continuous emulsion polymerization process under monomer-starved conditions. The seeded process affords easy control of particle size while the slower-than-polymerization feed rates for the monomers avoid composition drift in the copolymers formed throughout the polymerization process. Two surfactants, a sulfated fatty alcohol ethoxylate and sodium dodecyl sulfate (SDS), were used. Two pairs of monomers were used in making up the backbones of the model copolymer latexes: methyl methacrylate (MMA) and n-butyl acrylate (n-BA). Functional acid monomers,
such as acrylic acid (AA), methacrylic acid (MAA), itaconic acid (IA), and vinylphosphonic acid (VPA) were incorporated for enhancing latex stability and paint compatibility (especially with the target component in this study: TiO$_2$ pigment particles).

The chemical structures of these functional acid monomers are shown in Figure 5.2. These functional acid monomers were neutralized to various degrees in the pre-emulsion prior to it being fed into the emulsion polymerization vessel. In addition to the functional acid monomers, a variety of other proprietary functional monomers (~ 4 to 6 %) were used in the emulsion polymerization to further promote latex stability and wet adhesion.

The latexes were neutralized with ammonia to pH 8 to 9 at the end of the synthesis. The copolymer compositions along with basic physical properties are listed in the following sections where they are studied. The particle sizes were determined using photon correlation spectroscopy. Particle sizes of the model latexes range from 216 to 246 nm unless noted otherwise when evaluating the role of particle size on TiO$_2$ efficiency.

![Figure 5.2 Chemical structures of functional methacrylic acid, acrylic acid, vinylphosphonic acid and itaconic acid monomers used in this study.](image)
5.2.2 Tint Strength Measurement

The tint strength was evaluated by an internal method where the respective paints were tinted with identical amounts of tint paste (phthalo blue) and mixed thoroughly. Tint strength is a comparative method and not an absolute one to quantify the degree of TiO$_2$ dispersion, therefore an internal control sample must be included and subsequent measurements are comparatively based on the control. The resulting tinted paint was then drawn down with a 7 mil blade or a 3 mil bird bar onto a Leneta chart Form WB or BYK Gardner AG-5342. The paint film was allowed to dry overnight. After drying, color difference was run between the control and the test paint using the SP62 X-Rite Spectrophotometer, which will measure the lightness of the dried paint films. A lighter film will have better TiO$_2$ utilization and a darker film will have worse TiO$_2$ utilization.

5.2.3 Scrub Resistance Measurement

The scrub resistance was evaluated in accordance with ASTM standard test method 2486. This test method mainly applies to testing dry film integrity and abrasion resistance. The test paint was drawn down side by side with a suitable control on a Leneta or BYK Gardner scrub test panels using 7 mil side of the Dow film caster. The samples are allowed to dry/cure for 6 to 8 days or as specified. The samples are then oriented over the shim on the glass plate in the Gardco scrub machine so that the coating direction is perpendicular to the direction of the brushes. 7 mL of scrub media (Leneta SC-2) is applied evenly into the brushes, which are then attached onto the moveable arm of the machine. Before starting the test, it was ensured that the samples were centered and the brushes would travel over all shims during its full cycle. Immediately after starting the
scrub machine, 5 mL of water was placed on the scrub test sample along the path of each brush. Approximately at every multiple of 400 cycles, the process was stopped and another 7 mL of scrub medium to the scrub brush and another 5 mL water to the scrub path was added. The sample was scrubbed to failure and the cycle number was recorded.

5.2.4 High Pressure Freezing, Fracture, Surface Treatment and Cryo-SEM

The detailed sample preparation procedure has been described elsewhere (Huang et al. 1999; Sutanto et al. 2000). A droplet of paint or TiO$_2$/latex mixture is sandwiched between two brass discs each with a cylinder-shaped indentation. The assemblage is quickly frozen in a Bal-Tec HPM 010 high pressure freezing machine at 2100 bar. High pressure freezing is critically important for minimizing disturbance by large ice crystals to the original morphology of an aqueous sample. It works as follows: high pressure lowers the temperature range of supercooled water from 233 – 273 K at atmospheric pressure to 183 – 251 K at 2100 bar so that freezing water has a better chance to reach the glass transition temperature and be vitrified (zone I$_{II}$) before ice crystals grow (zone I$_{I}$). This phenomenon is clearly described in Figure 5.3. The frozen sandwich is then fractured in a liquid nitrogen bath. One side of the fractured sample is mounted on a cryo-transfer stage and is sublimed for 18 minutes to improve the topographic contrast. The fracture surface is then sputter-coated at – 130 °C with platinum to a nominal thickness of 4 nm to avoid the charging effect. The metal-coated fracture surface sits on the cold stage and is examined in the in-lens Hitachi S900 field emission scanning electron microscopy. Both secondary electron (SE) and backscattered electron (BSE) images are recorded. The former provides better topographic contrast while the latter is more preferred for maximum contrast between organic and inorganic phases. Unless
otherwise specified, the electron micrographs shown in this chapter are BSE images.

Figure 5.3 Phase diagram of supercooled water: high pressure lowers the temperature range of supercooled water from 233–273 K at atmospheric pressure to 183–251 K at 2100 bar, which makes it easier for the freezing water to reach the glass transition temperature and be vitrified before ice crystals grow.
5.3 Results and Discussion

5.3.1 Direct Observation of Paints in Wet State by Cryo-SEM

As mentioned in the introduction, this chapter explores the influence of functional acid monomers incorporated into polymer latex dispersions for their ability to effectively disperse TiO$_2$ in flat paint applications. We decided to examine both commercial and experimental latexes to first gain an assessment to their performance of TiO$_2$ efficiency of the paints. In this regard, we were able to obtain an excellent qualitative differentiation through cryo-SEM images of the paints in their wet state as well as mixtures (in the same proportions as in the paint formulation) of the latex and TiO$_2$ slurry in their wet state. Initial studies targeted commercial binders in order to get an accurate assessment of the pigment efficiency of products already in the market place. For example, Figure 5.4 and 5.5 show the cryo-SEM images of the wet formulated paints based on two commercially available latex products. Figure 5.4 shows a good TiO$_2$ dispersion with a tint strength value of 100, which is also the control of this study. Figure 5.5 shows a poor TiO$_2$ dispersion with a tint strength value of 89.6. In both images, it can be clearly seen that the TiO$_2$ dispersibility has a correlation with the tint strength value. In Figure 5.4, the TiO$_2$ particles are more homogeneously distributed in a random fashion throughout the paint film whereas in Figure 5.5 TiO$_2$ particles heavily aggregated together with very poor efficiency. The clustering of TiO$_2$ particles severely decreases the scattering efficiency of the pigment and leads to lower tint strength values (~10% less).
Figure 5.4 Direct observation of a paint with good TiO$_2$ dispersion in its wet state by cryo-SEM. The tint strength value of the dried paint film is measured as 100.
Figure 5.5 Direct observation of a paint with poor TiO$_2$ dispersion in its wet state by cryo-SEM. The tint strength value of the dried paint film is measured as 89.6.
### Table 5.1 Flat paint formulation used in TiO₂ efficiency study.
The TiO₂ used in this study is Dupont Ti-Pure R-746.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex Solids%</td>
<td>60</td>
</tr>
<tr>
<td>Latex MFFT (°C)</td>
<td>4</td>
</tr>
<tr>
<td>Water</td>
<td>150</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>5.1</td>
</tr>
<tr>
<td>Natrosol 250 MHBR</td>
<td>3.1</td>
</tr>
<tr>
<td><strong>DuPont Ti-Pure R-746</strong></td>
<td>255</td>
</tr>
<tr>
<td>AMP 95</td>
<td>1.53</td>
</tr>
<tr>
<td>Drewplus L-475</td>
<td>2.86</td>
</tr>
</tbody>
</table>

**Mix for 5 min at medium speed**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Igepal CTA 639</td>
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<td>Minex 4</td>
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**Grind at high speed for 20 min.**

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**Premix next 3 items and add**

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**Total Paste**

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**Latex (amount normalized to 60% solids)**

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<table>
<thead>
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<tbody>
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</tr>
<tr>
<td>Total</td>
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</table>
All latexes, experimental or commercial, were formulated in the same flat paint formulation, which has an amount of volatile organic compounds (VOC) at 50 g/L, a pigment volume composition (PVC) of 45% and the solids volume of the paint is at 39.0%. The flat paint formulation used in this study is shown below in Table 5.1.

