SYNTHESIS OF HYBRID LATEXES AND POLYMERIZATION KINETICS OF FUNCTIONAL LATEXES

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Serkan Bas
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SYNTHESIS OF HYBRID LATEXES AND POLYMERIZATION KINETICS OF FUNCTIONAL LATEXES

Serkan Bas
Dissertation

Approved: ______________________________
Advisor
Dr. Mark D. Soucek

Accepted: ______________________________
Department Chair
Dr. Sadhan C. Jana

_______________________________
Committee Member
Dr. H. Michael Cheung

_______________________________
Committee Member
Dr. Sadhan C. Jana

_______________________________
Committee Member
Dr. Thein Kyu

_______________________________
Committee Member
Dr. Alex Lubnin

_______________________________
Committee Member
Dean of the College
Dr. Stephen Cheng

_______________________________
Committee Member
Dean of the Graduate School
Dr. George R. Newkome

_______________________________
Date


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ABSTRACT

Hydrophilic or hydrophobic functional monomers impart unusual properties to latexes. The type, amount, and addition sequence of functional monomers affect the colloidal stability, film formation and mechanical properties of latexes. Carboxylic acid and hydroxyl functional monomers provide reactive sites for crosslinking. The colloidal stability of latex particles can be enhanced by functional groups such as carboxylic acids. The latexes with functional groups can also be used to graft inorganic materials to form hybrid materials. Functional groups on the latexes not only determine the morphology of the latexes, but also the polymerization kinetics. The present work focused on assessing the effects of the type and the amount of functional monomers on the physical properties of hybrid latexes (particle size, solid content, and glass transition temperature, etc.), polymerization kinetics of core-shell latexes and mechanical properties of thermoset latex films.

The first aim was to investigate the effect of hydrophobic groups such as polysiloxane on the physical properties of latexes. Polysiloxane-functionalized acrylic latexes were prepared by three different grafting techniques. In the first method, an acrylic core was prepared with the addition of a coupling agent, 3-(trimethoxysilyl) propyl methacrylate, after which a cyclic siloxane monomer (octamethylocyclotetrasiloxane, D₄) was grafted onto the coupling agent. In the second method, a
methacrylate-terminated polysiloxane was copolymerized with ethyl acrylate (EA) and 2-ethylhexyl acrylate (EHA) in batch emulsion polymerization. In the third method, D₄ was added during emulsion polymerization of EA, EHA and 2-hydroxyethyl methacrylate. A core-shell morphology was observed in transmission electron microscopy (TEM) for the first preparation method. Microphase separation was observed by atomic force microscopy (AFM) after polysiloxane-functionalization for all latex films. Energy dispersive X-ray data indicated that only the hybrid latex by copolymerization of methacrylate-terminated polysiloxane (second grafting method) resulted in higher silicon content at the film-air interface than the film-substrate interface. In all methods, storage modulus and surface energy of latex films decreased after polysiloxane-functionalization of latexes.

Secondly, the effect of polymerization of hydrophilic functional monomers with different types of surfactant on the polymerization kinetics was investigated. A semi-batch emulsion copolymerization of butyl acrylate (BA), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and methacrylic acid (MAA) was performed in which the concentration of HEMA (in core), MAA (in shell) and the type of surfactant (two anionic and two nonionic) were varied. New particle formation occurred throughout the polymerization even under almost starved-monomer conditions. The instantaneous rate of polymerization was inversely proportional to the concentration of HEMA and MAA. Secondary nucleation and limited coagulation were more significant when the anionic surfactant (Triton X-200) was used. In general, the smallest particle size was obtained when Triton X-200 was used. Generally, the anionic surfactant (Aerosol MA-
yielded slower polymerization reactions which were attributed to high critical micelle concentration (CMC) compared to the other surfactants.

Finally, the latexes with hydrophilic functional monomers were crosslinked to study the effects of crosslinker type on mechanical properties. The latexes with varying concentrations of HEMA, MAA and two types of surfactants (Tergitol XJ, Triton X-200) were crosslinked with five different types of crosslinkers. Melamine-formaldehyde (MF) resin was employed to crosslink hydroxyl functionalities in the core. Carboxylic acid groups in the shell were crosslinked with zinc ammonium carbonate and N,N-dicyclohexylcarbodiimide. Cycloaliphatic diepoxide and hexamethylene diisocyanate (HDI) isocyanurate were used to crosslink with hydroxyl or carboxyl functional groups in the core and the shell. The toughest films were obtained when MF resin was used as crosslinker in the tensile test. However, zinc crosslinker yielded brittle films with very low toughness and pencil hardness. The highest Young’s modulus was obtained for the latex films when HDI isocyanurate or carbodiimide were used as crosslinker. In general, anionic surfactant (Triton X-200) showed higher crosslink density compared to nonionic surfactant (Tergitol XJ). This was attributed to the broader particle size distribution of the latexes with Triton X-200.

Dual-cure (thermal/visible light process) amide- and acrylate-functionalized latexes were prepared via semi-batch emulsion polymerization. Thermoset latex films were prepared by blending amide- and acrylate-functionalized latexes in different fractions (50/50, 40/60, 60/40 wt/wt%). The tensile, dynamic mechanical and thermal properties of the thermoset films were evaluated. The effect of the photosensitizer (camphorquinone) concentration was also investigated on mechanical and thermal
properties. Amide- and acrylate-functionalized latexes (50/50 wt/wt.) were mixed with different amounts of methanolic camphorquinone and \( t \)-butyl hydroperoxide relative to the amount of trimethylolpropane triacrylate (1, 2, 4, and 6 wt% methanolic camphorquinone and \( t \)-butyl hydroperoxide). The highest tensile modulus and elongation % was observed in amide- and acrylate-functionalized latex with 50/50 wt% blend ratio. As the concentration of photosensitizer (camphorquinone) increased, storage modulus of films increased. Two glass transition temperatures were observed for the latex films. This could be attributed to the induced phase separation after the crosslinking of acrylic functionalities followed by thermally crosslinking between acetoacetoxy and amide functionalities.
DEDICATION

To my loving parents without whose sacrifices none of this would be possible.
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1.1 Hybrid Latexes

Hybrid latex is one of the most active research fields in literature due to the wide variance in end properties.\textsuperscript{1-4} Hybrid latex is prepared by mixing two classes of polymer by employing different procedures. Polysiloxanes have been used as inorganic substances to modify organic resins to improve some physical properties. Polysiloxanes are rarely handled due to their very soft nature. Preparation of polysiloxane hybrid materials with acrylic polymers can solve this problem. Preparation of polysiloxane hybrid materials can be achieved by blending, reacting, and grafting of polysiloxane with acrylic polymers. Blending is not an effective method since the system results in macroscopic phase separation. The blending of polysiloxane and polyacrylate results in phase separation due to low surface energy of polysiloxane.\textsuperscript{5} There are several benefits of hybrid latexes prepared from polyacrylate and polysiloxane.\textsuperscript{6} Polyacrylate can be modified with different functional groups to be crosslinked. Additionally, several physical properties of polyacrylates can be adjusted such as glass transition temperature (Tg). However, some polyacrylates do not have sufficient toughness and water resistance.\textsuperscript{7} These deficiencies can be improved by adding polysiloxane.\textsuperscript{8} Polysiloxane can also improve the thermal
Acrylic polysiloxane latexes in particular bear several benefits similar to those of acrylic latexes such as low viscosity, lower VOC and high UV-resistance. The effect of different modification methodologies on physical properties has not still been reported. Different synthesis methodology can lead to distinction in microstructure that has an impact on macroscopic properties due to possible differences in the extent of phase separation. The degree of phase separation profoundly influences the physical properties of the latexes. The final properties of the hybrid polymers depend on not only the amount and the type of the polymers but also the phase morphology and interfacial region between two polymers. Hybrid latexes synthesized by using different preparation methodologies were studied. A subsequent addition of organic (polyacrylate) and inorganic (polysiloxane) led to core-shell morphology where interfacial tension between the phases was moderated by alkoxyisilane.

Simultaneous preparation of hybrid latex can lead to very homogeneous interpenetrating network (IPN) opposed to subsequent addition of the phases. In this preparation method, the formation of organic and inorganic phase competes. The competition of the polymerization kinetics is followed by the thermodynamics of phase separation between two phases. The copolymerization of methacrylate-terminated polysiloxane with acrylic monomers in a batch reactor was studied in which simultaneous preparation method can minimize phase separation. Similarly, ring opening polymerization of cyclic siloxane monomers was conducted while free radical polymerization of acrylic monomers continues. The amount of polysiloxane added into polyacrylates has to be optimized to have properties such as lower surface tension or higher toughness. Modification of acrylic polymers with polysiloxane enhances some
properties like water resistance, temperature stability, and toughness of acrylic polymers. Additionally, film-forming of latex particles can be facilitated due to easy mobility of polysiloxane chains.

1.2 Polymerization Kinetics of Functional Monomers

Studies of emulsion polymerization kinetics have been extensively reported. However, controlling factors of latex stability leading to bimodal PSD are not well understood. Controlling PSD is important since better film formation and rheology characteristics can be obtained via bimodal PSD. Pedraza and Soucek obtained latexes with a bimodal particle size distribution (PSD) when a very high concentration (21 wt%) of functional monomers such as HEMA and MAA were used. The HEMA and MAA increased the solubility of monomer feed in water; therefore, colloidal stability decreased as the concentration of HEMA and MAA was increased, resulting in homogeneous nucleation and secondary particle formation. There are several reports on the polymerization kinetics of HEMA and MAA. Cheng and Chang studied emulsion polymerization of HEMA. They showed that nucleation ability of HEMA was weak relative to the persulfate initiator. Most of the HEMA was consumed in the first stage and located around the particle surface during the copolymerization of styrene with HEMA. The rate of polymerization increased in miniemulsion polymerization when the amount of HEMA increased. As the amount of methacrylic acid increased in styrene and butadiene pre-emulsion, the rate of polymerization increased. Another study also showed that a higher rate of polymerization was obtained in a batch reactor when the concentration of methacrylic acid increased. However, Dos Santos et al. showed that
MAA had a decelerating effect on the rate of polymerization due to desorption of oligomeric radicals.\textsuperscript{17}

In this study, the seeded two-stage latexes were prepared to investigate the effect of concentration of functional hydrophilic monomers (HEMA and MAA) on the polymerization kinetics and particle morphology. It was anticipated that change in hydrophilicity of monomer composition in core or shell would influence polymerization kinetics, interfacial tension, and morphology of latex particles. Latexes with varying core and shell composition were synthesized. Previously, the effects of varying monomer\textsuperscript{18} and seed compositions,\textsuperscript{19} feeding rate,\textsuperscript{20} the concentration of initiator\textsuperscript{21} and surfactant\textsuperscript{22} on polymerization kinetics have been reported. However, no study has been published on the effect of hydrophilic monomers (HEMA and MAA) on polymerization kinetics when the neat monomer and pre-emulsion is fed into a reactor. Additionally, no study has been reported on the morphology prediction of composite latex particles when the core and shell carry functional monomers such as HEMA and MAA and also very close theoretical glass transition. The effect of critical micelle concentration of the surfactants on polymerization kinetics was also discussed in this part.

1.3 Thermoset Acrylic Latexes

Thermoset latexes have drawn much attention due to their improved mechanical properties and chemical resistance compared to thermoplastic latex films.\textsuperscript{23,24} Thermoset latexes allow the use of polymers with low glass transition temperature, which facilitates the film formation at lower temperatures. A subsequent crosslinking of thermoplastic latexes leads to better physical properties due to increase in cohesive strength.\textsuperscript{25}
However, crosslinking degree has to be optimized to control desired properties such as high impact resistance and toughness. Therefore, crosslinking can be performed at different domains of latex particles such as homogeneous, interfacial, and interstitial sites to control physical properties. Several crosslinkers were studied such as amino resins, isocyanates, carbodiimides, aziridines, oxazolines, aromatic epoxides, zinc salts and silanes. However, there is not a variety of reports on the quantitative comparison of the coating and the mechanical properties of thermoset latexes, which could give an insight about the best crosslinker for different applications such as sealants or paints. The functional latexes (see introduction 1.2) were crosslinked by using five different crosslinkers. Core, shell or both core-shell was crosslinked with MF, zinc, N,N-dicyclohexylcarbodiimide, HDI isocyanurate and cycloaliphatic diepoxide. The distribution of crosslinking loci was expected to influence the mechanical strength of the film since the crosslinkers have different proximities to the functional groups in the core or shell. The mechanical properties of coatings were evaluated in terms of cross-hatch adhesion, pencil hardness, and impact resistance. In addition, tensile properties of thermoset films were tested. Design of experiment (DOE) was utilized to investigate the effect of variables on mechanical properties of crosslinked thermoset films.

In this part, dual-cure (thermal/visible light process) latexes were also prepared via semi-batch emulsion polymerization. Dual-cure systems carry unsaturated bonds cured by free radicals formed through radiation and also functional groups cured by thermal energy. The synthesis of thermal and visible light curable latex has not been previously reported. The duration of the film curing process can be decreased by the addition of visible light curing into the thermal curable formulation. The coating sagging
can be minimized. Additionally, dual-cure coatings can be used in multi-shaped substrates such as an auto-body. Amide- and acrylate-functionalized latexes were synthesized in separate batches by two-stage polymerization. In order to form a thermoset latex film, amide- and acrylate-functionalized latexes were blended in different fractions (50/50, 40/60, 60/40 wt/wt.) to find the best blend that yields the highest tensile properties such as elongation percentage. After the best weight ratio was determined, the mechanical properties as a function of the concentration of photosensitizer were studied.

1.4 Outline of the Dissertation

This dissertation is mainly composed of three related parts. The first part is presented in Chapter IV. The synthesis and characterization of polysiloxane-polyacrylate hybrid latexes is discussed. The morphology of hybrid latex particles is characterized via transmission electron microscopy (TEM). The morphology of film is characterized by AFM. The dynamic mechanical properties are also analyzed and presented in the same chapter. This part of the dissertation will have an impact on the improvement of some physical properties of industrial acrylic latexes such as toughness and water repellency.