Four classes of experimental latexes were used in the formulation and evaluated through the following test/methods to show the influence of the functional acid monomer with regard to TiO\textsubscript{2} efficiency: comparative cryo-SEM imaging of the paint in its wet state; comparative tint strength measurements of dried paint film and scrub/abrasion resistance measurements of dried paint film.

Although measuring hiding power is another way to determine TiO\textsubscript{2} efficiency, it is very difficult to differentiate between the samples used in this study, because all the paints are formulated to give a very high degree of reflectance (~ 95%) at the required film thickness for the test method. In this regard it is easy for the differences of the values to lie within the degree of error for the measurement. Due to this high degree of variability and lack of reproducibility, we decided to focus primarily on tint strength measurements over those of hiding power. Note, the only variable that is changed in this series of experimental latexes is the type of functional acid monomer used; all other recipe ingredients/parameters in this particular series are identical (including degree of acid neutralization in pre-emulsion) unless otherwise noted.
5.3.2 Acid Type and TiO\textsubscript{2} Dispersibility

The functional acid monomers employed in this series are acrylic acid, methacrylic acid, vinylphosphonic acid, and itaconic acid. VPA was evaluated in this series, in addition to the other three functional acid monomers that contain carboxylate groups, due to recent work which promotes its use and the use of other monomers that contain dibasic phosphate groups for the improvement of TiO\textsubscript{2} efficiency (Emmons et al. 1993; Emmons et al. 1993; Emmons et al. 1994; Brown et al. 2004). Figure 5.6, 5.7, 5.8 and 5.9 show the influence of acid type on the performance properties that reflect on TiO\textsubscript{2} efficiency. The micrographs represent the formulated flat paints in their wet state. Both the tint strength and scrub resistance data of the dried paint films show a clear correlation to the qualitative SEM-images, as shown in Figure 5.10.

As shown in Figure 5.6 to 5.9, latexes where vinylphosphonic acid or itaconic acid is incorporated give superior pigment efficiency when compared to acrylic acid or methacrylic acid functional acid monomers. This can be seen by the degree of clustering of the TiO\textsubscript{2} particles in the cryo-SEM micrographs. In Figure 5.6 and 5.7, TiO\textsubscript{2} particles are evenly dispersed throughout the wet paint and most of them remain as individual particles. The degree of clustering of the TiO\textsubscript{2} particles is very low. This can be explained by the chemical nature of the phosphonic acid moiety in vinylphosphonic acid and the structural orientation of the two carboxyl groups in itaconic acid, make both monomers suitable for scattering TiO\textsubscript{2} particles very effectively. While in Figure 5.8 and 5.9, latexes incorporated with AA or MAA functional monomers produce paints that have much higher degrees of clustering. Clusters of TiO\textsubscript{2} particles can easily be observed throughout the image.
Figure 5.6 Cryo-SEM image of a wet paint made from a latex in which acrylic acid monomers were incorporated. A high degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were poorly dispersed in the wet sample.
Figure 5.7 Cryo-SEM image of a wet paint made from a latex in which methacrylic acid monomers were incorporated. A high degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were poorly dispersed in the wet sample.
Figure 5.8 Cryo-SEM image of a wet paint made from a latex in which vinylphosphonic acid monomers were incorporated. A low degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were dispersed evenly in the wet sample.
Figure 5.9 Cryo-SEM image of a wet paint made from a latex in which itaconic acid monomers were incorporated. A low degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were dispersed evenly in the wet sample.
Figure 5.10 Influence of acid type on tint strength and scrub resistance of dried paint film.

Better TiO$_2$ efficiency gives better tint strength value and higher scrub resistance.
To further evaluate the sole interaction between the latex binder and TiO\textsubscript{2} pigment particles, raw blends of the latex dispersion and TiO\textsubscript{2} slurry were mixed together and stirred thoroughly for 30 minutes by a mechanic motor. Samples of the mixture were then frozen and analyzed through cryo-SEM. Figure 5.11 to 5.14 show these micrographs for the same series of latexes at a low magnification of 5K. At low magnification, we can have a broader view of the TiO\textsubscript{2} dispersibility throughout the wet samples. Figure 5.15 to 5.18 show cryo-SEM images of the TiO\textsubscript{2}/latex mixture at a much higher magnification of 100K. At such a high magnification, it is easier to observe how latex particles and TiO\textsubscript{2} particles interact with each other. One can clearly distinguish the latex’s ability to disperse the pigment throughout the paints when observing the different SEM magnifications of the TiO\textsubscript{2} slurry/latex blends.

In Figure 5.11 and 5.12, it is clear that the TiO\textsubscript{2} particles were poorly dispersed in the wet sample and form clusters. As shown in Figure 5.15 and 5.16, the high magnification cryo-SEM images reveal that latex binder incorporated with acrylic acid and methacrylic acid monomers did a poor job to promote the TiO\textsubscript{2} dispersibility.

In Figure 5.13 and 5.14, the TiO\textsubscript{2} particles were evenly dispersed in the wet state. Most of them remain as individual particles. At a high magnification, Figure 5.17 and 5.18 show that latex binders are surrounding the TiO\textsubscript{2} particles and formed a polymeric steric barrier between the pigment particles.
Figure 5.11 Low magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which acrylic acid monomers were incorporated. A high degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were poorly dispersed in the wet sample.
Figure 5.12 Low magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which methacrylic acid monomers were incorporated. A high degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were poorly dispersed in the wet sample.
Figure 5.13 Low magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which vinylphosphonic acid monomers were incorporated. A high degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were poorly dispersed in the wet sample.
Figure 5.14 Low magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which itaconic acid monomers were incorporated. A low degree of clustering of the TiO$_2$ particles can be seen throughout the image. TiO$_2$ particles were evenly dispersed in the wet sample.
Figure 5.15 High magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which acrylic acid monomers were incorporated. TiO$_2$ particles adhere to each other and form clusters.
Figure 5.16 High magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which methacrylic acid monomers were incorporated. TiO$_2$ particles adhere to each other and form clusters.
Figure 5.17 High magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which vinylphosphonic acid monomers were incorporated. TiO$_2$ particles were surrounded by latex particles. These latex particles work as a polymeric barrier to prevent the TiO$_2$ to form clusters.
Figure 5.18 High magnification cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which itaconic acid monomers were incorporated. TiO$_2$ particles were surrounded by latex particles. These latex particles work as a polymeric barrier to prevent the TiO$_2$ from forming clusters.
5.3.3 Degree of Neutralization and TiO\textsubscript{2} Dispersibility

In addition to evaluating acid type for its ability to influence TiO\textsubscript{2} efficiency, it was also of interest to investigate the degree of neutralization of the functional acid monomers before they were incorporated during the emulsion polymerization. In this regard the pre-emulsion was neutralized to various degrees which influence how the functional acid monomers are partitioned and distributed during the emulsion polymerization throughout the latex particles (particle interior/ particle surface) and in the serum of the dispersion. At higher degrees of neutralization the acid groups will be driven more to the aqueous phase as seen in previous publications (Vijayendran et al. 1979; Santos et al. 1997; Oliveira et al. 2006). Just as importantly, however, the influence of the degree of neutralization strongly relies on the type of acid monomer used. From our series of latexes we chose two binder prototypes with high TiO\textsubscript{2} efficiency (dispersions containing either 1% itaconic acid or vinylphosphonic acid) and varied the degree of neutralization of these functional monomers before they were fed into the emulsion polymerization. Figure 5.19 to 5.21 show the influence of the degree of neutralization on the TiO\textsubscript{2} dispersibility for latexes incorporated with itaconic acid functional monomer and Figure 5.22 shows the influence of the degree of neutralization on its tint strength and scrub resistance. Figure 5.23 to 5.25 show the influence of the degree of neutralization on the TiO\textsubscript{2} dispersibility for latexes incorporated with vinylphosphonic acid and Figure 5.26 shows the influence of the degree of neutralization on its tint strength and scrub resistance.
Figure 5.19 Cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which itaconic acid monomers were incorporated. The itaconic acid monomers were neutralized in the pre-emulsion to a low degree of neutralization.
Figure 5.20 Cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which itaconic acid monomers were incorporated. The itaconic acid monomers were neutralized in the pre-emulsion to a medium degree of neutralization.
Figure 5.21 Cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which itaconic acid monomers were incorporated. The itaconic acid monomers were neutralized in the pre-emulsion to a high degree of neutralization.
Figure 5.22 Influence of the degree of neutralization of the itaconic acid in the pre-emulsion on the tint strength and scrub resistance of the dried paint film.
Figure 5.23 Cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which vinylphosphonic acid monomers were incorporated. The vinylphosphonic acid monomers were neutralized in the pre-emulsion to a low degree of neutralization.
Figure 5.24 Cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which vinylphosphonic acid monomers were incorporated. The vinylphosphonic acid monomers were neutralized in the pre-emulsion to a medium degree of neutralization.
Figure 5.25 Cryo-SEM image of a mixture of TiO$_2$ slurry and a latex in which vinylphosphonic acid monomers were incorporated. The vinylphosphonic acid monomers were neutralized in the pre-emulsion to a high degree of neutralization.
Figure 5.26 Influence of the degree of neutralization of the vinylphosphonic acid in the pre-emulsion on the tint strength and scrub resistance of the dried paint film.
With the use of itaconic acid, as the degree of neutralization increases, the TiO$_2$ efficiency of the binder also increases. This trend is evident in the dramatic increase of scrub resistance and tint strength data along with qualitative comparative assessment of the different TiO$_2$/Latex blends with the cryo-SEM. At low degrees of neutralization, clustering of the TiO$_2$ particles take place. With higher degrees of acid neutralization the TiO$_2$ is more evenly distributed across the micrograph. This clearly demonstrates the sole interaction between pigment particles and latex particles without any interference from the other ingredients in the paint formulation. Interestingly, in the cryo-SEM evaluation of the wet paint (not shown here) containing the same latexes with different degrees of neutralization, it is difficult to differentiate between the micrographs despite the contrast in the tint strength numbers of the same paints in their dried state. Room temperature SEM images of the dried paints provide similar results and it is very difficult to differentiate between high and low levels of neutralization in the latex, despite its evident effect in the tint strength and scrub resistance results. Further investigations will center on observing how the TiO$_2$ particles are distributed in the different strata of the coating’s thickness.

When vinylphosphonic acid is employed, as seen in Figure 5.23 to 5.25, we see a opposite effect as the degree of acid neutralization increases. Lower degrees of neutralization of VPA in the pre-emulsion yield latexes with better TiO$_2$ efficiency. This is opposite to the trend that we see in using itaconic acid. At low pH values (<2), vinylphosphonic acid is thought to be readily incorporated onto the polymer particle surface and effectively interacts with TiO$_2$ particles (Brown et al 2004). While both VPA (pK$_{a1}$=2.6; pK$_{a2}$=7.3) and IA (pK$_{a1}$=3.8; pK$_{a2}$=5.4) are very water soluble at high degrees of neutralization in the pre-emulsion, they behave very differently during the emulsion
polymerization. Vinylphosphonic acid is more likely to couple with itself and remains in the aqueous phase as water soluble oligomers. These species apparently do not have the ability to disperse TiO₂ effectively. This is seen in the cryo-SEM images of the latex/TiO₂ blends for VPA, where it appears that the TiO₂ particles tend to aggregate at higher levels of acid neutralization. This observation is further confirmed by lower tint strength and scrub resistance values of the dried paint films.

In contrast, itaconic acid doesn’t oligomerize with itself but instead copolymerizes with other monomers (i.e. n-butyl acrylate and methyl methacrylate) to form oligomers which are believed to eventually localize themselves onto the polymer particle surface. Further work could prove and elucidate the behavior of latexes containing these functional acid monomers.

5.3.4 Particle Size of Latex and TiO₂ Dispersibility

Finally, the effect of particle size was examined for its influence over TiO₂ efficiency. We looked primarily at the tint strength and scrub resistance measurements of the dried paint films to quantify this phenomenon. Figure 5.27 and 5.28 show the effect of particle size on tint strength and scrub resistance for latexes which contain 1 part of itaconic acid and vinylphosphonic acid respectively.

As polymer particle size increases within a series (designated by the type of functional acid monomer used) the scrub resistance decreases. Note that TiO₂ efficiency has a major influence between series over the property of scrub resistance only when particle sizes are identical or close to identical. As seen in all the examples, when particle sizes of the
latex vary in large degrees, there are differences in effectiveness of film formation that have the greatest influence over scrub resistance. Also, for latexes with higher particle sizes the likelihood of defects increases and greatly influences the integrity of the consequent dried latex or paint film.

Figure 5.27 Effect of particle size on tint strength and scrub resistance for latexes which contain 1 part of itaconic acid.
Figure 5.28 Effect of particle size on tint strength and scrub resistance for latexes which contain 1 part of vinylphosphonic acid.
5.4 Closure

In this chapter, the main contributing factors in latex design which have a positive influence over TiO$_2$ efficiency were defined. Both functional acid monomer type and degree of acid neutralization in pre-emulsion before the emulsion polymerization greatly influence the ability of the latex and TiO$_2$ particles to interact with each other which consequently prevents TiO$_2$ particle aggregation. The chemical nature of the phosphonic acid moiety in vinylphosphonic acid and the structural orientation of the two carboxyl groups in itaconic acid, make both monomers suitable for scattering TiO$_2$ particles very effectively. However, functional acid monomers with one carboxylic acid group appear not to disperse the TiO$_2$ pigments effectively, as seen with latexes that contain the acrylic acid or methacrylic acid functional acid monomer. In the example using itaconic acid, the increase of its degree of neutralization in the pre-emulsion before emulsion polymerization takes place greatly influences the TiO$_2$ efficiency of the latex. The trend observed in this instance is that higher degree of neutralization leads to better TiO$_2$ efficiency. The reverse is seen when vinylphosphonic acid is used as the functional acid monomer: the lower the degree of acid neutralization prior to polymerization yields latexes with improved TiO$_2$ efficiency. Finally, the effect of particle size was examined and the general trend shows that as particle size decreases the TiO$_2$ efficiency of the latex increases. This is also the general trend observed in the decrease of the scrub resistance property of the paint film as latex particle size increases.
Disordered Network Nanostructure of PEO-PB Diblock Copolymer Solutions

6.1 Introduction

Self-assembly of amphiphilic molecules such as surfactants, soaps, and lipids can produce a rich assortment of ordered and disordered supramolecular structures. At low concentrations these substances form spherical (S) and cylindrical (C) micelles, and self-intersecting bilayers (B) known as vesicles. Such dispersions have found uses as foaming and emulsifying aids, wetting agents, viscosity modifiers, compatibilizers and drug delivery vehicles (Israelachvili 1983; Evans and Wennerstrom 1998). As the concentration increases, ordered structures can be observed, notably lamellae (L), hexagonally packed cylinders (H), and arrangements of spherical nanodomains on cubic (BCC, FCC) lattices. Morphology selection is governed by a host of factors, particularly the shape and volume fraction of the hydrophobic and hydrophilic portions of the molecule, which govern interfacial curvature (Israelachvili 1983). Combinations of small or zero mean interfacial curvature and negative Gauss curvature (i.e., saddle surfaces) may result in bicontinuous morphologies (Scriven 1976) such as triply periodic cubic phases (gyroid and double diamond), disordered bicontinuous microemulsions (Scriven 1976), and the disordered “sponge” (L₃) phase (Roux et al 1992).