The second part focuses on the polymerization kinetics of functional monomers such as HEMA and MAA in the presence of two anionic (Triton X-200, Aerosol MA80) or two nonionic (Tergitol XJ, Triton X100) surfactants. This part is presented in Chapter V. In Chapter VI, the effect of hydrophilicity of either core or shell of latex particles on the particle morphology is presented. The concentration of HEMA in core and MAA in shell is varied similarly. The extent of diffused phase between core and shell, interfacial tension, and the morphology are studied. Additionally, this chapter includes the
comparison of polymerization kinetics when either neat monomer or pre-emulsion is used as feed. The second part of dissertation is believed to contribute optimization of polymerization kinetics of functional monomers such as HEMA and MAA in the emulsion polymerization area where there are not so many reports in the literature. These functional emulsion polymers also carry crosslinking sites that can be cured and ultimately enhance mechanical properties of the latexes for many coating applications.

In the third part of the dissertation, the synthesis and characterization of thermoset latexes is presented. The functional latexes (presented in the second part) are crosslinked with external crosslinkers and cured. The coating and mechanical properties of thermoplastic (non-crosslinked) and thermoset (crosslinked) are characterized. The mechanical properties of coatings are evaluated in terms of tensile and dynamic mechanical properties, cross-hatch adhesion, pencil hardness, and impact resistance. This part is given in Chapter VII.

The dual-cure (thermal/visible light process) amide- and acrylate-functionalized latexes are synthesized. These two latexes are blended in different ratios to obtain thermoset latex films. Tensile and dynamic mechanical properties are studied as a function of weight ratio of these functional latexes. After the best mechanical properties are obtained, the mechanical properties are analyzed as a function of photoinitiator concentration for the optimum weight ratio. The details are given in Chapter VIII. The conclusions of the study are summarized in Chapter IX.
CHAPTER II

LITERATURE REVIEW

2.1 Definition of Latex

Latex is stable colloidal dispersion in the liquid (continuous phase) where polymer is not soluble. Latexes are lyophobic (not diffusing into solution) sols. Therefore, the latex particles are metastable compared to coagulated particles. There is a thermodynamic tendency favoring the coagulation of particles by Brownian motion since the coagulation decreases the free energy of the system due to a decrease in interfacial area. Polymer colloids in latexes aggregate into gelled state in which particles are very small in macroscopic scale. However, polymer solutions in the organic solvents are completely mixed with the solvent in microscopic state. This distinction in microscopic states of latex and solvent-based polymer leads to very high viscosity difference, even if the polymer solutions have very low concentrations. As the molecular weight of polymer increases, viscosity increases dramatically. Therefore, solvent-based polymer solutions require more complicated machinery for processing than water-borne systems.\(^{28}\)

Latex can be classified according to the origin, physical nature of polymer, chemical nature of polymer, and polarity of particles. If one classifies according to origin, latex can be divided into natural lattices (from plants), synthetic lattice (emulsion polymerization), artificial lattice (bulk polymer dispersed in liquid), and modified
lattice (modification of existing latex). The physical nature of lattice is classified into rubber (rubbery at room temperature) and resin (glassy polymer at room temperature) lattices. Classification can be made according to electric charge of latex. Anionic lattice (particles bear negative charges), cationic lattice (particles bear positive charges), and neutral lattice (neutral particles) are the divisions of this classification.28

2.2 Emulsion Polymerization

Emulsion polymerization, the heterogeneous reaction initiated by free radicals, is a method to prepare dispersions of monomers having limited solubility in water. Emulsion polymerization offers many advantages. Specific architectures, e.g., core-shell, can be obtained through emulsion polymerization. The emulsion polymer particles can be designed in respect to the end use. Functional groups are added on shell so particles are crosslinkable to enhance mechanical properties. Emulsion polymer having either hard or soft shell/core can be formulated for different applications. The glass transition temperature (T_g) can be modified in the acrylic latex. Minimum film forming temperature (MFFT) can be decreased below room temperature by virtue of monomers and core-shell architecture. Volatile organic content can be minimized in emulsion polymerization. Thus, environmentally friendly coatings, adhesives, sealants and paints are prepared.

Emulsion polymerization is carried out by stabilizing components (polymers) by virtue of stabilizers into emulsion. Emulsion refers to a two-phase system. One phase is continuous that is water and the other one is small droplets, which is the dispersed phase. Latex is the final product having fine and stabilized polymer particles by surfactants. Particle sizes are typically sub-micrometer (0.1-0.5 μm). Latexes have 10^{16} particles per
liter and very high surface area (2000 m²/liter). Aqueous emulsion polymers are now the highest volume resins used in the coatings industry due to easy modification of resins for different applications.\textsuperscript{29}

Emulsion polymerization has some advantages and disadvantages. Advantages can be summarized briefly as:

- Heat, evolved due to free radical polymerization, is easily absorbed by continuous phase.
- Polymer has higher molecular weight than polymer obtained from bulk polymerization.
- Higher rate of polymerization is obtained in emulsion polymerization than corresponding bulk polymerization.
- Viscosity of dispersion is much lower than that of polymers in organic solvents. Therefore, processing of polymer is easy.
- Volatile organic content (VOC) is reduced, which allows one to decrease costs and environmental hazards.
- Very high conversion is obtained due to low viscosity of medium.

On the other hand, emulsion polymerization has some disadvantages, such as:

- Many kinds of additives are used for emulsion polymerization such as surfactants, co-stabilizers, and buffering agents. This makes it very costly to purify emulsion polymers.
- In order to separate polymer from water, organic solvents (coalescence agents) might be needed. This also increases production expenses.
- Polymerization is very hard to control due to complex mechanism.\textsuperscript{30}
2.2.1 Components in Emulsion Polymerization

The main components in emulsion polymerization are monomers, dispersing medium (water or solvent), emulsifying agent, and initiator. Monomers used in the industry can be divided into five main categories;

- Butadiene-styrene-acrylonitrile
- Vinyl chloride-vinyl acetate
- Vinlylidene chloride
- Acrylate and methacrylates
- Water-soluble monomers, e.g., (meth)acrylic acid and acrylamide

The most suitable monomers for emulsion polymerization are the ones that have enough water solubility, but not too much. Gaseous monomers such as ethylene might need a special reactor. Monomers such as (meth)acrylic acid are used as adhesion promoters and crosslinking sites. Monomers with low glass transition temperature as polymer form decrease minimum film-forming temperature (MFFT). Lower MFFT of formulation is especially preferred in highly pigmented resins.

The dispersing medium of emulsion polymerization is generally water. Emulsifiers are used to stabilize polymer particles after and during polymerization. Emulsifiers (surfactants) also form a locus (swollen micelles with monomers) which is one of the possible nucleation sites. Surfactants are categorized into ionic (cationic and anionic), nonionic and amphoteric (zwitterionic). Dispersion is stabilized by electrostatic repulsions in anionic surfactants. Nonionic surfactants provide steric stabilization.

Polymerization is initiated by free radicals. Initiators (water or oil soluble) are the source for free radicals. A good initiator should have high free radical efficiency at
reasonable temperatures. Dissociation energy of an initiator lies between 100 and 170 kJ/mole. Water-soluble initiators, sodium or ammonium persulfates, decompose at 50-90 °C. Oil soluble initiators are peroxides and azo compounds. Persulfate-bisulfite and persulfate-hydrosulfite are two common redox initiators employed at lower temperatures.\(^{31}\)

Water-reducible resins are prepared by reacting carboxylic acid-functionalized resins with amine compounds. After the reaction between carboxylic acids and amines, the stability of resin is increased due to electrostatic repulsions. However, neutralizing agents have a dramatic effect on the viscosity of resin. Therefore, a neutralizing agent has to be selected carefully.\(^{32}\) The presence of carboxylic groups might not suffice for the solubility of water-reducible resin in water. The addition of solvent is required to increase the solubility of organic resin. Solvent is selected based on the viscosity, gloss and substrate wetting of final coating formulation.

Film-forming agents are used to decrease minimum film forming temperature (MFFT). A film-forming agent with low odor is desired. Additionally, the film-forming agents should be good plasticizers for the polymer resin and also yield no saponification with alkaline. Good film-forming agents should not cause coagulation and viscosity increment for the latex particles. The film-forming agent functions faster during film-formation when the residence time of the agent in the outer layer of the particle is higher than the residence time in the core of the particle or water phase.

Thickeners are also utilized as additives to increase viscosity of dispersion and prevent settling of pigments. Thickeners are also used in order to attain high enough viscosity for polymer processing. The ideal thickener must not influence gloss, leveling,
and soiling. Thickeners can be divided into 4 main groups: a) inorganic, silicates like montmorillonite, b) organometallic, cellulose ethers with addition of titanium chelates c) organic, carbomethoxy/methyl cellulose d) synthetic organic, polyacrylates, polyvinylpyrrolidones.33

2.2.2 Emulsion Polymerization Stages

When water-insoluble monomers are employed, most of the monomers take place in micelles if surfactant concentration exceeds critical micelle concentration (CMC). The surface area of micelles is higher than surface area of droplets, which feeds micelles during polymerization. Therefore, polymerization mostly occurs in micelles due to high surface area and high solubility of monomers. The polymerization in droplets is insignificant (<0.1 wt%).

During the progress of emulsion polymerization, three distinct intervals are observed, according to Harkins.34 Particle formation, initiation and nucleation take place in interval I. Micelles are used up due to growth of particles. Interval I ends when maximum number of particles is formed and the highest rate of polymerization is reached. In interval II, the number of particles remains constant while the volume of monomer droplets decreases. At this stage, surfactant concentration decreases below CMC. Monomer droplets supply monomer and surfactant to growing particles. At the beginning of interval III, polymer droplets completely disappear. The polymerization rate increases in interval I since new particles are formed. On the other hand, the rate is constant in interval II. The rate of polymerization decreases in interval III since monomer concentration is low.
2.3 Film Formation of Latex

Latexes can be used in two different forms in industry: coagulated latex films or dispersed form. The film formation of dispersed form of latex follows three main steps:\(^35\):

- Figure 2.1 shows the schematic representation of film formation mechanism of latex. It starts with the formation of a closed-packed layer when water evaporates. As water evaporates, particles approach each other. Thus, void-free arrays are formed.

- Deformation of particles from their spherical shapes into polyhedral shapes by virtue of capillary forces that are formed by spaces between particles. Initial interfaces gradually vanish. To complete deformation of particles, a temperature higher than minimum film formation temperature (MFFT) is required. Capillary forces have to overcome steric and electrical repulsions. Reduction in free energy of particles due to a decrease in the surface area of particles has to be taken into account in particle deformation. Broader particle distribution is also helpful to attain a rapid film formation.

- Inter-diffusion of chains occurs across boundaries. Entanglements between polymer chains form a totally continuous film. Initial granular structure is lost. This step is crucial to strengthen the film. In order to have complete inter-diffusion, temperature has to be higher than the glass transition temperature (\(T_g\)) of polymers. If the \(T_g\) of polymer is greater than room temperature, baking is needed for a totally continuous film. Rate of inter-diffusion depends on the \(T_g\) of polymers, which is a function of free-volume and chain length of polymer chains. Less branched polymers diffuse more rapidly compared to more branched...
polymer chains. The distance of inter-diffusion is much smaller than the diameter of particle. Full strength of film is achieved if polymer chains near interfaces diffuse a distance equivalent to their root-mean squared radius of gyration ($R_g$) across inter-particle boundary.$^{23}$
Figure 2.1. Schematic representation of main steps in latex film formation (a) particles approach each other as water evaporates. (b) flocculation of particles. (c) deformation of particles from their spherical shapes into polyhedral shapes. (d) inter-diffusion of chains occurs across boundaries.\textsuperscript{36}
Film properties depend on the diffusion rate of chains and crosslinkers. If the reaction rate of crosslinking is higher than the diffusion rate, mainly intra-cellular crosslinking occurs. This kind of pre-crosslinked latex particles results in films having brittle structure and insufficient cohesive strength, especially when the molecular weight between crosslinking points ($M_c$) is smaller than the molecular weight between two entanglements ($M_e$).\(^{37}\) Diffusion rates in negatively charged particles, e.g. neutralized acrylic acids, are slower due to electron repulsion.\(^{38}\)

Cohesive strength of the film depends on friction between polymer chains and the concentration of chain segments cross boundaries during the application of tensile force. The chain breaking-up dominates over chain pullout in glassy polymers.\(^{39}\) Adhesion strength of particles depends on the diffusion rate of polymer chains. When the crosslinkers are used, polymer diffusion is more complicated. Compromise between diffusion rate and rate of crosslinking has to be obtained. Inter-diffusion slows down when the molecular weight of chains and the rate of crosslinking are higher.\(^{40}\) If the rate of crosslinking is smaller than the diffusion rate, particle interfaces have perfect coalescence. In this case, tear strength of the film is almost equal to cohesive strength. When the rate of crosslinking is almost the same as the diffusion rate, the boundary is crosslinked before reaching equilibrium. If the rate of crosslinking is very fast, no crosslinking across boundaries is formed. The concentration of polymer segments passing through interface is smaller.\(^{41}\)
2.4 Thermoplastic and Thermosetting Latexes

Thermoset latexes have several advantages over thermoplastic latexes. Low molecular weight is converted to infinite molecular weight and viscosity increases during crosslinking of thermoplastic systems. Thermosetting polymers have higher solvent, moisture, abrasion resistance, and cohesive energy density than thermoplastic latexes. Shear and tensile moduli are also larger than in thermoplastic polymers. Thermoset polymer is swollen in suitable solvents, instead of dissolving like in thermoplastic latexes. On the other hand, elasticity of polymer decreases as extent of crosslinking increases. Crosslinking in polymers delivers a rapid network formation when molecular weight of polymer increases. Crosslinking sites in polymer chains, however, bring some problems. Particles in latex are stabilized by electrostatic and steric forces. If there are some functional groups that crosslink in the pot, particles cannot remain stable and the molecular weight of the polymer becomes extremely large. This shortens the pot life of the formulation. Ideal latex formulation should crosslink preferably at room temperature. However, latexes that can be crosslinked under special conditions (desired pH and temperature) are also industrially available.

Crosslinking has to be controlled after the latex is cast. The latex film might have cracks and brittle structure if crosslinking occurs so quickly. Additionally, the film might form some craters. In order to have effectively crosslinked film, functional groups must have regular spacing along the chain to enhance collision rates of the functional groups. In order to obtain polymers with regularly spaced functional groups, polymerization with gradual feeding (starved-feed condition) can be employed.
Latex formulation can be cured at a higher temperature than the minimum film formation temperature in order to improve the coherency and strength of the film. Extent of crosslinking is enhanced at temperatures higher than MFFT. Catalyst is also used to aid crosslinking. To keep latex system stable, volatile ammonium salts can be employed where interaction between carboxylic acid and crosslinkers can be blocked in the pot.42

2.4.1 Network Formation of Thermoset Latexes

A network of polymer chains is formed through crosslinks. As linking proceeds, larger branched polymers are obtained from “sol,”--that is, soluble species in solvent. Finally, the structure becomes a huge molecule that is not soluble in any solvent. This theoretically infinite structure is called as network or gel. Transition from sol to gel is called a sol-gel transition and it occurs through physical or chemical crosslinking. This mechanism is explained by using a bond percolation model in which all monomers in polymer chain occupy sites of a lattice.43 Crosslinks are randomly formed between active sites and available functional groups of neighboring sites. If solvents are included in the model, solvent replaces crosslinking neighboring groups.44 Flory45 based the evolution of network structure on quantitative mean-field theory. He proposed:

- All functional groups are equally reactive.
- Reactivity is not dependent on the size of functional groups.
- Intramolecular cycles are not present in finite species.46

Gel fraction depends on the concentration of functional groups, which is the ratio of crosslinked functional groups to initial functional group concentration.42 Gel fraction is
calculated by the swelling ratio in which the chemical potential for solvent penetration into film is balanced by elastic deformation of the network. Change in chemical potential of crosslinked network after interaction with solvent is higher if crosslink density is higher.\textsuperscript{47} If average molecular weight between crosslinks ($M_c$) decreases, higher crosslink density, i.e. lower swelling ratio ($Q$), is obtained for a given Flory-Huggins parameter ($\chi$). If the Flory-Huggins parameter ($\chi$) increases (proportional to difference of Hildebrand solubility parameters of polymer network and solvent), interaction enthalpy for swelling becomes higher.\textsuperscript{23} Some authors claimed the Flory-Huggins parameter ($\chi$) is not constant but depends on volume fraction of polymer in solvent.\textsuperscript{48} Polydispersity index (PDI) also has a very important influence on the extent of crosslinking. As PDI increases, the extent of crosslinking decreases due to the decrease of the number of crosslinked monomers as average molecular weight increases.

2.4.2 Physical Crosslinking

When the solvent is removed, secondary bonds like hydrogen and van der Waals forces are formed between chains. The H-bonds are formed through dipole-dipole interaction of polar functional groups such as –COOH and -OH. The VDW forces arise from electrostatic attraction of one nucleus of one molecule and the electrons of another. An appropriate distance between functional groups is needed to have secondary bonds. Secondary bonds have thermoreversible character dissimilar to chemical crosslinking. Therefore, secondary bonds have finite lifetimes. The secondary bonds form and break continuously. When the network is heated up, secondary bonds are broken and reformed during cooling. Secondary bonds form inter-molecular and intra-molecular secondary
bonds. The H-bonding is three or four times stronger than VDW forces. Therefore, networks with polar functional groups are stronger than films having only VDW bonding.

2.4.3 Chemical Crosslinking

Chemical crosslinking involves formation of covalent bonds, which results in strong gel. To obtain chemical crosslinking, appropriate functional groups, e.g. -COOH and -NH₂, have to be closer to react. This situation is observed when sufficient water evaporates. This is followed by deformation of particles due to capillary forces. Solvent moisture and temperature resistant networks are obtained by adding crosslinkers. Cohesive strength of network also increases.

Chemical crosslinkers can be added externally or copolymerized (internally) into the backbone of polymer chain. Both of the crosslinkers should be soluble in water or solvent. The internal crosslinkers are vinyl or acrylate monomers containing functional groups such as -Si(OCH₃)₃ and/or -NH₂-CH₂-OH. The external crosslinkers are used for dispersion. In this type of coating, two-pot (2K) coating formulations are prepared where the polymer is mixed with crosslinker just before application. Selection of external crosslinker is very important. Side reactions of crosslinker with other species, e.g. substrate and hydrolysis with solvent, are undesirable.

2.5 Types of Crosslinkers

Crosslinking agents are used to enhance the hardness, abrasive resistance, and chemical resistance. Crosslinking agents can be a part of latex formulation but
crosslinkers should not ruin the stability of latex or decrease the pot-life. Crosslinkers can be added into polymer backbone during polymerization. Alternatively, crosslinkers having multiple crosslinkable sites can be added into formulation after latex is synthesized. Formaldehyde and glyoxal can be added into synthesized polyvinyl acetate and polyvinyl alcohol latexes, respectively. Several crosslinking agents have been proposed in literature. The mechanisms of crosslinking chemistries are shown below.42

2.5.1 Derivatives of Acrylamide

Curing reaction between carboxyl and amide containing acrylic polymers can eliminate self-condensation of alkylol acrylamide derivatives.49 The presence of acrylamide as comonomer can eliminate evolution of formaldehyde that occurs in alkylol acrylamide derivatives in basic medium.35 Polyacrylamide is also used as a flow modifier or thickener in latexes. Because of the high rate of equilibration, polyacrylamide modifiers showed more Newtonian rheology than most other commercial modifiers.50 Stable dispersions containing acrylamide can be obtained when the pH of water is less than or equal to pK_a of the carboxylic group. The carboxylic acid groups can be deprotonated, which allows the formation of stable particles via electrostatic charges.51

2.5.2 Radiation Curing

Curing can also be initiated by radiation. Crosslinking starts when functional groups are radiated. Hence, radiation-curable coating formulations have longer pot-life than thermal curing coatings. Curing can be completed at room temperature very rapidly. Therefore, heat sensitive substrates can be coated with coatings. Ultraviolet, infrared,
electron beam cure, γ-rays and microwave can be used for curing of unsaturated functional groups. Visible light curing of latexes was also reported.\textsuperscript{52} Figure 2.2 shows the schematic representation of radiation curing.

Energy requirement and volatile organic content are minimized by employing radiation curing. Thermal curing needs more space than any radiation curing. On the other hand, radiation curing is only applicable to flat sheets or webs. Curing in pigmented coatings is limited since radiation can reach just into a top layer of coating.\textsuperscript{52} The shrinkage during curing of unsaturated functional groups causes poor adhesion of coating.

Photopolymerization can be initiated by free-radical or cationic photoinitiators. The photoinitiator should have high absorption coefficient in the range of activation and a high quantum yield. The photoinitiator also should be soluble in resin, odorless, and nontoxic.\textsuperscript{53} Two classes of photoinitiators are used to cure unsaturated functional groups. These can be either unimolecular (e.g. acylphosphines, iron arene salts, peresters), or bimolecular, formulated with photosensitizer like N-phenylphthalimide. In bimolecular initiators, hydrogen is abstracted from photosensitizer to form free radicals.\textsuperscript{54} A small amount of the photoinitiators is consumed during curing.\textsuperscript{35}

Visible light curing shows potential in the use of latex paints since rate of drying is faster than conventional drying. However, the rate of radiation curing should be insensitive to presence of oxygen and slow enough to allow painting. Final film should be white, implying there was no oxygen interference with unsaturated bonds.\textsuperscript{54} Intensity of the light should be adequate to obtain a complete crosslinking.\textsuperscript{52} Visible light curing of unsaturated functional groups by camphorquinone in dental applications was already
reported by several authors. Camphorquinone was the least oxygen sensitive photoinitiator. Additionally, clear films were obtained after curing.

![Figure 2.2. Schematic representation of curing of unsaturated bonds by radiation.](image)

2.5.3 Isocyanate Curing

Multi-functional aliphatic or aromatic polyisocyanates can be used as external crosslinkers to improve tackiness and cohesive strength of film. Isocyanates, -NCO, are reactive with many functional groups such as amines, acids, polyols and water as shown in Figure 2.3. The reactivity of isocyanates can be decreased by using blocking agents in pot, e.g. phenol, but the film needs to be baked at high temperatures like 150 °C for curing. The isocyanate (isopropenylidimethylbenzyl isocyanate (TMI)) reacting slowly with water was previously reported as comonomer in a self-crosslinkable latex. Self-crosslinkable latexes were synthesized when TMI is copolymerized with monomers having functional groups such as -COOH, -NH₂, -OH. The TMI retarded new particle formation due to slow reactivity ratio. Pot life of latexes containing isocyanates is relatively short due to hydrolysis. Therefore, the formulation needs immediate casting after the latex is synthesized. The rate of hydrolysis is decreased by neutralizing medium and copolymerizing TMI in the interior part (core) of the latex particle. By copolymerizing TMI in core, intra-particle crosslinking was prevented.
Figure 2.3. Schematic representation of curing of isocyanate-modified latex with (a) amine functionality. (b) carboxylic acid functionality. (c) hydroxyl functionality.

2.5.4 Vinyl Ester Curing

Vinyl acetate (VAc) is one of the most common and oldest curable monomers. It is cheaper than (meth)acrylic esters and mainly used with cellulosic substrates. However, VAc latexes have poorer hydrolytic and photochemical stability than (meth)acrylic esters. Hydrolysis of VAc monomers is triggered through the anchimeric effect of hydrolyzed VAc monomer that yields acetic acid. This mechanism can be retarded by means of the umbrella effect via copolymerizing branched vinyl or acrylic ester comonomers like 2-ethylhexyl acrylate. Vinyl acetate polymers might undergo creep so coating sags. The glass transition temperature of PVAc homopolymer is 33 °C, which is too high to coalesce. In order to decrease MFFT, VAc was copolymerized with low Tg acrylic asters. On the other hand, reactivity ratio of VAc is slower than butyl acrylate, but
solubility in water is higher. This leads to unreacted VAc monomers in last stages of polymerization. Therefore, the reaction should be held under starved-monomer conditions to obtain uniform polymer.\textsuperscript{60} Partially hydrolyzed PVAc is crosslinked through hydroxyl (–OH) groups with urea- and melamine-formaldehyde resins, dialdehydes like glyoxal and glutaraldehyde. Inorganic salts such as boric acid, titanium, zirconium, vanadium or chromium compounds also have been suggested to crosslink PVAc. However, the rate of crosslinking is high, and the reaction rate has to be controlled. Self-crosslinkable latex was synthesized with co-monomer, N-(alkoxymethyl)-acrylamide, to control polymerization rate.\textsuperscript{61} Copolymerization of VAc with diacids and anhydrides also yields self-crosslinkable resins. As hydrolysis of VAc increases, crosslink density increases. Itocanic acid is found to be among the best crosslinking co-monomers with PVAc among fumaric acid, maleic acid, and maleic anhydride.\textsuperscript{62} A schematic representation of vinyl acetate latexes crosslinking after hydrolysis is shown in Figure 2.4.

![Figure 2.4. Schematic representation of vinyl acetate functionalized latexes.](image)

2.5.5 Acetoacetate Curing

Acetoacetate esters can be copolymerized with acrylic monomers to synthesize self-crosslinkable latexes forming enamine bonds. Crosslinking occurs at room
temperature in the presence of diamine. Acetoacetate esters are less hazardous than isocyanates and oxirane rings. However, acetoacetoxy esters like acetoacetoxyethyl methacrylate (AAEMA) have hydrolytic stability problems. Decarboxylation of AAEMA yields 2-hydroxy ethyl methacrylate (HEMA). To increase the stability of AAEMA, AAEMA was reacted with ammonia.\(^63\) The reaction between AAEMA and ammonia yields amino-enamine. The modification of AAEMA blocks extends the pot life of formulation. Diamine starts crosslinking after casting the film after ammonia evaporates. The increase in MFFT of latex is prevented by blocking the hydrolysis of AAEMA since AAEMA has lower \(T_g\) than HEMA.\(^64\) Post-curing with diamine improved transparency and mechanical strength of film. Diamine functioned as crosslinker of soft-segments and flocculating agent for hard segments.\(^65\) Figure 2.5 shows the crosslinking reaction of acetoacetoxy with amines.

Figure 2.5. Schematic representation of crosslinking of acetoacetoxy functionalized latexes with amines.
2.5.6 Aldehyde Curing

Glyoxal and gluteraldehyde are used to crosslink hydroxyl groups to yield transacetal groups in acidic medium. Glutaraldehyde yielded higher modulus than glyoxal. Curing is accelerated at higher temperatures, which increases the storage modulus of film. To keep latex stable, the ratio of dialdehyde was adjusted to 0.3 wt% of the total amount of functional group. Curing with dialdehydes was employed to convert hydrophilic surfaces to hydrophobic surfaces to improve oxygen and moisture permeability. Figure 2.6 shows the curing reaction between glyoxal and polymers carrying functional groups such as hydroxyl, amine, and carboxylic acid. Unfortunately, pot-life of dispersion is short when two-pot (2K) formulations are prepared. Blocking of glyoxal with cyclic urea was proposed to increase pot-life.

![Figure 2.6. Schematic representation of crosslinking of hydroxyl- and amine-functionalized latexes with glyoxal (a) hydroxyl functionalized, (b) amine functionalized latexes.](image)

2.5.7 Curing with Water-Soluble Polymers

Vinyl pyrrolidone (VP) is water-soluble monomer. The vinyl pyrrolidone copolymers form lattices that have freeze-thaw stability, chemical stability and good
mechanical strength. Films have superior adhesion on substrate due to polarity of VP. Poly(vinyl pyrrolidone) films show high grease resistance and moisture absorption. Vinyl pyrrolidone undergoes ring-opening reaction in presence of acids so it can be crosslinked. On the other hand, the reactivity ratio of VP is lower than ethyl acrylate so VP might polymerize as homopolymer in the later stages of polymerization. This led to latex instability resulted in coagulation. The PVP undergoes ring-opening at elevated temperatures in the existence of acid or base catalyst. Afterward, carboxylic acid groups that crosslinked with amine groups evolved.

Polyamines are reacted with crosslinkable groups such as epoxy, diacids, acyl halides, etc. Epoxy was hardened with amine derivatives for anticorrosion purposes, but curing was relatively slow. Aliphatic epoxy derivatives were used to reduce MFFT and VOC. Polyethyleneimines are branched polyamines made out of ethyleneimine. Figure 2.7 shows the chemical structure of polyethyleneimines where primary, secondary, and tertiary amines are available functional groups.

![Chemical structure of polyethyleneimine](image)

Figure 2.7. Chemical structure of polyethyleneimine.
2.5.8 Curing with Zinc and Zirconium salts

Zinc salts offer non-formaldehyde curing with (meth)acrylic acid containing polymer dispersions via ion bridging. Stable one-pack polymer dispersion is prepared with amine complex zinc compounds. This complex makes very hard and water-resistant coatings. Figure 2.8 shows a schematic representation of the crosslinking reaction between zinc ions and carboxylic acid groups via Coulombic interactions where ammonia neutralizes carboxylic acid. Molecular weight and thermosetting character of network increased after curing with zinc.