Comparing with conventional amphiphilic systems, polymeric surfactants such as poly(butadiene-b-ethylene oxide) (PEO-PB) offer some significant advantages, including continuously tunable chemical structures, larger domain dimensions that permit chemical
modification such as cross-linking, resulting in robust control over physical properties (Won, Davis and Bates 1999). And, as in the case of conventional surfactant, the morphology can be controlled by addition of a second component (usually a selective solvent) that swells one of the polymer domains, leading to materials with adjustable periodicities and microstructures. Over the past decade, extensive experimentation with macromolecular surfactants has unveiled a rich self-assembly behavior and identified many potential applications, e.g., in biomedical devices (Wright et al. 2003), photonic crystals (Bendejacq et al. 2002), mesoporous media (Alexandridis and Lindman 2000), semiconductors (Braun, Osenar and Stupp 1996), arrayed metal nanoparticles (Puvvada et al. 1994) and polymer gels (Desai et al. 1996).

Synthetic advances in the past decade have simplified the preparation and investigation of amphiphilic block copolymers containing hydrophilic segments such as PEO and poly(acrylic acid) (Hillmyer and Bates 1996). Nonionic macromolecular surfactants containing a hydrocarbon block (e.g., PEO-PB), poly(isoprene-\(b\)-ethylene oxide) (PI-PEO), and poly(styrene-\(b\)-ethylene oxide) (PS-PEO)) can be synthesized using anionic polymerization. Chemically, these block copolymers resemble the generic nonionic C\(_i\)E\(_j\)-type surfactants and, hence, represent an attractive model system for comparing the aggregation behavior of polymeric and low molecular weight surfactants. Low glass transition temperatures for PB and PI blocks (\(T_g<-10^\circ\text{C}\)) permit unencumbered chain movement facilitating efficient dispersion of the copolymers in water at all concentrations and at ambient temperature. Moreover, poly(diene) blocks can be cross-linked, resulting in the enhancement of certain physical properties (Foerster et al. 2001; Messe et al. 2002); cross-linking self-assembled lipids and oligomeric surfactants usually disrupts the targeted morphology (Alexandridis and Lindman 2000).
Aqueous mixtures of nearly symmetric PEO-PB diblock copolymers were characterized by Förster et al. (2001) using polarized light optical microscopy and transmission electron microscopy. They observed a familiar set of structural transitions, from disordered spherical micelles ($M$), to spheres ordered on a BCC lattice ($BCC$), to hexagonally packed cylinders ($H$), and finally, to lamellae ($L$) as the polymer concentration increased. Hentze et al. (1999) used PEO-PB to template mesoporous silica. A PEO-PI diblock copolymer with an average volume ratio of PEO $f_{PEO} = 0.64$ was shown by Messe et al. (2002) to exhibit the sequence of phases $M$-$I$-$L$, with decreasing water content; curiously, the hexagonal phase ($H$) is conspicuously absent.

Network structures with interconnected domains have attracted scientific attention for many years because they provide tantalizing opportunities for the design of materials with controllable mechanical, transport, and optical properties. Porous, bicontinuous, materials with well-defined pore sizes have generated technological interest, based on applications in aerogels (Long et al. 2004), membranes (Castro-Roman 2001), and low-density materials (Foerster 2001; Goltner et al. 1998). Several protocols, including spinodal decomposition (Chen and Choi 1998), etching, nucleation and growth, and self-assembly (Hentze et al. 1999), have been employed to create these materials. A variety of fascinating bicontinuous morphologies, including the sponge-phase (Strey et al. 1990), double-diamond (Ciach 1996), hexagonally perforated lamellae (Funari and Rapp 1999), and gyroid (Imai et al. 2000), have been reported in solvated surfactant systems. A few publications have documented bicontinuous cubic morphologies in binary and ternary systems containing block copolymers (Alexandridis and Spontak 1999).
Twenty-five PEO-PB diblock copolymers, derived from a PB precursor polymer (PB degree of polymerization $N_{PB} = 170$), with different compositions and formulated with varying amounts of water, have been studied in this chapter. Cryogenic scanning electron microscopy (cryo-SEM) and small angle x-ray scattering (SAXS) techniques have been employed to characterize these mixtures. This effort has revealed that the random network morphology (denoted $N$) formed from interconnected struts with predominately cylindrical symmetry, situated at concentrations and compositions between those associated with hexagonal and lamellar phases, disappears as the molecular weight is reduced. Remarkably, Tlusty et al. (2000) and Hyde et al. (1998) have anticipated the sequence of topological transitions that we document at higher molecular weight for conventional three-component (surfactant/oil/water) microemulsions. These findings suggest that cylinder branching and network formation may be a universal feature of self-assembling amphiphilic systems.

6.2 Experiments

6.2.1 Materials

Poly-(ethylene oxide)-poly(butadiene) (OB) block copolymers were synthesized by Sangwoo Lee (a Ph.D. candidate in the department of Chemical Engineering & Materials Science in the University of Minnesota) by a two-step living anionic polymerization technique (Hillmyer and Bates 1996), characterized by a constant core molecular weight. Sizeable batches ($\sim 120$ g) of 1,3-butadiene (Aldrich) were polymerized using sec-butyl lithium initiator in tetrahydrofuran (THF) forming poly(1,2-butadiene), which was subsequently end-capped using ethylene oxide and followed by termination with acidic (HCl) methanol to form hydroxyl-terminated poly(butadiene). Small quantities ($\sim 5$ g) of
hydroxyl-terminated poly(butadiene) were reinitiated in purified THF using potassium napthalenide, followed by addition of quantitative amounts of ethylene oxide and termination with acidic methanol, to obtain OB diblock copolymers. The advantage of using this two-step synthesis scheme in this study is that it yields different diblock copolymers derived from a single identical hydrophobic core (B) block.

Polydispersity indices (PDI) were determined by gel permeation chromatography (GPC) using a Waters 150C instrument fitted with Phenogel columns (10000, 5000 and 500 Å pore size). Measurements were done at 25 °C with THF as the mobile phase and the columns were calibrated with polystyrene standards (Pressure Chemical Co.). In all cases, GPC traces were characterized by a single, monomodal peak, indicative of the efficient reinitiation of hydroxy-poly(butadiene), and the absence of homopolymer in the diblock product. Proton (1H) NMR spectroscopy was used to determine the PB microstructure (i.e., 90% 1,2 addition). Diblock copolymer molecular weights ($M_n$) and compositions (weight fraction of PEO, $W_{PEO}$) were determined from the reaction stoichiometry and 1H NMR spectroscopy, using a Varian 300 MHz instrument, with all samples dissolved in deuterated chloroform.

Five different diblock copolymers were synthesized with a core molecular weight of 9200 g/mol ($N_{PB} = 170$) and PEO weight fractions ranging from 0.3 to 0.49. They were then hydrated to 25 different diblock copolymer solutions. A complete listing of these compounds is provided in Table 6.1. In the present study, the material chosen for the hydrophobic core is 1,2-polybutadiene, having a glass transition temperature of -12 °C (Ferry 1980).
Table 6.1  Molecular Characteristics of Block Copolymers

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<td>90</td>
<td>1.06</td>
</tr>
</tbody>
</table>

<sup>a</sup> Diblock copolymers of poly(ethylene oxide) (PEO) and Poly(butadiene) (PB).  
<sup>b</sup> Concentration of diblock copolymer (wt%) in its solution.  
<sup>c</sup> Weight fraction of PEO block in diblock copolymer.  
<sup>d</sup> Number-average molecular weight determined from reaction stoichiometry and ¹H NMR.  
<sup>e</sup> Number of monomer repeat units in PEO block.  
<sup>f</sup> Polydispersity index determined from gel perfeation chromatography.

6.2.2 Small Angle X-ray Scattering (SAXS)

These SAXS measurement data were previously published by Sumeet Jain et al. (2005, 2006 and 2008). This section will briefly review the sample preparation procedure. There will be a follow-up paper focus on the cryo-SEM data obtained.