Zirconium ammonium carbonate is also used for the same purpose. This salt can enhance adhesion on low surface energy substrates. It is also used as a viscosity modifier in paints due to interactions with carboxylic anions. Cohesion of film increased after curing with zirconium salts while tackiness decreased. Crosslinking efficiency of zinc or zirconium ammonium complexes increases as pH of dispersion decreases.

![Figure 2.8. Schematic representation of crosslinking of carboxylic-functionalized latexes with zinc compounds.](image)

2.5.9 Oxirane Curing

Oxirane (epoxide) groups react with functional groups such as amines, carboxylic acids and alcohols. The significant properties of cured epoxy are attributed to the
chemical structure of epoxy ring. Once epoxy group opens, polar hydroxyl group is formed, which helps adhesion to substrate through hydrogen bonding. Other carbon on the ring is available for reaction with functional groups.\textsuperscript{29} It is stable to hydrolysis, so self-crosslinkable latexes can be prepared via copolymerizing glycidyl methacrylate (GMA).\textsuperscript{74} Hydrolysis of GMA can be prevented by increasing the rate of monomer feeding in semi-batch reactor. This results in a higher concentration of GMA in the interior part of the particles due to higher rate of polymerization. Therefore, GMA has less interaction with water. Decrease in polymerization temperature also helps to prevent hydrolysis.\textsuperscript{75} Glycidyl methacrylate has almost same reactivity ratio with methyl methacrylate (MMA). The reactivity ratios are 0.75 for GMA and 0.69 for MMA. Uniform copolymer of MMA and GMA is obtained. Uniform terpolymer of ethyl acrylate (EA), MMA and GMA is obtained if the addition of GMA is delayed to the last stage. Glycidyl methacrylate was copolymerized with polymerizable acids such as maleic or itaconic acids to synthesize catalyzed self-crosslinkable latexes.\textsuperscript{42} Water resistant and curable films at room temperature were synthesized by polymerizing GMA in core and methacrylic acid (MAA) in shell. If the mixture of two types of particles with either GMA or MAA shell was used, then high temperature (125 °C) was needed for curing.\textsuperscript{75} Figure 2.9 shows the crosslinking reactions of oxirane rings with various reactants (amine, carboxylic acid, and hydroxyl groups).
2.5.10 Silane Curing

Alkoxy silane derivatives are used for clear, moisture- and weather-resistant coatings. Additionally, films with low glass transition and surface tension can also be obtained via silane curing. These properties can be adjusted by preparing different architectures. Silane moiety can be catalyzed for self-condensation through moisture in air. Therefore, resin is kept stable in pot due to absence of any catalyst. The thermogravimetric analysis (TGA) showed the weight loss of films decreased as content of alkoxy silane increased due to stronger carbon-silicon (C-Si) bonds. Glass transition of shell in particles increased since silane groups were crosslinked. Incorporation of vinyl triethoxysilane (VTES) is more convenient than methacryloxypropyl trimethoxysilane (MATS) to prepare stable latexes because silane in MATS is easily hydrolysable due to flexible propyl (-C₃H₇) functionality. Therefore, using MATS in the formulation causes premature crosslinking and shorter pot-life. On the other hand, closer ethoxy groups to vinyl functionality in VTES prevent silane hydrolysis. The volume shrinkage during film
formation is less in latex with VTES than in latex with MATS. However, VTES has higher Tg and lower reactivity ratio than MATS. The VTES might remain unreacted in the reactor or form low molecular weight homopolymers. Polydimethylsiloxane-functionalized latex by MATS showed a higher pot life. Water and toluene resistance was also improved. Figure 2.10 shows the schematic representation of crosslinking reaction for silane-functionalized latexes.

![Figure 2.10. Schematic representation of crosslinking for silane-functionalized latexes.](image)

2.6 Hybrid Systems

Acrylic or vinyl latexes find a wide range of applications. But there are some deficiencies of these polymers such as poor toughness. In order to improve physical and chemical properties of latexes, other generic polymers such as organic (polyurethane) or inorganic (polydimethylsiloxane) can be used. The formulations with more than one type of materials such as epoxy-acrylics and urethane-acrylics are called as hybrid systems. Hybrid systems may contain inorganic and organic substances to enhance the overall properties of the final product. Inorganic materials increase hardness and stiffness whereas organic materials form the network and improve the toughness of the final product.

Hybrid systems are gradually more utilized in coating formulations. Blending of polymers from different generics might result in microphase separation if polymers are
not completely compatible. On the other hand, stable systems and smaller domain sizes of each phase are obtained by preparing grafted polymers. Hybrid latex systems are prepared by free radical polymerization of one generic class of polymer onto another generic class of preformed polymer. If the preformed polymer is water dispersible, it is used as seed and other type of monomers is polymerized onto that seed. If the preformed polymer is not water soluble, stable emulsion seeds are prepared by the high shear rate in the presence of surfactant. Alkyd/acrylic latexes are prepared by emulsifying alkyd and then acrylic monomers polymerized around alkyd. In some instances, preformed polymer has pendant functional groups that are used for grafting of other polymer chains. This preparation method brings improved mechanical properties over blending of two polymers.80

Hybrid systems are prepared to combine superior properties of thermal properties of inorganic materials and elastic properties of organic materials. Organic materials act as network formers and modifiers. The final material can have good elasticity, fracture toughness, low density by organic material, and hardness, stiffness, abrasion resistance and thermal stability by inorganic material. On the other hand, higher content of inorganic material increased stress-cracking.81 Impact strength can be enhanced by preparing hybrid systems. Acrylonitrile-Butadiene-Styrene (ABS) has very high impact strength due to its hybrid nature. Therefore, ABS is frequently used in the automotive industry. Surface-modified latexes find applications in medical diagnosis due to the high surface area of the system and simple modification of shell according to applications. Unlimited applications of hybrid materials are possible by post-polymerization modification.
2.6.1 Silicone-Modified Resins

Silicone coatings have improved water, UV resistance and exterior durability. These coatings also have very high mobile character at a wide temperature range due to easy rotation of siloxane (Si-O-Si) bonds. On the other hand, silicone coatings have less tear resistance, low modulus and high dirt pick-up. Silicone-modification of other polymers can improve water and UV resistance of overall film. After silicon modification of polymer, processing of the final product is easier due to very low surface energy and melt viscosity. Silicone-modification enhances non-flammability and thermal stability of the final resin. These properties can also be modified by changing functional groups, molecular weight and degree of branching of polysiloxane.

Silicon modified-alkyds show better exterior durability than unmodified-alkyd resin. These coatings are generally used in air-dry coatings. Silicon-polyesters are used in coil coatings. These coatings also show better exterior durability than unmodified polyester or acrylic films. Yellowing resistance, hydrolytic stability and flexibility of polyester/polysiloxane coatings were enhanced by utilizing cycloaliphatic monomers. In addition, viscosity of cycloaliphatic monomers was lower than linear monomers. The brittle character of epoxy resins was lessened by grafting silicone rubber. Siloxane rubber was employed as toughening agent. Polyurethane/polysiloxane systems combined superior properties of each resin; for example, good mechanical properties of polyurethanes, and good adhesion and corrosion protection from polysiloxane. Moisture-curable polyurea/poly-siloxane system showed great adhesion on aluminum substrate, good corrosion inhibition and self-priming properties.
The hydroxyl-functionalized acrylic resins are reacted with methoxysilane (Si-OCH₃) modified polysiloxane in the presence of catalyst such as tetraisopropyltitanate. These resins showed better defoaming properties than unmodified-acrylic resins. Impact strength is increased by integrating siloxane on acrylic polymers. On the other hand, hardness and tensile strength decreased. Siloxane-polyimide hybrid coatings were prepared through sol-gel process. Adhesive melting flow reduced. In addition, crosslink density and storage modulus increased due to crosslinking between silanes. Thermal stability was also improved relative to pure polyimide films. Siloxane-epoxy systems that showed excellent chemical resistance were prepared at a lower cost than multi-layer coatings. Corrosion and moisture resistance also increased.

Hybrid latexes with hard core and soft shell particles can be prepared. Polysiloxane chains are grafted onto hard acrylic core. MFFT is decreased due to soft polysiloxane shell. However, this structure has poor paintability due to the low surface tension of polysiloxane. When vinyl-modified siloxane was grafted onto shell, morphology of particle was distorted.

2.6.2 Other Classes of Hybrid Systems

Hybrid systems provide better physical properties than corresponding blend systems due to their unique particle morphology. Acrylic polymers can be combined with other organic polymers such as polyurethanes, alkyds, and polyesters to be used in multiple applications. Polyurethane hybrid systems find several applications such as wood lacquer, plastic coatings, and adhesives due to their flexible chemistry. Polyurethane-seeded acrylic dispersions can be prepared after isocyanate functionalities
are extended by diamines. Polyurethane tends to remain on the surface due to polarity of multiple ionic groups whereas acrylic phase penetrates to the core. This morphology forms a continuous film in polyurethane phase other than polyurethane/acrylic phase. These dispersions have higher exterior durability, better solvent resistance, and wear resistance.\(^9\)

Combination of alkyds with acrylics also offers many synergistic advantages such as price and mechanical properties. Alkyd-acrylic composite water dispersions are prepared from colloidal alkyd droplets. Polymerization might be retarded due to the presence of double bonds in alkyds. In water-borne systems, film-forming properties were poorer than corresponding solvent-borne resins. Mechanical properties of alkyd-acrylic can be enhanced by crosslinking with melamine-formaldehyde (MF) derivatives. Copolymerization of N-methylol acrylamide with acrylic monomers has been proposed to synthesize self-crosslinkable resins.\(^4\)

Several types of hybrid materials containing inorganic pigments such as silica gel, CaCO\(_3\), and TiO\(_2\) can be prepared through miniemulsion technology. The shell is formed by absorbing polymers or monomers onto core. Encapsulation of pigments is performed by decreasing in interfacial tension between pigment and polymer. These hybrid systems are used in coatings, inks, and paints.

2.7 Emulsion Polymerization Kinetics

An emulsion polymerization system involves water, monomers, surfactants, initiator, and buffer agents. Monomers mostly take place in a monomer reservoir called a droplet. Droplet diameters range from 1 to 10 \(\mu\)m. Surfactants form micelles above
critical micelle concentration, which leads to a sudden decrease in surface tension of system. Only small fraction of monomers is present in micelles.

Figure 2.11 shows the possible scenarios of particle nucleation during emulsion polymerization. Particle formation might occur by micellar, homogenous and droplet nucleation. Initiation starts in aqueous phase. Radical species add monomers (z-mer) and become surface active. These oligomeric free radicals grow until they are insoluble \( (j_{\text{crit}}) \) in water \( (j_{\text{crit}}=5 \text{ for styrene}) \). Oligomers precipitate and become swollen by monomers to form particles. Growing oligomers absorb surfactant until a stable particle is formed.\(^92\) This mechanism is called homogeneous nucleation and happens below critical micelle concentration (CMC).

Every one of the 100-1000 micelles is converted into particles through this mechanism. After enough particles are formed to capture all z-mers, particle formation stops. The z-mers enter existing particles or micelles other than those undergoing homogeneous nucleation. This is valid when all particles have very high surface area to volume ratios. Particle nucleation might occur entirely in micelles after radicals formed in aqueous phase enter the monomer containing micelles above CMC. Single or oligomeric radicals enter micelles and initiate polymerization to form monomer-swollen particles. Nucleation occurs in micelles if very large oil-water surface area is created.\(^93\) Monomer droplets cannot compete with micelles for nucleation sites due to their small ratio of area to volume. In droplet nucleation, radicals generated in aqueous phase enter monomer emulsion droplets as single radicals or oligoradicals and propagate to form particles. This mechanism generally occurs in microemulsion and miniemulsion polymerizations.
Particle size and particle size distribution (PSD) depend on the amount of surfactant. The number of particles is proportional to the amount of surfactant with power (0.6). Generally, unimodal PSD is obtained in emulsion polymerization due to very short nucleation time. Nucleation time can be decreased by lowering the amount of surfactant. Additionally, particle size becomes bigger. Utilizing excess surfactant causes too many colloids in the system due to the longer nucleation period. This results in the reduction in
mean free path between particles. Particles collide more when there are more particles in the system. This phenomenon might lead to flocculation.94

The particles serve as loci for the polymerization. There are several models for emulsion polymerization kinetics. The rate of polymerization is given by;

\[ R_{pol} = -\frac{d[M]}{dt} = k_p[M][R·] \]  

where \( R_{pol} \) is the rate of polymerization per unit volume, \( k_p \) the propagation rate coefficient, \([M]\) the monomer concentration, and \([R·]\) the radical concentration. Since polymerization occurs in particles, the number of particles has to be included in this equation. Rate of polymerization in Interval II for case II leads to;

\[ R_p = \frac{k_p \bar{n}C_m N}{N_a} \]  

where \( C_m \) is the monomer concentration in the particles, \( \bar{n} \) is the average number of radicals per particle, and \( N_a \) is Avogadro’s number. This kinetic model, shown by eq. (2), is based on following assumptions: 1) Nucleation and coagulation of particles do not occur. Namely, the number of particles per unit volume of water is constant; 2) Particle size distribution is assumed as uniform; 3) Desorption of free radical from particles does not take place; 4) Bimolecular termination is instantaneous.

The value of \( \bar{n} \) is determined by absorption of radicals from the water phase into particles, desorption of radicals from particles, and bimolecular termination of radicals in the particles. If the entry of a second radical into a particle having already a radical
occurs, then average number of radicals per particle is 0.5. In this case, monomer-swollen particles contain either one radical or none (case II). This assumption is correct especially for hydrophobic monomers like styrene since the rate of desorption is very low. The styrene monomers keep growing until another radical enters. If \( \bar{n} \) is much less than 0.5 (case I), the desorption rate of the radical is much faster than absorption. The particle can contain maximum one radical at a time. If \( \bar{n} \) is much higher than 0.5 (case III), bimolecular termination occurs. This results in no instantaneous entry of a radical into a particle.

The kinetic model is based on the assumption that monomer concentration in monomer-swollen particles is constant in Interval II. Interval II ends after monomer is consumed in droplets. This stage is followed by the start of interval III. The rate of polymerization starts decreasing due to a reduction of the rate of bimolecular termination after the reaction medium becomes viscous.