Samples for scattering measurements were prepared by dissolution of measured amounts of diblock copolymer in methylene chloride in a glass vial. The samples were then slowly
dried, leaving behind a thin film of copolymer along the walls of the vial. Subsequently, defined amounts of high-purity water (HPLC grade) were added, and the sample vials were capped and sealed using laboratory film (Parafilm). Samples were then stirred and centrifuged at room temperature for a week. Initial mixing was followed by homogenization through repeated cycles of stirring, centrifugation, annealing at a moderate temperatures (ca. 40 °C), and thermal cycling across the melting point of the PEO block for a period of six weeks, to facilitate complete dispersion. There was no appreciable loss of water as estimated from sample weight measurements at regular intervals during the homogenization process. Samples with polymer concentration less than 25% were transferred to quartz capillaries, 1.5 mm in outer diameter, which were then sealed with commercial epoxy (Loctite Quick-set epoxy). Melt and concentrated samples were sandwiched between Kapton windows separated by an O-ring just prior to measurement. This protocol minimizes the loss of water. Multiple measurements were performed with the concentrated samples to ensure reliability and reproducibility of the results. Morphological assignments were made on the basis of the diffraction peaks that occur at specific wavevector ratios.

SAXS measurements were conducted on the DND-CAT at the Advanced Photon Source at Argonne National Laboratory and using beamlines maintained at the University of Minnesota (Jain 2005). Samples (in capillaries) were investigated at 25, 40, and 60 °C. The limited range of temperatures was employed in order to minimize water loss and to avoid seal failure. No morphology changes were recorded over this temperature range. (Although the domain spacing decreases slightly upon heating, this change was insignificant compared to the variations in domain spacing encountered upon changing the concentration).
6.2.3 Cryogenic Scanning Electron Microscopy (cryo-SEM)

Cryo-SEM studies were conducted on concentrated copolymer samples identical or equivalent to the samples prepared for SAXS measurements. The highly viscous samples were smeared into two “freezing hats” each about 100 μm deep, which were carefully angled together to exclude air. The assemblage was loaded into a Bal-Tec HPM 010 high-pressure freezing machine (Balzers, Lichtenstein), quickly pressured to 2100 bar, and rapidly cooled (~10 ms) by jets of liquid nitrogen. The high pressure lowers the supercooling limit of water and greatly elevates its viscosity (already high at atmospheric pressure in the concentrated PEO-PB samples), thereby yielding fast-frozen samples with negligible freezing artifacts. The sample assembly was transferred into a liquid nitrogen bath where it was pried open to fracture the sample longitudinally. One side was mounted in a Gatan 626 cryo-transfer stage (Gatan, Pleasanton, CA) and transferred into a precooled Balzers MED 010 freeze-drying and sputtering device (Balzers Union, Balzers, Lichtenstein) against a counterflow of cold dry nitrogen gas. Vitrified water in and immediately below the fracture surface was partially sublimed away at -96 °C and approximately $2 \times 10^{-9}$ bar for about 9 min to expose the less volatile structure while avoiding recrystallization of the remaining vitrified water. The exposed surface topography was coated at -130 °C with a conducting deposit of platinum, nominally 2-3 nm thick. The coated sample was then transferred at -150 °C into a Hitachi S900 in-the-lens field emission scanning electron microscope, maintained at about -170 °C, and examined at a low acceleration voltage of 3 keV to avoid excessive charging and radiation damage of the areas imaged.
6.3 Results and Discussion

The nanostructure of aqueous mixtures of the OB9 ($N_{PB} = 170$) diblock copolymers was studied by cryogenic scanning electron microscopy as a complement to small angle x-ray scattering. Experimental results of the cryogenic scanning electron microscopy (cryo-SEM) are discussed in this section. First, however, the small angle x-ray scattering (SAXS) studies will be reviewed.

6.3.1 Small Angle X-ray Scattering results

Phase behavior of poly(butadiene-$b$-ethylene oxide) diblock copolymer has been previously studied by extensively small angle x-ray scattering and to a limited extent by cryogenic transmission electron microscopy techniques (Jain 2005, Jain et al. 2008). This section will briefly review the SAXS results of PEO-PB diblock copolymer solutions.

Figure 6.1 to 6.5 show SAXS data for various copolymer concentrations of five diblock copolymer samples, beginning with bulk (100 wt %), followed by dilution in regular increments down to a concentration of 10 wt %.

From Figure 6.1, it was inferred that the undiluted sample contains the hexagonal ($H_2$) phase and the SAXS pattern obtained at 80 wt % shows sample establishes a lamellar ($L$) morphology. At 60 wt % the primary scattering peak broadens into what was interpreted as the convolution of two reflections, hence a two-phase ($L + N$) region. The 20 wt % SAXS data shows at least 12 orders of diffraction leading to the $H_1$ phase. At a composition of 10 wt %, OB9-1 is disordered, and the resulting SAXS pattern can be
quantitatively modeled using a solid cylindrical form factor with $R_c = 16.2$ nm and $\Delta R_c/R_c = 0.06$ (solid curve).

In Figure 6.2, the scattering pattern of pure copolymer (100 wt%) also indicates an $H_2$ phase; between 50 and 90 wt% concentration it indicates the $L$ phase; and a disordered $N$ phase can be identified between 26 to 45 wt% copolymer concentration.

In Figure 6.3, the scattering pattern indicates that the 100 wt% copolymer contains the lamellar ($L$) phase; at 85 wt%, a two-phase ($H_2 + L$) region can be identified, which may also have structural elements of disordered network morphology; 30 wt% copolymer implies again the disordered network phase.

The undiluted block copolymer in Figure 6.4 indicates a $H_2$ phase, which transforms to lamellar ($L$) phase between 70 and 90 wt % concentration; the scattering trace for samples at 55 and 60 wt% exhibits two principal peaks suggesting a coexistence of two morphologies, probably lamellar ($L$) and disordered network ($N$) morphologies; between 26 to 50% concentration shows the disordered network structure; a $H_1$ phase can be observed at 20 wt% concentration.