2.7.1 The Effect of Surfactant on Kinetics

Surfactants are employed to synthesize stable dispersions. Surfactants increase freeze-thaw, mechanical, and shelf-life stability. Polymerization kinetics differs for the different types of surfactants. The nature and amount of surfactants affect final number of particles and nucleation mechanism. Anionic surfactants, in which the hydrophilic part is anion, stabilize organic polymer colloids through electrostatic repulsions. Nonionic surfactants provide a steric stabilization to colloids.

Nonionic surfactants mostly partition in the oil phase. Therefore, the initial rate of kinetics is slower when nonionic surfactant was used as sole emulsifier. As particles grow,
nonionic surfactant is released from droplets. The instantaneous increase in concentration of surfactant in polymerization medium causes secondary nucleation. Systems with the mixture of surfactants (low ratio of anionic to nonionic surfactant) lead to homogeneous nucleation due to the absence of micelles. Mixture of emulsifiers prevents secondary nucleation due to high surface area. The ratio of nonionic to anionic surfactant also determines the kinetics of polymerization. At a low ratio, limited coagulation occurs due to insufficient surfactant. On the other hand, no secondary nucleation is observed at high ratios. Rate of polymerization is also increased relative to same amount of sole nonionic or anionic surfactant.\textsuperscript{96} Boutti et al. showed type of surfactant (mixture or anionic) did not significantly influence particle size distribution.\textsuperscript{97} Masa et al. studied effects of surfactant and initiator on kinetics of polymerization. Rate of polymerization was not affected by type of surfactant. However, bimodal PSD was obtained when the amount of surfactant was increased. Latexes were coagulated when surfactants having short ethoxy lengths were used. Amount of surfactant is also important parameter influencing particle size and particle size distribution. Novak developed a model relating amount of surfactant to particle size. Novak has proposed that diameter of particle size is proportional to the weight percentage of surfactant with power (-1/3).\textsuperscript{98} A lower amount of surfactant shortened nucleation period and caused larger particle size. However, a low amount of surfactant did not stabilize many of particles, which led to decrease in number of particles due to limited flocculation.\textsuperscript{96}
2.7.2 The Effect of Monomer on Kinetics

Polarity of monomer plays a crucial role in kinetics of polymerization. As the polarity of monomer increases, the rate of nucleation in aqueous phase increases. This phenomenon has been observed in copolymerization of vinyl acetate and butyl acrylate. The number of radicals per particle was very high; therefore, the kinetic model did not follow the Smith-Ewart theory.\textsuperscript{99} Homopolymerization of butyl acrylate (BA) and methyl methacrylate (MMA) was investigated in the presence of nonionic surfactant (Triton X-405). The rate of nucleation and polymerization of BA was much higher than corresponding rates of MMA. This was attributed to reduced CMC value of surfactant in presence of MMA probably as a result of higher water solubility of MMA than BA. This led to a constant number of particles after a certain time due to flocculation of homogeneously nucleated particles onto primary particles.\textsuperscript{100} Another study reported that the amount of coagulum increased with increase in the weight ratio of MMA to BA.\textsuperscript{94} However, hydrophilic monomers such as HEMA and acrylic acid can be used as stabilizers in particles. These monomers bring a steric stabilization to particles.\textsuperscript{101} Smith-Ewart theory held only for the hydrophobic functional monomers (m-diisopropenylbenzene) were copolymerized with butyl methacrylate as opposed to copolymerization of ethylene glycol methacrylate with butyl methacrylate. This was attributed to decreased particle growth rate and prolonged nucleation period.\textsuperscript{102} The rate of surfactant-free polymerizations and number of particles per unit volume increased in the presence of acrylic acid as comonomer.\textsuperscript{103} Nonionic polymerizable surfactants showed higher electrolyte stability. The same study showed particle size decreased as the amount of surfactant increased.\textsuperscript{104}
2.7.3 The Effect of Initiator on Kinetics

Type of initiator is another factor influencing the polymerization kinetics as well as polydispersity index of polymer chains. Solubility of initiator determines where the initiation takes place. Oil-soluble initiator such as AIBN was rarely used in emulsion polymerization since free radicals evolved from that kind of initiator enter the micelles due to poor solubility in water. This increases probability of bimolecular termination in micelles or monomer-swollen particles. Initiation in aqueous phase has been proven by Luo and Schork in emulsion polymerization containing oil-soluble AIBN as initiator and radical scavenger soluble in water. In their study, no nucleation was observed in the presence of an aqueous-phase radical scavenger. In the absence of an aqueous-phase radical scavenger, the initiator entered the particles and followed the expected the particle growth. Very hydrophilic monomers (HEMA) were successfully polymerized and stabilized only with hydrophobic surface active initiator and persulfates with alkyl (decyl group) chains. Water-soluble initiators yielded a higher rate of polymerization than oil-soluble initiators. Electrostatically charged initiators such as ammonium persulfate had a very effective stabilizing outcome on particles. Particles that were polymerized in the presence of nonionic surfactant underwent coagulation without electrically charged initiators even though five times higher surfactant was used. Therefore, uncharged initiators (hydrogen peroxide) could be used only in polymerization in the presence of anionic surfactants. The higher rate of polymerization was obtained when initiator was fed into reactor as opposed to the rate of polymerization when initiator was used in batch reactor.
2.8 Control of Particle Morphology

Controlling particle morphology is possible through emulsion polymerization. Controlling particle morphology is important in managing the physical and chemical properties of the final latex. The tuning of the toughness of latex particles is achievable through core-shell morphologies. Heterogeneous particles, namely core-shell, are obtained by locating first polymer in core, then covering the shell polymer over core. Heterogeneous morphology development of particle was determined based on calculations of in free energy change.\textsuperscript{108} Equilibrium morphology is developed by minimum interfacial free energy in a system with two kinds of polymers and water. The free energy of the particle is expressed as:

\[
G_s = \sum \gamma_{ij} A_{ij}
\]

(3)

where \(G_s\) is the free energy of system, \(A_{ij}\) is interfacial area between components, \(\gamma_{ij}\) is interfacial tension between components. The difference in interfacial free energy between polymers leads to different morphologies, e.g., core-shell, inverted core-shell, hemispheres, and individual particles. Core-shell is favored when the interfacial tension between seed and water is higher than interfacial tension between second stage polymer and water (i.e. \(\gamma_{1w} \gg \gamma_{2w}\)). Inverted core-shell is obtained if second-stage polymer becomes incorporated at the centre of particle and the seed of polymer found on the periphery of composite particle.\textsuperscript{109} Several morphologies, e.g., sandwich and multiple lobes, are observed within single emulsion. On the other hand, these structures may not be as thermodynamically stable as core-shell and inverted core-shell. Morphology is determined through minimization of interfacial tension of the system.\textsuperscript{113} Interfacial
energies of polymers depend on hydrophilicity of each component, temperature\textsuperscript{110}, and amount and type\textsuperscript{111} of initiators\textsuperscript{112}. Studies showed surfactants also play very important role. Surfactants with higher interfacial tension, such as pectin, lead to core-shell formation\textsuperscript{113}.

The morphology development of composite latexes complied with spreading coefficients of two different kinds of oil phases dispersed in water. Incompatible oil phases in water form a predictable morphology when the interfacial tension of each component is known\textsuperscript{108}. Effect of phase ratio is another important parameter determining final morphology. Different morphologies were obtained when the amount of the second polymer increased while the amount of first one was constant. Figure 2.12 shows the morphologies obtained when the second polymer had either lower or higher surface tension than first polymer. When the second polymer had lower surface tension than first polymer, partial engulfing occurred due to very close interfacial tension of both polymers. When the second polymer had higher surface tension, the first polymer partially covered the second polymer\textsuperscript{114}. Morphology can be controlled by adjusting the volume ratio of each polymer. Figure 2.13 shows the morphology development of PS seeds as a function of volume fraction of PMMA introduced\textsuperscript{80}. 
Figure 2.12. Equilibrium morphologies for non-crosslinked systems as a function of the ratio of second polymer to first polymer.\textsuperscript{114}

Figure 2.13. Morphology development in PS (seed)/PMMA (polymer) system as a function of PMMA in system.\textsuperscript{80}
CHAPTER III
EXPERIMENTAL

3.1 Materials

2-ethylhexyl acrylate (EHA), ethyl acrylate (EA), benzyl methacrylate, 3-(Trimethoxysilyl)propyl methacrylate (MATS), butyl acrylate (BA), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA), dodecylbenzene sulfonic acid (DBSA), sodium bicarbonate (NaHCO₃), ammonium persulfate (APS), ethylene glycol dimethacrylate, n-hexane, Amberlyst® 15, 0.5 wt% ruthenium tetroxide (aq) (RuO₄), and Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) were purchased from Aldrich Chemical Co. Octamethylcyclotetrasiloxane (D₄) was obtained from Gelest, Inc. Sodium dodecyl sulfate (SDS) was purchased from Fluka. Sodium phosphotungstate was purchased from SPI Supplies, Inc. Spectra/Por® dialysis membrane, MWCO 6000 to 8000, with flat width, 23mm, was purchased from VWR. Sulfoethyl methacrylate (SEM), Triton X-200 (sodium salt of an alkylaryl polyether sulfonate), and Tergitol-XJ (polyalkylene glycol monobutyl ether) were received from Dow Chemical. Triton X-100 was purchased from Aldrich. Aerosol MA-80 was received from Cytec Co. All reagents were used without further purification. Figure 3.1 shows the chemical structure of the anionic and nonionic surfactants.
3.2 Synthesis

The details and characterization of hybrid latexes were described in the following sections.

3.2.1 Synthesis of polysiloxane-polyacrylate hybrid latexes

Nomenclature of neat and hybrid latexes is as follows: SC-CS is a semi-continuous polymerization through core-shell formation. B-MS is a batch polymerization of acrylic monomers with methacrylate-terminated polysiloxane. However, B-RH is a batch polymerization and concurrent ring-opening of D₄. PA is for polyacrylate without siloxane.
3.2.1.1 Synthesis of SC-CS (grafting of polysiloxane on shell via semi-continuous reaction)

In formation of core, all components were mixed vigorously to prepare pre-emulsion given in Table 3.1. Pre-emulsion was added into reactor, heated up to 80 °C, and polymerized with stream of 2 wt% of ammonium persulfate (APS) (0.4 g of APS/20 mL water) solution for 2 h. Coupling agent (MATS) in water (5 mL) fed into reactor along with 2 wt% of APS (0.01 g of APS/5 mL water) within 30 min. Polymerization was continued afterward for 1 h. To form a polysiloxane shell, octamethylcyclotetrasiloxane (D₄) emulsified with dodecylbenzene sulfonic acid (DBSA) fed into reactor within 1 h. pH was measured as 1.5 during polymerization. After addition, ring-opening polymerization proceeded for 5 h more. After synthesis was completed, latex was extracted in n-hexane (3×100 mL) to remove unreacted siloxane derivatives. NMR for SC-CS: \(^1\text{H NMR (CDCl}_3\text{)} 0.03 (-CH}_3\text{-Si}), 0.55 (-CH}_3\text{-Si-OC}_3\text{H}), 0.93 (-CH}_3\text{(EHA)}), 1.29 (-CH}_3\text{(EA)}), 1.36 (-CH}_2\text{-Si-O-Si}), 1.60 (CH}_2\text{-CH}_2\text{-Si-O}), 1.66, 1.99, 2.31 (Main chain -CH}_2\text{-CH}_2\text{-}), 3.55 (Si-OCH}_3\text{), 3.85 (COO-CH}_2\text{(EHA)}), 3.91 (COO-CH}_2\text{(EA)}), 4.08 (COO-CH}_2\text{(EHA)}). 20 wt% siloxane monomer was added, but grafting yield was determined as 17.6 wt% in which 1,2-dichlorethane was used as internal standard. Figure 3.2 shows the NMR spectrum of core-shell hybrid latex (SC-CS). Table 3.1 lists all amounts and components for synthesis of hybrid latexes.
In order to study the morphology of core-shell hybrid latex (SC-CS) in transmission electron microscopy (TEM), benzyl methacrylate was used as monomer in core. Ethyl acrylate (4 g) was replaced with benzyl methacrylate to obtain a higher contrast in core.
Table 3.1. Composition and synthesis methodology of polysiloxane functionalized acrylic latexes.

<table>
<thead>
<tr>
<th>Components</th>
<th>SC-CS*</th>
<th>B-MS</th>
<th>B-RH</th>
<th>PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis methodology</td>
<td>semi-continuous, core-shell</td>
<td>batch, copolymerization of polysiloxane</td>
<td>batch, ring-opening D₄ on HEMA</td>
<td>batch</td>
</tr>
<tr>
<td>1st step 2nd step</td>
<td>10</td>
<td>-</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2-ethylhexyl acrylate (EHA) (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acrylate (EA) (g)</td>
<td>6</td>
<td>-</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Polysiloxane</td>
<td>-</td>
<td>3.6 g of D₄</td>
<td>4 g of MS ‡</td>
<td>3.6 g of D₄</td>
</tr>
<tr>
<td>Coupling agent</td>
<td>-</td>
<td>0.4 g of MATS †</td>
<td>-</td>
<td>0.4 g of HEMA †</td>
</tr>
<tr>
<td>NaHCO₃ (g)</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS) (g)</td>
<td>0.48</td>
<td>-</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Dodecylbenzene sulfonic acid (DBSA) (g)</td>
<td>-</td>
<td>0.12</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>Water (g)</td>
<td>20</td>
<td>5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Conversion</td>
<td>&gt; 85%</td>
<td>&gt; 90%</td>
<td>&gt; 85%</td>
<td>&gt; 95%</td>
</tr>
<tr>
<td>Coagulum (g)</td>
<td>4.38</td>
<td>0.89</td>
<td>3.86</td>
<td>-</td>
</tr>
</tbody>
</table>

* (a) Semi-continuous core-shell hybrid latex (SC-CS). (b) batch, methacrylate-terminated polysiloxane (B-MS). (c) batch, ring opening polymerization of D₄ on HEMA (B-RH).

‡ MS: methacrylate-terminated polysiloxane.