The Figure 6.5 scattering pattern indicates a hexagonal ($H_2$) phase between 90 to 100 wt% copolymer and lamellar phase between 50 to 80 wt% concentrations; in the range of 30 to 40%, sample displays the disordered $N$ phase.
Figure 6.1 SAXS patterns obtained from OB9-1 ($W_{PEO} = 0.42$) copolymer as a function of polymer concentration in water. Relative peak positions and assigned morphologies: 100% ($1:\sqrt[4]{4}:\sqrt[7]{9}:\sqrt[12]{13}:\sqrt[16]{16}$, hexagonal, $H_2$); 80% ($1:2:3:4:5:6$, lamellar, $L$); 60% (1:2:3:4:5:6 (inverted triangles), lamellar, $L$ and disordered network (solid like), $N$); 20% ($1:3:4:7:9:12:13:16:19:21:27:28:37:48$, hexagonal, $H_1$); 10% (disordered cylinders, $C$) (Jain 2005).
Figure 6.2 SAXS patterns obtained from OB9-4 ($W_{\text{PEO}} = 0.34$) copolymer as a function of polymer concentration in water. Relative peak positions and assigned morphologies: 100% ($\sqrt{1}:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$, hexagonal, $H_2$); 90% - 50% (1:2:3:4:5:6, lamellar, $L$); 45% - 26% (disordered network, $N$); 20% and 10% (form-factor scattering). Arrows indicate the characteristic peak positions for the assigned morphology; some peaks are extinct which may be due to the form-factor extinction or the lack of long-range order (Jain 2005).
Figure 6.3 SAXS patterns obtained from OB9-5 \(W_{PEO} = 0.49\) copolymer as a function of polymer concentration in water. Relative peak positions and assigned morphologies: 100\% \((1:2:3:4, \text{lamellar, } L)\); 85\% \((\sqrt{1}:\sqrt{4}:\sqrt{9}:\sqrt{12}:\sqrt{16}, \text{hexagonal and lamellar, } H_2 \text{ and } L)\); 55\% - 30\% (disordered network, \(N\)); 10\% (form-factor scattering). Arrows indicate the characteristic peak positions for the assigned morphology; some peaks are extinct which may be due to the form-factor extinction or the lack of long-range order (Jain 2005).
Figure 6.4 SAXS patterns obtained from OB9-11 ($W_{PEO} = 0.39$) copolymer as a function of copolymer concentration. Relative peak positions and assigned morphologies: 100% ($\sqrt{1}:\sqrt{4}:\sqrt{7}:\sqrt{9}:\sqrt{12}$, hexagonal, $H_2$); 90% - 70% (1:2:3:4:5:6, lamellar, $L$); 60% - 55% (coexistence of probably lamellar ($L$) and disordered network ($N$) morphologies). 50% - 26% (disordered network, $N$). 20% ($\sqrt{1}:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}:\sqrt{12}$, hexagonal, $H_1$); 10% (form-factor scattering). Arrows indicate the characteristic peak positions for the assigned morphology; some peaks are extinct which may be due to the form-factor extinction or the lack of long-range order (Jain 2005).
Figure 6.5 SAXS patterns obtained from OB9-15 ($W_{PEO} = 0.30$) copolymer as a function of copolymer concentration. Relative peak positions and assigned morphologies: 100% and 90% (√1:√3:√4:√7:√9, hexagonal, $H_2$); 80% - 50% (1:2:3:4:5:6, lamellar, $L$); 40% - 30% (disordered network, $N$); 10% (form-factor scattering). Arrows indicate the characteristic peak positions for the assigned morphology; some peaks are extinct which may be due to the form-factor extinction or the lack of long-range order (Jain 2005).
Figure 6.6 Experimental phase portrait for the OB9 diblock copolymer solutions. Structures are identified as a function of the composition of diblock copolymer ($W_{\text{PEO}}$) and the concentration of copolymer in solution (by weight fraction). Solid lines mark approximate phase boundaries, and thin horizontal lines identify co-existence regions. The following ordered structures are present: spheres of PEO packed with body-centered symmetry in a PB matrix ($BCC$); cylinders ($H_2$); lamellae ($L$); cylinders of PB packed on a hexagonal lattice in a PEO/water matrix ($H_1$); spheres ($FCC$). A disordered network morphology is denoted by ($N$). Two phase coexistence regions separate single phase regions. Upon dilution, the ordered structures disintegrate into disordered micelles ($S$, $C$) and bilayer vesicles ($B$), as delineated by the long-dashed line (Jain 2005). Black filled circles represent samples that were prepared for cryo-SEM study.
Figure 6.6 summarizes the lyotropic phase behavior of the PEO-PB diblock copolymer solutions as a function of weight fraction of PEO \( W_{\text{PEO}} \) and the concentration (by weight fraction) of copolymer in water, as deduced from the small angle x-ray scattering results. At low concentration, spherical (S) and cylindrical (C) micelles, vesicles (B) and a narrow two-phase band containing water and a network morphology (N) were revealed (Jain and Bates 2003). Several ordered phases were identified at higher concentration, including lamellae (L), normal and inverse hexagonally packed cylinders \( (H_1 \text{ and } H_2) \) and spheres packed on cubic lattices \( (BCC \text{ and } FCC) \). The most intriguing feature of this phase portrait is the morphological window referred to as the network \( (N) \) morphology, located between 26 wt% and 55 wt% diblock copolymer with \( 0.28 < W_{\text{PEO}} < 0.50 \).

To better characterize the nanostructure of this disordered network \( (N) \) region identified in Figure 6.6, twenty five hydrated OB9 samples listed in Table 6.1 were studied using cryogenic scanning electron microscopy (cryo-SEM), a powerful microscopy technique capable of imaging nanometer scale topographical features in concentrated fluids and soft solids. These diblock copolymer solution samples were chosen within and around the disordered network region. Contrast is obtained with this technique by subliming water from the surface layer of a cryo-fractured sample, leaving behind the original nanostructure of the frozen material as dispersed in the aqueous medium.
6.3.2 OB9-1 (W_{PEO} = 0.42) Diblock Copolymer Solutions

First, we examine samples of OB9-1 (W_{PEO} = 0.42) with compositions outside the random network (N) region in Figure 6.6. Figure 6.7 shows a cryo-SEM image of a 20 wt% solution of OB9-1 in water, which according to the SAXS data is in the hexagonal (H1) phase region. The predominant structural feature in this image is some locally close packed cylindrical micelles with limited degree of ordering, but not as ordered as expected for hexagonal packing. And all the cylindrical micelles are pointing to the upper right direction, which is indicative of a nematic phase. Although it is impossible to determine the aspect ratio with any certainty, these cylinders appear to be rather long.

By increasing the concentration to 26 wt%, the sample crosses the SAXS-determined phase boundary between the hexagonal (H1) and the network (N) region and enters the N region. Figure 6.8 shows a structure of disordered wormlike micelles and they are significantly more curved than those shown in Figure 6.7. Figure 6.9 is a higher magnification image of Figure 6.8 and we can clearly see some interconnected micelles with branches in between them.

The dispersion behavior of PEO-PB copolymers in water at low (ca. 1% by weight) concentrations was previously studied (Jain and Bates 2003). As W_{PEO} decreases spherical micelles transform to cylindrical micelles followed by the formation of ‘‘Y junctions’’ (three-fold connectors) with network formation and macroscopic phase separation in the vicinity of W_{PEO} \approx 0.34; fragmentation of the network produces an assortment of reticulated (meta-stable) micelles (Jain and Bates 2003). Further reduction in the fraction of PEO results in vesicles. These features are identified on the left-hand
side of the experimental phase portrait (Figure 6.6). Thus, the tendency to form Y branches at low concentration is manifested through a sizable region of network formation as the water content is reduced. Significantly, the $N$ phase is absent from the phase portrait for $N_{PB} = 45$ (Jain et al. 2008). Apparently cylinder branching and network formation are contingent on higher core molecular weights.

Figure 6.7 Cryo-SEM image of sample OB9-1 at 20 wt% concentration (in water). The nanostructure shows some locally close packed cylindrical. With the cylindrical micelles pointing to the upper right direction, it is more likely to be a nematic phase.
Figure 6.8 Cryo-SEM image of sample OB9-1 at 26 wt% concentration (in water). The nanostructure shows disordered wormlike micelles with branches interconnect them.

Figure 6.9 Higher magnification cryo-SEM image of Figure 6.8, which clearly shows the branching feature of these cylindrical micelles.
Increase of copolymer concentration to 30% results in another quite different morphology, as shown in Figure 6.10. A densely interconnected random network structure can be easily identified. Strands of block copolymer, roughly 200-300 nm in length, are linked together at junctions that range from simple 3-fold unions to larger, flat, multifunctional connections. The basic structural element of the random network appears to be approximately cylindrical, with a diameter of 34-38 nm, consistent with the dimension extracted from the form factor scattering (Jain et al. 2006), which was calculated based on a cylinder diameter of 32 nm. (Note that the structures evident in the cryo-SEM pictures contain both the PB (core) and PEO (shell) blocks, whereas the SAXS patterns reflect primarily core scattering).

Figure 6.10 Cryo-SEM image of sample OB9-1 at 30 wt% concentration (in water). The image shows a random network nanostructure.
Superficially the random network phase appears to be an analog of the sponge phase ($L_3$) documented in surfactant-water systems. However, the conventional sponge phase is associated with a sheetlike bilayer geometry (Roux, Coulon and Cates 1992), whereas the SAXS data (Figure 6.1) and cryo-SEM images (Figure 6.10) establish a three-dimensional network morphology with cylinder geometry. Also different is the location and extent of the $N$ phase in the overall phase diagram relative to the $L_3$ phase. Whereas the $N$ state is nested primarily between the $H_1$ and $L$ phases (Figure 6.6), the $L_3$ sponge phase usually occupies a narrow slice of compositions between ordered lamellae (referred to as $L_a$ in the surfactant literature) and pure water (Roux, Coulon and Cates 1992). Based on these observations, the $N$ phase as shown in Figure 6.10 appears to reflect a different state of self-assembly than $L_3$.