† Couples to PDMS obtained from ring-opening of D₄.
3.2.1.2 Synthesis of B-MS (copolymerization of methacrylate-terminated polysiloxane with acrylic monomers) via batch reaction

All components shown in Table 3.1 were mixed vigorously before polymerization. Pre-emulsion was added into reactor and polymerized at 60°C for 6 h. pH was measured as 6.5 during polymerization. Initiator, 2 wt% of ammonium persulfate (APS) in 20 mL water, and extra SDS (0.2 g) were fed into reactor during polymerization. After synthesis was completed, latex was extracted in \( n \)-hexane (3×100 mL) to remove unreacted siloxane derivatives. \(^1\)H NMR (CDCl\(_3\)) for B-MS: \( \delta = 0.02 \) to 0.08 (CH\(_3\)-Si), 0.91 (-CH\(_3\) (EHA)), 1.29 (-CH\(_3\) (EA)), 1.60, 1.80 (CH-CH\(_2\)-Si(-CH\(_3\))-O), 1.64, 1.99, 2.25 (Main chain -CH\(_2\)-CH\(-\)), 3.18 (-O-CH\(_2\)-CH\(_2\)-O- (EGDMA)), 3.85 (COO-CH\(_2\) (EHA)), 3.92 (COO-CH\(_2\) (EA)), 4.06 (COO-CH\(_2\) (EHA)), 4.36 (-O-CH\(_2\)-CH\(_2\)-O-). 20 wt% siloxane monomer was added, but grafting yield was determined as 12.9 wt% in which 1,2-dichloroethane was used as internal standard. Figure 3.3 shows the NMR spectrum of B-MS.
Synthesis of ethylene glycol methacrylate-terminated polysiloxane: Octamethylcyclotetrasiloxane (D₄) (25 g) and 1,1,3,3-tetramethyldisiloxane (6.7 g) was mixed with Amberlyst-15 at 60°C for 15 h. Unreacted 1,1,3,3-tetramethyldisiloxane was removed in vacuo. Ethylene glycol dimethacrylate was added to silane-terminated polysiloxane in the presence of Karstedt catalyst until silane absorption (2160 cm⁻¹) disappeared in FT-IR. Number-average molecular weight (Mₙ) and polydispersity index (PDI) of methacrylate-terminated polysiloxane was measured as 3550 g/mol and 1.92 in gel permeation chromatography (GPC). Figure 3.4 shows the H-NMR spectrum of methacrylate-terminated polysiloxane used for the synthesis of BMS. Chemical analysis in NMR analysis of methacrylate-terminated polysiloxane was assigned in $^1$H NMR (CDCl₃) as δ = 0.05 (CH₃-Si), 1.22 (COCH-CH₃), 1.87 (CH-CH₂-Si), 1.95 (-CH₃-CH₂=C-), 2.61 (COCH
\((-\text{CH}_3)\)-\text{CH}_2-\text{Si}\), 4.35 \((-\text{OCH}_2\text{CH}_2\text{O}-\) 5.52 \((-\text{CH}_2=\text{C-CH}_3\)\), 6.08 \((-\text{CH}_2=\text{C-CH}_3\)\). $^{29}\text{Si}$ NMR as $\delta = -22.5$ to $-19.1$ (Si(\text{CH}_3)_2), 6.2 (\text{CH}_2-\text{CH}_2(-\text{CH}_3)-\text{Si})$. Figure 3.5 shows the Si-NMR spectrum of methacrylate-terminated polysiloxane used for the synthesis of B-MS.

Figure 3.4. H-NMR of methacrylate-terminated polysiloxane used for the synthesis of B-MS.
3.2.1.3 Synthesis of B-RH (ring-opening and grafting of polysiloxane through 2-Hydroxyethyl methacrylate via batch reaction)

All components shown in Table 3.1 were mixed vigorously and sonicated for 10 min in ice bath in power 3.5 to prepare pre-emulsion. Pre-emulsion was added into reactor and polymerized at 80 °C for 6 h. pH was measured as 1.5 during polymerization. Initiator, 2 wt% of ammonium persulfate (APS) solution and extra SDS (0.2 g) fed into reactor during polymerization. After synthesis was completed, latex was extracted in n-hexane (3×100 mL) to remove unreacted siloxane derivatives. Chemical $^1$H NMR (CDCl$_3$) for B-RH: $\delta$= -0.05 to 0.05 (-CH$_3$-Si), 0.90 (-CH$_3$ (EHA)), 1.23 (-CH$_3$ (EA)), 1.85, 2.07, 2.41 (Main chain -CH$_2$-CH$_2$), 3.62 (COO-CH$_2$ (EHA)), 3.95 (CH$_2$-O-Si-O-Si), 4.11 (COO-CH$_2$ (EA)), 4.26 (COO-CH$_2$- (HEMA)). 20 wt% siloxane monomer was
added, but grafting yield was determined as 11.8 wt% in which 1,2-dichlorehane was
used as internal standard. Figure 3.6 shows the NMR spectrum of B-RH.

![NMR Spectrum of B-RH](image)

Figure 3.6. NMR spectrum of hybrid latex B-RH (ring-opening and grafting of
polysiloxane on HEMA via batch reaction.

3.2.1.4 Synthesis of PA (polyacrylate via batch reaction)

Components shown in Table 3.1 were mixed vigorously. Pre-emulsion was
polymerized at 60 °C for 6 h in a batch reactor. During polymerization, pH was measured
as 6.5. Initiator, 2 wt% of ammonium persulfate (APS) solution, and 0.2 g of extra SDS
fed into reactor during polymerization. Chemical shifts were assigned to functional
groups in $^1$H NMR (CDCl$_3$) as $\delta$ = 0.88 (-CH$_3$ (EHA)), 1.26 (-CH$_3$ (EA)), 1.71, 1.88, 2.28
(Main chain -CH$_2$-CH-), 3.94 (COO-CH$_2$ (EA)), 4.08 (COO-CH$_2$ (EHA)).
3.2.2 Synthesis of core-shell latexes with neat monomer addition

Seeded latex synthesis was obtained via a semi-batch feeding under continuous nitrogen flow and 200 rpm stirring rate. Synthesis procedure reported by Pedraza and Soucek\textsuperscript{11} was followed but with addition of neat monomer. Sixteen latexes with varying functionalities in terms of hydroxyl from HEMA in core and carboxylic acid from MAA in shell and surfactants (two anionic and two nonionic) were synthesized. These parameters are shown in Table 3.2. Polymerizations were run under monomer-starved conditions with 95% conversion and insignificant macroscopic coagulum. Nomenclature is as follows for H18M12: H18 designates the weight percent of 2-hydroxyethyl methacrylate (HEMA) in core, and M12 shows weight percent of methacrylic acid (MAA) in shell.
Table 3.2. Amount of constituents for core and shell compositions of latexes.

<table>
<thead>
<tr>
<th>Component</th>
<th>1 - H18M12 - Tergitol</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
<th>2 - H18M17 - Triton X-200</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
<th>3 - H25M12 - Triton X-200</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
<th>4 - H25M17 - Tergitol</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>21.85</td>
<td>24.03</td>
<td>21.85</td>
<td>23.27</td>
<td>20.34</td>
<td>24.03</td>
<td>20.24</td>
<td>10.03</td>
<td></td>
<td>23.27</td>
<td>10.03</td>
<td></td>
</tr>
<tr>
<td>MMA</td>
<td>10.95</td>
<td>11.17</td>
<td>10.93</td>
<td>10.05</td>
<td>9.76</td>
<td>11.17</td>
<td>9.76</td>
<td>10.05</td>
<td></td>
<td>10.05</td>
<td>10.05</td>
<td></td>
</tr>
<tr>
<td>HEMA</td>
<td>7.2 (0.055 mol)</td>
<td>-</td>
<td>7.2</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>10 (0.077 mol)</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MAA</td>
<td>-</td>
<td>4.8 (0.055 mol)</td>
<td>-</td>
<td>6.6 (0.077 mol)</td>
<td>-</td>
<td>4.8 (0.055 mol)</td>
<td>-</td>
<td>- (0.077 mol)</td>
<td></td>
<td>- (0.077 mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NaHCO3</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.1 (0.077 mol)</td>
<td>-</td>
<td></td>
<td>0.1 (0.077 mol)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Triton X-200</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tergitol XJ</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>80</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>5 - H25M17 - Triton X-200</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
<th>6 - H18M17 - Tergitol</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
<th>7 - H25M12 - Triton X-200</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
<th>8 - H18M12 - Triton X-200</th>
<th>Core weight (g)</th>
<th>Shell weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>9.76</td>
<td>10.05</td>
<td>10.95</td>
<td>10.05</td>
<td>9.76</td>
<td>11.17</td>
<td>11.17</td>
<td>10.95</td>
<td></td>
<td>11.17</td>
<td>10.95</td>
<td></td>
</tr>
<tr>
<td>HEMA</td>
<td>10 (0.077 mol)</td>
<td>-</td>
<td>7.2</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>7.2 (0.055 mol)</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MAA</td>
<td>-</td>
<td>6.6 (0.077 mol)</td>
<td>-</td>
<td>6.6 (0.077 mol)</td>
<td>-</td>
<td>4.8 (0.055 mol)</td>
<td>-</td>
<td>- (0.055 mol)</td>
<td></td>
<td>- (0.055 mol)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NaHCO3</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.1 (0.077 mol)</td>
<td>-</td>
<td></td>
<td>0.1 (0.077 mol)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Triton X-200</td>
<td>3.6</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tergitol XJ</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>80</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
3.2.2.1 Seed synthesis

Water (150 g), NaHCO₃ (1.5 g), and Triton X-200 (0.5 g) were charged into a flask and heated up to 75 °C. This was followed by addition of butyl acrylate (41.68 g, 0.326 mol) and methyl methacrylate (38.32 g, 0.3832 mol), Triton X-200 (3.6 g), and
NaHCO\textsubscript{3} (0.1 g). After solution reached 75 °C, 100 g aqueous ammonium persulfate (APS) solution (2 wt\% APS, 0.4464 mol APS) was added. Polymerization was continued for 30 min at 75 °C.

3.2.2.2 Synthesis of core and shell latex

Water, seed (20 wt\% of monomer weight for core), surfactant, and sodium bicarbonate were initially added into reactor. The reactor was heated to 75 °C. Neat monomer composition for core (see Table 3.2) was fed into reactor for 180 min. After feeding was over, reaction was run for 180 min to complete conversion. Shell composition was fed into reactor within 240 min and reaction was continued for 240 min after feeding was completed. Initiator solution (50 g aqueous APS solution with 1 g of APS) was fed along with monomer mixture during core and shell synthesis.

3.2.3 Synthesis of core-shell latexes with pre-emulsion monomer addition

The synthesis of core-shell latexes were performed according to the reaction scheme given below.

3.2.3.1 Preparation of latexes

Seeded two-stage latex was synthesized via semi-batch feeding under continuous nitrogen flow and 200 rpm stirring rate. Synthesis procedure reported by Pedraza\textsuperscript{11} et al. was followed. Four latexes with different composition in terms of hydroxyl (HEMA) and carboxylic acid (MAA) were synthesized. The composition of latexes is shown in Table 3.3. Nomenclature is as follows for H9M6: H9 designates 9 wt\% of 2-hydroxyethyl
methacrylate (HEMA) in the core, and M6 shows 6 wt% of methacrylic acid (MAA) in the shell. Same nomenclature is also valid for other samples.

Table 3.3. Amount of constituents for core and shell compositions of latexes for the pre-emulsion feed.

<table>
<thead>
<tr>
<th>Component</th>
<th>1 - H9M6</th>
<th>2 - H9M17</th>
<th>3 - H5M6</th>
<th>4 - H5M17</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Core weight (g)</td>
<td>Shell weight (g)</td>
<td>Core weight (g)</td>
<td>Shell weight (g)</td>
</tr>
<tr>
<td>BA</td>
<td>43.14</td>
<td>46.29</td>
<td>43.14</td>
<td>46.53</td>
</tr>
<tr>
<td>HEMA</td>
<td>7.14 (0.11 mol)</td>
<td>-</td>
<td>7.14 (0.11 mol)</td>
<td>-</td>
</tr>
<tr>
<td>MAA</td>
<td>-</td>
<td>4.73 (0.11 mol)</td>
<td>-</td>
<td>13.2 (0.154 mol)</td>
</tr>
<tr>
<td>BenzylMA</td>
<td>1</td>
<td>-</td>
<td>1 (0.11 mol)</td>
<td>-</td>
</tr>
<tr>
<td>SEM</td>
<td>-</td>
<td>0.57</td>
<td>-</td>
<td>0.57</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Triton-200</td>
<td>3.6</td>
<td>3.6</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Tergitol-XJ</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Water</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Water⁺</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

* Amount of water was charged into reactor before polymerization started.

3.2.3.2 Preparation of seeds

The seed synthesis was given in the section 3.2.2.1. Same polymerization scheme and reactants were used.

3.2.3.3 Synthesis of core and shell latex with pre-emulsion addition

The procedure that was given in section 3.2.2.2 was followed but with Table 3.3. Same polymerization scheme and reactants were used.
3.2.3.4 Synthesis of core and shell latex with neat monomer addition

The constituents of H25M17 with Tergitol XJ and H25M17 with Triton X-200 were given in Table 3.2. The synthesis details were given in section 3.2.2.2.

3.2.4 Synthesis of core-shell latexes used for thermoset latex films

The composition of the latexes was given in Table 3.2. The procedure was followed as described in section 3.2.2.

3.2.5 Synthesis of dual-cure thermoset latexes

The synthesis of dual-cure thermoset latexes was performed according to the reaction procedures given in section 3.5.2.1 and 3.5.2.2.

3.2.5.1 Synthesis of amide-functionalized latex

Table 3.4 shows the first- and second-stage compositions to synthesize amide-functionalized latex. Water (50 g) was placed into the reactor and heated to 75 °C. The pre-emulsion mixture (10 wt%) was added into flask and the seed polymerization was performed at 75 °C for 30 min with ammonium persulfate (APS) (0.1 g) as initiator. After the seed was formed, the rest of pre-emulsion was fed into reactor within 3 h along with aqueous APS solution (0.8 g APS in 20 g water). The reaction was conducted 3 h more to obtain high conversion. The second-stage composition was fed into reactor within 1 h along with aqueous APS solution (0.1 g APS in 10 g of water). Reaction was continued for 1 h more.
Table 3.4. Composition of first- and second-stage for amide-functionalized latex.

<table>
<thead>
<tr>
<th>Components</th>
<th>Amide-functionalized Latex</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; stage (g)</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; stage (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethylhexyl acrylate</td>
<td></td>
<td>81</td>
<td>8</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td></td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Acrylamide</td>
<td></td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td></td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene glycol dimethacrylate (EGDMA)</td>
<td></td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Aerosol MA 80</td>
<td></td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td></td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Solid %</td>
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<td></td>
<td>57.5</td>
</tr>
<tr>
<td>Coagulum</td>
<td></td>
<td></td>
<td>8.7</td>
</tr>
</tbody>
</table>

3.2.5.2 Synthesis of acrylate-functionalized latex

Table 3.5 shows the first- and second-stage compositions to synthesize acrylate-functionalized latex. Water (50 g) was placed into the reactor and heated to 75 °C. The pre-emulsion of the mixture (10 wt%) was added into flask and the seed polymerization was conducted at 75 °C for 30 min with ammonium persulfate (APS) (0.1 g) as initiator. After the seed was synthesized, the rest of pre-emulsion was fed into reactor within 3 h along with aqueous APS solution (0.97 g APS in 20 g water). The reaction was conducted for 3 h more to obtain high conversion. After the first-stage of polymerization, the residual monomers in the latex were chased with a mixture of aqueous t-butyl hydroperoxide (0.1 g in 5 g water) and aqueous sodium formaldehyde sulfoxylate (0.1 g in 5 g water) at 50 °C for 1h. For the second-stage polymerization, trimethylolpropane triacrylate (3 g) was added into latex and mixed for 30 min. The mixture of aqueous t-
butyl hydroperoxide (0.025 g in 1 g water) and aqueous sodium formaldehyde sulfoxylate (0.025 g in 1 g water) was added into the reactor and mixed for 1h at 40 °C. The amount of the redox initiator added in the second stage was based on trial and error experiments. The amount of redox initiator was determined according to NMR analysis where free acrylic groups were observed after second stage polymerization. Chemical shifts were assigned to functional groups in $^1$H NMR (CDCl$_3$) as $\delta$ = 0.88 (-CH$_3$ (EHA)), 1.32 (-CH$_3$ (EA)), 1.81, 2.16, 2.30 (Main chain -CH$_2$-CH-), 3.55 (C(=O)-CH$_2$-C(=O) (AAEMA)), 3.96 (COO-CH$_2$ (EHA)), 4.13 (COO-CH$_2$ (EA)), 5.81 (CH$_2$=CH (TMPTA)), 6.45 (CH$_2$=CH (TMPTA)). The iodine number of acrylate-functionalized latex was determined as 1.51 by ASTM D-5902.

Table 3.5. Composition of first- and second-stage for acrylate-functionalized latex.

<table>
<thead>
<tr>
<th>Components</th>
<th>Acrylate-functionalized Latex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st stage (g)</td>
</tr>
<tr>
<td>2-ethylhexyl acrylate</td>
<td>50</td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td>30</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>10</td>
</tr>
<tr>
<td>Acetoacetoxyethyl methacrylate (AAEMA)</td>
<td>3</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>4</td>
</tr>
<tr>
<td>Trimethylolpropane triacrylate (TMPTA)</td>
<td>-</td>
</tr>
<tr>
<td>Aerosol MA 80</td>
<td>1</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.1</td>
</tr>
<tr>
<td>Water</td>
<td>30</td>
</tr>
<tr>
<td>Solid %</td>
<td>59.3</td>
</tr>
<tr>
<td>Coagulum</td>
<td>5.8</td>
</tr>
</tbody>
</table>
3.3 Instruments

The specifications of characterization tools for the latex films and the latex particle were given in the following sections.

3.3.1 Instruments for the characterization of polysiloxane-polyacrylate hybrid latexes

Particle size and distribution was analyzed in dynamic light scattering, Brookhaven BI-200SM equipped with He-Ne laser operated at 633 nm. Philips Tacnai-12 model with a combination of high-resolution imaging scanning transmission electron microscope (STEM) was employed for studying morphology. Dynamic mechanical properties of latex films were studied in Perkin Elmer Instruments, Pyris Diamond DMA. Thermo Scientific, Nicolet 380 was used for FT-IR. Quanta 200 of FEI, EDAX model was run for energy dispersive X-ray (EDX) analysis. Differential scanning calorimeter analysis was completed in TA Instruments DSC 2920. Analysis of NMR was done in Varian Mercury 300. Contact angle measurement was performed using the Rame-Hart, Inc. Goniometer, Model 100. Atomic force microscopy (AFM) images were taken in Veeco (Digital Instruments) Multimode. Number-average molecular weight ($M_n$) of methacrylate-terminated polysiloxane was obtained in gel permeation chromatography (GPC, Waters Co.) equipped with HPLC pump with THF at 0.5 mL/min.

3.3.2 Instruments for the characterization of core-shell latexes with functional monomers (HEMA and MAA)

Contact angle measurement was performed using the Rame-Hart, Inc., Goniometer, Model 100 in ambient conditions. Philips Tacnai-12 model with a
combination of high-resolution imaging scanning transmission electron microscope (STEM) was employed for studying particle morphology. The DSC thermograms were recorded on a TA Instruments DSC 2920. Solid state 2D-WISE NMR measurements were made on Varian, VNMRS-500 spectrometer with dipolar decoupling field (70K).

3.3.3 The Basics of Dynamic Light Scattering

Dynamic light scattering (DLS) is one of the fastest methods to characterize particle size and particle size distribution of colloids. The scattering of photons by moving particles is quasielastic in DLS analysis. DLS is a nondestructive technique which does not require a blank solvent calibration. On the other hand, DLS has limited resolution, especially for samples with multimodal particle size distribution. The range of particle size that can be measured is also limited. The samples must be extremely free of impurities such as dust since the scattered light is proportional to sixth power of the particle diameter.

Dynamic light scattering (DLS) is based on the analysis of constructive and destructive interference arising from the scattered light from particles. The interference varies by time due to the Brownian motion of particles. The larger particles diffuse more slowly while smaller particles diffuse faster, which influences the scattered intensity by time. When the sample is exposed to the laser beam, the scattered light is measured as a function of time intervals called delay times. The correlator builds the autocorrelation function and compares the scattered intensity at time t to time with the very small time interval t+τ. In order words, the intensity autocorrelation function can be described as the group average of the intensity signal as a function of the delay time. The intensity signal
is defined as the number of photons counted in the detector. Correlation function is an exponential function where correlation is high at short delay times. However, correlation diminishes to zero and the exponential decay of the correlation function is characteristic of the diffusion coefficient of the particles as a function of time. Delay time of the data collection is almost 100 ns, which depends on the diffusivity of the colloids. The correlator function is given as \( G(\tau) = \langle I(t)I(t+\tau) \rangle \). The intensity autocorrelation function \( G(\tau) \) can also be described as: 
\[
G(\tau) = 1 + e^{(-2Dq^2 \tau)}
\]
where \( q \) is the wave vector \((q = 4\pi n/\lambda \sin(\theta/2))\), \( n \) is the refraction index of solvent, and \( \lambda \) is the wavelength of the light source. The analysis of the autocorrelation function is based on the numerical fitting of the calculation with theoretical distribution where the theoretical assumption is established on standard deviation of particle size. A multimodal distribution has several exponential functions, which causes more complicated fitting than that of a monodisperse system. The scattering intensity is not correlated when the time is long. The decay of correlation of smaller particles is faster. The hydrodynamic particle size (R) can be obtained by using Stokes-Einstein relationship: 
\[
D = kT/6\pi\eta R
\]
where \( D \) is the diffusion constant, \( k \) is the Boltzmann constant, \( R \) is the average hydrodynamic radius, \( \eta \) is the solvent viscosity, and \( T \) is temperature in Kelvin. The decay constant, \( \Gamma \), (time to diffuse a distance for a particle) is measured as follows: 
\[
\Gamma = Dq^2
\]

3.4 Characterization methods

The details of the characterization of latexes including the film formation and morphology were given in the following section.
3.4.1 Characterization of polysiloxane-polyacrylate hybrid latexes

Before characterization, surfactants were removed from latexes by dialysis in which latexes were mixed for 24 h in deionized water (1 L) at room temperature. Latexes were diluted to 0.1 vol. % in water. Intensity-average particle size and particle size distribution were analyzed in dynamic light scattering at 25 °C. Each sample was run for 15 min and analyzed by using non-negative least squares (NNLS) algorithm. Transmission electron microscopy that had 120 kV illumination system, maximum magnification of 500K, and maximum resolution of <1nm was operated. Samples were diluted to 0.1 wt% and dropped onto copper TEM grids. Samples were stained with 1 wt% aqueous sodium phosphotungstate. Additionally, SC-CS contained 20 wt% of benzyl methacrylate in core composition and stained with vapor of 0.5 wt% aqueous ruthenium tetroxide (RuO₄) for 15 min to compare polyacrylate core with staining and without staining.

Films were cast on glass substrate and dried at room temperature for 3 days. FT-IR analysis was run with 32 scans in 4000-400 cm⁻¹ on attenuation total reflection (ATR) apparatus. Differential scanning calorimeter analysis was run under 20 psi nitrogen flow. Latex films were heated and annealed at high temperatures (150 °C). Without removing the pan, second calorimetry was run for films between -150 and 100 °C at 20 °C/min heating rate. Nuclear magnetic resonance (NMR) of samples was taken in CDCl₃ solvent. The latex samples were mixed with excess amount of tetrahydrofuran (THF) to coagulate latex particles. The water and THF was removed. 1,2-dichloroethane was used as internal standard in order to calculate the amount of grafted-polysiloxane on polyacrylate. The amount of siloxane units (Si(CH₃)₂) was determined by the equation: 

\[ m_{\text{Si(CH₃)₂}} = \]
(2/3)\times n_{\text{DCE}}\times (A_{(\text{Si(CH}_3)_2)} / A_{\text{DCE}})\times MW_{(\text{Si(CH}_3)_2)}, \text{ where } m_{(\text{Si(CH}_3)_2)} \text{ is the weight of siloxane units, } n_{\text{DCE}} \text{ is the mole of 1,2-dicholoroethane, } A_{(\text{Si(CH}_3)_2)} \text{ is the area of siloxane units (Si(CH}_3)_2), } A_{\text{DCE}} \text{ is the area of 1,2-dichloroethane, and } MW_{(\text{Si(CH}_3)_2)} \text{ is the molecular weight of siloxane units (58 g/mol). The weight } \% \text{ of grafted-polysiloxane on polyacrylate is determined by equation: Weight } \% \text{ (Si(CH}_3)_2) = (m_{(\text{Si(CH}_3)_2)} / m_{\text{polymer}}) \times 100\%, \text{ where } m_{(\text{Si(CH}_3)_2)} \text{ is the amount of siloxane units in NMR tube and } m_{\text{polymer}} \text{ is the amount of polymer in NMR tube. Surface composition was measured by energy dispersive X-ray. Pressure was measured as 0.45 Torr inside chamber. Voltage, filament current, and emission current was adjusted to 30 kV, 2.60 A, 102 μA, respectively. The resolution and depth profiling of EDX analysis were 2 and 10 nm, respectively. Contact angle measurements were performed ten times for each sample. Consistent angles were averaged and standard deviation was calculated. Latex particles were diluted to 1 wt\% and dried for 16 h on PET substrate at room temperature for the analysis of the films in atomic force microscopy. Dynamic mechanical analysis was run at heating rate of 4\degree C/min under 40 psi nitrogen flow at constant oscillating frequency, 1 Hz. Storage modulus, } G', \text{ at plateau of rubbery region was converted to crosslink density by the expression: } \nu_e = G'/3RT \text{ where } \nu_e \text{ is crosslink density of network in mol/m}^3 \text{ and } G' \text{ (storage modulus at rubbery plateau) was expressed in Pa.}^{116} \text{ Molecular weight between crosslinks was calculated as } M_c = \rho RT / G' \text{ where } R \text{ is the gas constant (8.3145 Pa.m}^3/ \text{mol.K), } T \text{ is the temperature in Kelvin, and } \rho \text{ is the density of polymer.}
3.4.2 Characterization of core-shell latexes with functional monomers (HEMA and MAA)

For all the latexes, 2 mL of latex sample was withdrawn from reactor during synthesis of core and shell as a function of time. A 2 wt% aqueous hydroquinone solution (0.05 mL) was added to latex aliquots to quench the polymerization reaction. The solid content of latex samples were calculated gravimetrically. Each latex sample was dried in an oven at 110°C until a constant weight is reached. Solid content was calculated by eq. (5):

\[
\text{Solid} \% = \frac{\text{weight of dried sample}}{\text{weight of latex sample}} \times 100\%
\]  

(5)

Conversion is calculated through eq. (6):

\[
\chi = \frac{w_{\text{solid}} - (w_{\text{seed}} + w_{\text{surf}} + w_{\text{ini}} + w_{\text{HQ}})}{w_{\text{mon}}}
\]  

(6)

where \(\chi\) is the conversion of fraction, \(w_{\text{solid}}\) is the fraction of solid content, \(w_{\text{seed}}\) is the fraction of seed, \(w_{\text{surf}}\) is the weight fraction of surfactant, \(w_{\text{ini}}\) is the weight fraction of initiator, \(w_{\text{HQ}}\) is the weight fraction of hydroquinone, \(w_{\text{mon}}\) is the weight fraction of injected monomer in overall weight of latex of each time interval. The amount of additives such as \(w_{\text{seed}}\) and \(w_{\text{surf}}\) was assumed constant during polymerization. The amount of initiator \(w_{\text{ini}}\) was included in eq. (6) as a function of time. The instantaneous rate of polymerization \((R_p, \text{g/L.min})\) was computed from eq. (7):
where $\Delta x/\Delta t$ is the ratio of conversion from time ($t_o$) to time ($t$). However, the amount of seed, surfactant, and initiator was assumed constant throughout the reaction. The number of particles ($N_p$, $1/dm^3$) was computed from eq. (8):

$$N_p = \frac{6 M_o x}{\pi \rho D_v^3}$$

where $M_o$ is the ratio of the monomer injected to the reactor during time intervals ($g/dm^3$), $x$ is the conversion fraction by time, and $D_v$ is the volume-average diameter of latex particle (dm) obtained from dynamic light scattering analysis. The density of polymer, $\rho$, is 1070 g/dm$^3$ which was calculated by weight-averaging of density of homopolymers ($d_{PBA}$= 1.033, $d_{PMMA}$= 1.16, $d_{PHEMA}$= 1.11, $d_{PMAA}$= 1.01 g/cm$^3$).