When the concentration reaches 45 and 50%, cryo-SEM reveals another interesting morphology of this OB9-1 block copolymer solution. As shown in Figure 6.11 and Figure 6.12, the PEO-PB copolymer forms a much denser structure than at 30 wt%. The spacing between the interconnected cylindrical micelles is almost too small to distinguish. A closer look at Figure 6.11 may reveal a faint shape of the cylindrical structure. While in Figure 6.12, this reticulated surface describes a honeycomb-like structure which appears to be very similar to another system we have studied, a bicontinuous water-oil-surfactant microemulsion system (Figure 6.13, will be published elsewhere). As discussed in the previous paragraph, this morphology is different from the random network ($N$) structure seen in Figure 6.10 and is an analog to the $L_3$ phase (Roux, Coulon and Cates 1992), or more precisely a two component sponge phase.
Figure 6.11 Cryo-SEM image of sample OB9-1 at 45 wt% concentration (in water). The image shows a densely packed nanostructure very similar to a bicontinuous.

Figure 6.12 Cryo-SEM image of sample OB9-1 at 50 wt% concentration. The image shows a densely packed nanostructure very similar to a bicontinuous phase of a water/oil/surfactant microemulsion (Figure 6.13).
By looking at the nanostructure of the diblock copolymer in Figures 6.11, 6.12 more closely, it is noticeable that many pullouts (bright spots) appear upon cryo-fracture during the sample preparation. As discussed by Ge et al. (2006), these pullouts are artifacts formed by the polymer elongation and plastic deformation during cryo-fracture, which can be used to identify the polymer phase.

Figure 6.13 Cryo-SEM image of a bicontinuous water-oil-surfactant microemulsion.

At 55 and 60 wt % of diblock copolymer OB9-1 ($W_{\text{PEO}} = 0.42$) solutions, a terraced lamellar morphology in the cryo-SEM images (Figures 6.14 and 6.15) clearly reinforces the assignment of a lamellar morphology. What is worth noticing is that the SAXS results show a two phase ($N + L$) region at these two concentrations. While in Figures 6.14 and 6.15, there is no sign of existence of the $N$ structure. Only distinguishable nanostructure appears to be the multilayer lamellar structure. The conflict between two techniques indicates that one or both technique may contain artifacts during sample preparation, or the actual bicontinuous structure is too small to be seen in the electron microscopy.
Figure 6.14 Cryo-SEM image of sample OB9-1 at 55 wt% concentration (in water). The image shows a terraced lamellar nanostructure without coexistence of $N$ phase.

Figure 6.15 Cryo-SEM image of sample OB9-1 at 60 wt% concentration (in water). The image shows a terraced lamellar nanostructure without coexistence of $N$ phase.
6.3.3 OB9-4 ($W_{\text{PEO}} = 0.34$) Diblock Copolymer Solutions

Three different concentrations of block copolymer OB9-4 ($W_{\text{PEO}} = 0.34$) were prepared near the phase boundaries between network ($N$) phase and bilayer ($B$) and lamellar ($L$) phase to better understand the phase behavior of the copolymer solutions. First sample with concentration of 30% was prepared inside the $N$ region but close to the $B$ region. Cryo-SEM image, as shown in Figure 6.16, shows clearly more than just the random network morphology. Many bilayer vesicles can be seen embedded in this random network of cylindrical micelles in Figure 6.16. Some of these vesicles were broken open during cryo-fracture and exposed the structure inside.

Figure 6.16 Cryo-SEM image of sample OB9-4 at 30 wt% concentration (in water). The image shows both random network and bilayer vesicle nanostructure, indicating the coexistence of both $N$ and $B$ phases.
At a higher concentration of 45%, the copolymer solution was again chosen inside the network region, but close to the lamellar ($L$) phase. Interestingly, the cryo-SEM image (Figure 6.17) also shows a coexistence of two phases, both random network ($N$) and lamellar ($L$) phases. It is clear that some sheet-like multilayer lamellar structures are embedded in the random network of cylindrical micelles. In the center of Figure 6.17, some small spheres can also be seen, which could again be bilayer vesicles. But these spheres do not represent the dominating nanostructure of the block copolymer solution.

Figure 6.17 Cryo-SEM image of sample OB9-4 at 45 wt% concentration (in water). The image shows both random network and lamellar, indicating the coexistence of both $N$ and $L$ phases.
The last sample in this group was picked inside the lamellar region, but still close to the network region, a polymer concentration of 50 wt%. Figure 6.18 shows a similar nanostructure of the copolymer solution to Figure 6.17, coexistence of both $N$ and $L$ phases. One obvious difference between Figure 6.17 and 6.18 though, is the spacing (shown as voids where used to be the water phase) between these interconnected cylindrical structures. In Figure 6.18, the spacing between network structure are apparently smaller than that in Figure 6.17, indicating a much denser random network structure, which can be easily explained by the higher polymer concentration. The spheres seen in Figure 6.17 is also absent in Figure 6.18.

Figure 6.18 Cryo-SEM image of sample OB9-4 at 50 wt% concentration (in water). The image shows both random network and lamellar, indicating coexistence of both $N$ and $L$ phases. The network structure appears denser than that in Figure 6.17 due to higher copolymer concentration.
6.3.4 OB9-5 ($W_{PEO} = 0.49$) Diblock Copolymer Solutions

The third group of samples was prepared close to the upper boundary of the network region in Figure 6.6. This group of samples is close to the phase boundary between hexagonal ($H_i$) phase, network ($N$) phase and the two-phase ($N + L$) region. First two samples, at concentrations of 26 and 30%, exhibit similar random network structures (Figure 6.19 and 6.20). Similar to sample OB9-1 30 wt%, cylindrical block copolymer micelles, roughly 200 nm in length, are interconnected with each other at junctions larger than 3-fold and form a robust random network structure. Again, the network structure in Figure 6.20 appears to be denser than that in Figure 6.19 due to higher copolymer concentration.

Figure 6.19 Cryo-SEM image of sample OB9-5 at 26 wt% concentration (in water). The image shows a robust random network structure.
Figure 6.20 Cryo-SEM image of sample OB9-5 at 30 wt% concentration (in water). The image shows a random network structure. The structure appears denser than that in Figure 6.19 due to higher copolymer concentration.

Increasing copolymer concentration to 40% yields another different nanostructure, as shown in Figure 6.21. Although a denser random network morphology is expected based on the SAXS results, Figure 6.21 doesn’t show anything like a random network structure. Figure 6.22 shows a higher magnification cyro-SEM image of Figure 6.21. A closer look at Figure 6.22 makes it plain that this structure is formed by a close packing of the cylindrical micelles. These micelles are very close-packed and all pointing to the normal direction of the fracture surface, which means the structure in Figures 6.21 and 6.22 is more likely to be the hexagonal ($H_2$) or nematic morphology, instead of the random network ($N$) morphology.
Figure 6.21 Cryo-SEM image of sample OB9-5 at 40 wt% concentration (in water). The image shows a close packing of cylindrical micelles.

Figure 6.22 Higher magnification cryo-SEM image of Figure 6.21. The nanostructure appears to be a close-packed hexagonal ($H_1$) or nematic morphology.
When the copolymer concentration reaches 55%, Figure 6.23 reveal another bicontinuous morphology as seen in Figures 6.11, 6.12 and 6.13. Pullout features from the polymer phase can be seen and are more obvious than in Figures 6.11 and 6.12, which could be caused by its higher weight fraction of the PEO block ($W_{\text{PEO}} = 0.49$ compares to 0.42 in sample OB9-1).

Figure 6.23 Cryo-SEM image of sample OB9-5 at 55 wt% concentration (in water). The image shows a similar bicontinuous structure to sample OB9-1 at intermediate concentrations of 45 and 50%.

At a high concentration of 60%, OB9-5 copolymer solution shows a pure lamellar structure, as Figure 6.24 makes plain. This is again in conflict with SAXS result, according to which this sample is in a two phase region and should show both random network and lamellar structures.
Figure 6.24 Cryo-SEM image of sample OB9-5 at 60 wt% concentration (in water). The image shows a simply lamellar structure instead of coexistence of $N$ and $L$ phases given by the SAXS data.

6.3.5 OB9-11 ($W_{\text{PEO}} = 0.39$) Diblock Copolymer Solutions

At an intermediate level of PEO block weight fraction ($W_{\text{PEO}} = 0.39$), another seven samples were prepared to study the random network nanostructure of the PEO-PB diblock copolymer solutions. First sample, prepared at 20% concentration, has similar SAXS results with sample OB9-1 at 20% concentration. Figure 6.25 also shows a similar nanostructure as seen in Figure 6.7. Again, some locally close packed cylindrical micelles appear to be the reason that SAXS picks up the hexagonal ($H_1$) signals. All the cylindrical micelles points to the lower right direction and a nematic phase may be a more proper
designation. One difference between Figure 6.7 and 6.25 is that “Y” junctions are noticeable in Figure 6.25, but not in Figure 6.7. As discussed in section 6.3.2, spherical micelles transform to cylindrical micelles followed by the formation of “Y” junctions as $W_{\text{PEO}}$ decreases. This can explain the presence of “Y” junctions in Figure 6.25 due to lower PEO block weight fraction.

![Image of sample OB9-11 at 20 wt% concentration in water showing locally close-packed cylindrical micelles.]

Figure 6.25 Cryo-SEM image of sample OB9-11 at 20 wt% concentration (in water). The nanostructure shows some locally close-packed cylindrical micelles. With the micelles pointing to the lower right direction, it is more likely to be a nematic phase. Presumably, “Y” junctions are visible due to lower PEO block weight fraction.

By increasing the concentration to 26 wt%, the sample enters the $N$ region. Figure 6.26 shows a structure of disordered wormlike micelles which is also similar to sample OB9-1 at the same concentration. These micelles are significantly more curved than those shown...
in Figure 6.25 and we can clearly see many interconnected micelles with branches in between them. This once again confirms the SAXS results and verifies the phase boundary of random network.

Figure 6.26 Cryo-SEM image of sample OB9-11 at 26 wt% concentration (in water). The nanostructure shows disordered wormlike micelles with branches interconnect them.

Chosen from the center of the network region, two OB9-11 diblock copolymer samples with concentration of 35 and 40% show clearly robust random network structures and are in support of SAXS results. Figure 6.27 and 6.28 are the cryo-SEM images of OB9-11 copolymer solutions at 35 and 40% concentration respectively. Both images show a very dense random network structure, with increasing size of the polymer structure and decreasing size of the spacing (water phase in solution before high pressure freezing) as the concentration increases.
Figure 6.27 Cryo-SEM image of sample OB9-11 at 35 wt% concentration (in water). The image shows a dense random network structure.

Figure 6.28 Cryo-SEM image of sample OB9-11 at 40 wt% concentration (in water). The image shows a dense random network structure.
The fifth sample in this group was chosen near the phase boundary of $N$ and the two phase ($N + L$) region. Given the SAXS result, the morphology of the copolymer solution with a concentration of 50% should be random network. Figure 6.29 is the cryo-SEM images of OB9-11 diblock copolymer solutions at 50% concentration. Interestingly, the predominant feature shown in Figure 6.29 is terraced lamellar structure, together with some onion-like lamellar structure in the upper left part of image, which could be caused by shearing during sample preparation (Zipfel et al. 1999).

Figure 6.29 Cryo-SEM image of sample OB9-11 at 50 wt% concentration (in water). The predominant morphology is terraced lamellar structure, together with some onion-like lamellar structure.

At high concentrations of 55 and 60%, OB9-11 diblock copolymer solutions reside in the two phase ($N + L$) region according to Figure 6.6. Figure 6.30 and 6.31 are the cryo-SEM images of these two OB9-11 copolymer solutions respectively. These images show only
Figure 6.30 Cryo-SEM image of sample OB9-11 at 55 wt% concentration (in water). The image shows a terraced lamellar nanostructure without coexistence of network phase.

Figure 6.31 Cryo-SEM image of sample OB9-11 at 60 wt% concentration (in water). The image shows a terraced lamellar nanostructure without coexistence of network phase.
the existence of lamellar structure with no sign of any random network structure, as seen in Figure 6.14, 6.15 and 6.24. It appears that all five samples chosen from this two phase region in between random network (N) phase and lamellar (L) phase show only lamellar structure.

6.3.6 OB9-15 (W_{PEO} = 0.30) Diblock Copolymer Solutions

The last group of sample was chosen near the lower boundary of the network (N) region. At W_{PEO} = 0.30, three block copolymer solutions were prepared to study the morphology close the phase boundary of bilayer (B), network (N) and lamellar (L) phases.

30% OB9-15 copolymer solution was prepared because it is inside the network region and close to both bilayer and lamellar phases. Figure 6.32 shows the nanostructure of this block copolymer solution, a co-existing of all three phases: bilayer vesicles, random network of cylindrical micelles and sheet-like multilayer lamellar structure. The random network structure is apparently more dominant, while the other two structures are both obvious.

Increasing the concentration to 40% yields a similar structure, as shown in Figure 6.33. At this concentration, the random network of cylindrical micelles co-exists with the onion-like lamellar structure, without the presence of bilayer vesicles. This can easily be explained as the sample is close to the phase boundary of network (N) and lamellar (L) phases, while far away from bilayer (B) phase.
Figure 6.32 Cryo-SEM image of sample OB9-15 at 30 wt% concentration (in water). All bilayer ($B$), random network ($N$) and lamellar ($L$) phases co-exist at this concentration.

Figure 6.33 Cryo-SEM image of sample OB9-15 at 40 wt% concentration (in water). Both random network ($N$) and lamellar ($L$) phases co-exist at this concentration.
Chapter 6  Disordered Network Nanostructure of PEO-PB Diblock Copolymer Solutions

The last sample in this group was picked inside the lamellar phase region. Figure 6.34 shows the nanostructure of OB9-15 block copolymer solution at 50% concentration. The cryo-SEM shows a beautiful terraced lamellar structure, which is in accordance with SAXS measurement.

![Cryo-SEM image of sample OB9-15 at 50 wt% concentration (in water). The image shows a terraced lamellar nanostructure.](image)

The stability of the random network (N) morphology was tested by analysis of samples after extended annealing (room temperature for two weeks) and thermal cycling (five cycles per day between room temperature and 60 °C for two days). No perceptible changes were documented in the SAXS or cryo-SEM measurements after annealing the samples. Also, no changes were recorded when selected solutions were examined six months after preparation.
Figure 6.35 Experimental phase portrait for the OB9 diblock copolymer solutions. The symbols in this figure are defined as: the filled circles represent samples that cryo-SEM data agree with SAXS measurement; the squares represent samples that show nematic phase instead of $H_1$ or $N$ phase; the triangles represent samples show sponge ($L_3$) phase instead of $N$ phase; the pentagons represent samples show lamellar ($L$) phase instead of network ($N$) or two phases ($N + L$); the rings represent samples show two or three coexisting phases ($B + N$, $N + L$, or $B + N + L$), instead of single phase.

Further study by cryo-SEM shows results in accordance to SAXS measurements in most cases. The cryo-SEM results of samples chosen near phase boundaries between bilayer ($B$), network ($N$) and lamellar ($L$) phases generally show co-existence of two or three phases. Cryo-SEM images of samples chosen from the two phase ($N + L$) region show only lamellar structure, which conflicts the SAXS measurement. This could indicate that
one or both technique may contain artifacts during the sample preparation, or the
certain structure is beyond the imaging capability of the scanning electron
microscope. Figure 6.35 shows the cryo-SEM results compared with the SAXS
measurement. Different symbols indicates whether cryo-SEM agree with SAXS or not.

6.4 Closure

Cryogenic scanning electron microscopy was employed to further understand the nature
of nanostructure deduced by small angle x-ray scattering for PEO-PB (OB) diblock
copolymers solutions, as a function of copolymer concentration (wt % copolymer in
water) and block copolymer composition (weight fraction of PEO block). At $N_{PB} = 170$,
the SAXS measurements and cryogenic scanning electron microscopy reveal a new type
of network morphology, comprised of a random arrangement of interconnected (branched)
cyinders, in addition to the other classical structures. This network phase, which occurs
over a sizable range of compositions ($0.28 < W_{PEO} < 0.5$) and concentrations (26-50 wt %
diblock copolymer), is characterized by a lack of translational order (as evidenced by
SAXS and cryo-SEM) and a solid-like dynamic elastic modulus.
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