The particle size and particle size distribution were obtained at 25 °C. The latex aliquots were diluted to 0.1 vol. % in water. Each sample was run for 5 min. Non-negative least squares (NNLS) algorithm was used to calculate particle size and particle size distribution. The volume-average diameter of particles was obtained from DLS analysis. The particle size and particle size distribution were obtained at 25 °C. The volume-average diameter and number of particles with error bars are shown in section 5.5. Particle morphology was evaluated in transmission electron microscopy (TEM). Latex samples were diluted to 0.5 wt% with deionized water and dropped over a copper grid. After dried at room temperature, core with benzyl methacrylate was stained with vapor of
0.5 wt% aqueous ruthenium tetroxide for 15 min before TEM analysis. The DSC thermograms were recorded at a scanning rate of 20 °C/min. Solid state 2D NMR measurements were made at room temperature. The sample was spun at 10 kHz in order to avoid peak overlapping. The 90° 1H pulse lengths were almost 3.5 µs. The mixing times of the domains were 100 and 1000 µs.

3.4.3 Film formation and characterization of thermoset latexes with functional monomers (HEMA and MAA)

The latex pH was modified to 7.0 by addition of 25 wt% ammonium hydroxide (NH₄OH) before crosslinker was added. Cycloaliphatic diepoxide (10 g) was emulsified in 20 g of water with 0.1 g of Triton X-200. A stoichiometric amount of cycloaliphatic diepoxide was added into latex. For 2 moles of functional groups, 1 mol of cycloaliphatic diepoxide was used. The mixture was mixed for 15 min and cast into a pyrex dish. Latex was dried for 48 h at room temperature. Films were cured at 170°C for 1 h. Melamine-formaldehyde resin was dissolved in water. The hexamethoxymethyl melamine (HMMM) solution (50 wt%) was prepared. The HMMM (1 eq. mole) was added for 3 moles hydroxyl functionality in latex. The mixture was dried at room temperature for 48 h and cured at 150°C for 30 min. Zinc ammonium carbonate was used as it was received. The zinc ammonium carbonate (1 eq. mole) was added per 2 moles of carboxylic acid into latex. Latex was cast into a pyrex dish and film was cured at room temperature for 48 h. N,N'-dicyclohexylcarbodiimide was employed to crosslink carboxylic acids in shell. The N,N'-dicyclohexylcarbodiimide solution (25 wt%) was prepared in isopropyl alcohol. N,N'-dicyclohexylcarbodiimide (1 mole) was added for 2 moles of carboxylic acid in
latex. The mixture was cast onto a pyrex dish and dried for 48 h at room temperature. Dried films were cured at 120 °C for 30 min. HDI isocyanurate (Desmodur N3300A) was used to crosslink hydroxyl and carboxylic acid functionalities in core and shell, respectively. The HDI isocyanurate solution (50 wt%) was prepared in acetone. The HDI isocyanurate (2 eq. moles) was added into latex for 3 moles of hydroxyl and carboxylic acid functionalities. Formulation was mixed for 30 min and cast onto a pyrex dish. Film was dried for 24 h at room temperature.

Films were removed with a razor blade and analyzed in Instron Universal Electromechanical Tester 5567. Tensile testing was performed with a load cell of 1 kN at crosshead speed of 10 mm/min. Films cast on aluminum substrate were used for coatings testing such as cross-hatch adhesion (ASTM D-3359), pencil hardness (ASTM D-3363-00), impact resistance (ASTM G-14). Gloss % (20°) was measured of coatings applied on aluminum plates according to ASTM D-523.

3.4.3.1 Design of Experiment

Two-level fractional factorial design of experiment was used with \( k \) factors on response. Each factor has only two levels, “low” and “high”. \( 2^k \) of experiments was tested. Two-level fractional design of experiment with 3 variables was run. The numerical factors for 2 variables HEMA and MAA, and 1 categorical factor (type of surfactant) were used. Analysis was performed in software Design-Expert 6.0.

Two-level factorial design was operated to study effect of variables on mechanical properties of latex films. For this purpose, concentration of hydrophilic monomers such as HEMA, MAA and type of surfactant were studied. Eight latexes were
synthesized with formulations as shown in Table 3.6. Bimodal particle size distribution (PSD) was obtained for the latexes.

Table 3.6. Composition and PSD of synthesized eight latexes.

<table>
<thead>
<tr>
<th>Run</th>
<th>HEMA (g)</th>
<th>MAA (g)</th>
<th>Surfactant</th>
<th>Particle Size Distribution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H18M12-tergitol</td>
<td>14.4</td>
<td>9.6</td>
<td>Tergitol-XJ</td>
<td>53.5 307.4</td>
</tr>
<tr>
<td>2-H18M17-triton</td>
<td>14.4</td>
<td>13.2</td>
<td>Triton X200</td>
<td>154.7 312</td>
</tr>
<tr>
<td>3-H25M12-triton</td>
<td>20</td>
<td>9.6</td>
<td>Triton X200</td>
<td>132.3 286.7</td>
</tr>
<tr>
<td>4-H25M17-tergitol</td>
<td>20</td>
<td>13.2</td>
<td>Tergitol-XJ</td>
<td>220.2 713.3</td>
</tr>
<tr>
<td>5-H25M17-triton</td>
<td>20</td>
<td>13.2</td>
<td>Triton X200</td>
<td>208.0 522.7</td>
</tr>
<tr>
<td>6-H18M17-tergitol</td>
<td>14.4</td>
<td>13.2</td>
<td>Tergitol-XJ</td>
<td>91.4 374.6</td>
</tr>
<tr>
<td>7-H25M12-tergitol</td>
<td>20</td>
<td>9.6</td>
<td>Tergitol-XJ</td>
<td>134.5 447.4</td>
</tr>
<tr>
<td>8-H18M12-triton</td>
<td>14.4</td>
<td>9.6</td>
<td>Triton X200</td>
<td>110.8 335.9</td>
</tr>
</tbody>
</table>

3.4.4 Film preparation and characterization of dual-cure thermoset latexes

Amide- and acrylate-functionalized latex with acetoacetoxy functionality were blended in different ratios (50/50, 40/60, 60/40 wt/wt). Methanolic camphorquinone and \( \tau \)-butyl hydroperoxide were added into latex blends. The amount of camphorquinone and \( \tau \)-butyl hydroperoxide was adjusted as 1 wt % of trimethylolpropane methacrylate amount in latex resin. After mixing for 30 min, latexes were cast onto glass substrate and dried at room temperature for 3 days. Nomenclature is as followed: 50acr50tri stands for amide-functionalized latex (50 wt%) was blended with acrylate-functionalized latex (50 wt %) with acetoacetoxy functionality. CQ1 in 50acr50triCQ1 stands for the amount of camphorquinone added into the formulation. Camphorquinone (1 wt%) was added into the latex relative to amount of double bonds. Tensile testing of latex films in size of
10mm × 30 mm was conducted in Instron 5567 at room temperature. The load (1 kN) was applied to films at 50 mm/min crosshead speed. Ten latex films were prepared for each formulation. Tensile values were averaged and standard deviation was calculated. The DSC thermograms were recorded on a TA Instruments DSC 2920 at a scanning rate of 20 °C. Dynamic mechanical analysis of latex films was conducted at heating rate (4 °C/min) and constant oscillating frequency (1 Hz) under 40 psi nitrogen flow. Crosslink density was calculated as given in section 3.4.1.
CHAPTER IV
PREPARATION OF POLYSILOXANE FUNCTIONALIZED ACRYLIC LATEXES

4.1 Introduction

Composite latexes with two phases are prepared from two polymers, which can be miscible or immiscible. By changing the monomer feed composition, composite latexes can be prepared.\textsuperscript{118,119} The gradation of monomer feed usually leads to a two-phase system which is miscible. By subtle changes in the polymer such as glass transition temperature (Tg) or crosslinking, a two-phase system can be achieved from ostensibly miscible polymers. Various morphologies can be obtained by the separation of two phases. These morphologies are core-shell, inverted core-shell, raspberry, sandwich and half-moon.\textsuperscript{109} Hybrid latexes are prepared from two polymers, which are immiscible.\textsuperscript{120} Hybrid systems are usually prepared by grafting or using a batch process in which one polymer is prepared inter-micellarly within the other.\textsuperscript{90}

The morphology of composite latexes is determined by several factors. Interfacial tension between two phases designates structures like core-shell, inverted core-shell, and hemi-sphere.\textsuperscript{121} Core-shell morphology is obtained if interfacial tension of core decreases after building of shell polymer. Otherwise, inverted core-shell is obtained. Phase
separation between polymers increases as difference in interfacial tension of shell and core polymer increases. Namely, latex particle inclines to phase separation, which depends on free energy of mixing of phases. Kinetic factors such as diffusion restriction of monomers also influence morphology. Water solubility and addition sequence of monomers, initiator amount, and amount of crosslinking agent are also parameters affecting final morphology of particle.

There are several benefits of hybrid latexes prepared from polyacrylate and polysiloxane. Polyacrylates have good chemical resistance, low glass transition temperature, and high pigment binding ability. Additionally, polyacrylates have superior weatherability and optical properties such as transparency, yellowing resistance, and gloss retention. Glass transition temperature and hydrophilicity of binder can be modified by copolymerizing monomers such as methacrylic acid (MAA). On the other hand, some polyacrylates such as poly(methyl methacrylate) are not tough enough, which makes polyacrylates less resistant to stress-cracking. Water-resistance of polyacrylates needs to be improved due to the hydrophilic characteristics of ester groups. Therefore, another generic of polymer is needed to improve these deficiencies. Polysiloxanes have high water-repellency, good toughness, and low surface tension. Polysiloxanes can be used to overcome the disadvantages of polyacrylates due to very low glass transition temperature, easy processability, excellent thermal stability, and high flexibility. The blending of polysiloxane and polyacrylate results in phase separation due to low surface energy of polysiloxane. Therefore, grafting of polysiloxane onto polyacrylate is needed to attain micro- or nano-phase separation. Grafting of polysiloxane onto acrylic emulsions is challenging due to high solubility difference with polyacrylates.
Several studies showed different methods for grafting. The acrylate-terminated polysiloxane was polymerized in miniemulsion. Polysiloxanes bearing vinyl groups were employed as seeds in emulsion polymerization. Ring-opening polymerization of octamethylcyclotetrasiloxane (D₄) and grafting in presence of acidic surfactants was accomplished with much less coagulum. In order to increase crosslink density of film, vinyl septamethylcyclotetrasiloxane (VD₄) was utilized as a coupling agent. Lin et al. used polydimethylsiloxane (PDMS) seeds to synthesize hybrid core-shell latexes. When PDMS core was used core-shell morphology was obtained, whereas vinyl terminated PDMS yielded particles with uneven surfaces due to crosslinking of particles. For better wet soak adhesion, polysiloxane emulsion was post-added to the acrylic latex formulation with dispersants. Polysiloxane rubber was synthesized by reacting octamethylcyclotetrasiloxane (D₄), tetraethyl orthosilicate (TEOS), and a coupling agent, methacryloxypropyl methyldimethoxysilane. In second step, acrylic monomers were polymerized with acrylic monomers. This hybrid latex showed better impact-resistance than non-hybrid latexes in sealants. Inverted core-shell morphology was obtained when polysiloxane was used in the second step. When polysiloxane seeds composed of octamethylcyclotetrasiloxane (D₄) and tetramethyl tetravinylcyclotetrasiloxane (VD₄) were used, core-shell morphology was obtained after the polymerization of methyl methacrylate in the second step.

In this study, three pathways used to prepare polysiloxane-polyacrylate hybrid latexes were investigated: 1) polyacrylate-polysiloxane with core/shell morphology was synthesized through a two-stage semi-continuous feeding of monomers; 2) a methacrylate-terminated polysiloxane was copolymerized with acrylic monomers; and 3)
ring-opening polymerization of a cyclic siloxane (D₄) and concurrent grafting of polysiloxane onto acrylic monomer (2-hydroxyethyl methacrylate) was carried out during polymerization in batch reactor. Grafting of polysiloxane onto polyacrylate was investigated by NMR and FT-IR. The hybrid latex particles and films were investigated with atomic force microscopy (AFM) and transmission electron microscopy (TEM). Stratification of the polysiloxane phase in the latex film was also investigated by FT-IR and energy dispersive X-ray (EDX) SEM. Surface tension values of polysiloxane-grafted and unmodified polyacrylates were also measured.

4.2 Results

The characterization results of the hybrid latexes were given in details in the following sections.

4.2.1 Synthesis of Siloxane-functionalized Latexes

Core-shell latex (SC-CS) was prepared by a two-stage semi-continuous emulsion polymerization method. Initially, core composed of 2-ethylhexyl acrylate and ethyl acrylate was synthesized in a batch reactor. In the second stage, an alkoxy silane coupling agent, 3-(Trimethoxysilyl)propyl methacrylate (MATS), was added to functionalize the periphery of the core with alkoxy silane groups. A polysiloxane shell was formed by feeding and ring opening polymerization of octamethylcyclotetrasiloxane (D₄) on coupling agent (MATS). Schematic representation for synthesis of SC-CS is shown in Scheme 4.1.

Hybrid latex (B-MS) of methacrylate-terminated polysiloxane, EHA and EA, was prepared in batch polymerization. Schematic representation for the synthesis of a hybrid latex with methacrylate-terminated polysiloxane (B-MS) is shown in Scheme 4.2. All the monomers including the methacrylate-terminated polysiloxane were added at the same time. Although the acrylic monomers (EHA, EA) would be transported from the monomer droplet via a Smith-Ewart mechanism, the methacrylate-terminated polysiloxane may not. The lack of polysiloxane transport through water could lead to latex particles with varying compositions and, as a consequence, morphologies.
As a third approach, concurrent grafting of cyclic siloxane monomer (D₄) onto acrylic monomer (HEMA) was investigated during batch copolymerization of HEMA with EHA and EA as shown in Scheme 4.3. Ring-opening polymerization of D₄ was carried out. As with other batch process (B-MS), copolymerization of acrylic monomers occurred first due to their higher diffusion constants into water. The HEMA preferentially reacted and, after entering the micelle, was located at the water-micelle interface, as a consequence of its hydrophilicity. This was followed by diffusion of D₄ into particles. The D₄ siloxane oligomers ring opened via the HEMA forming a second phase.
Scheme 4.3. Synthesis of hybrid latex via ring-opening polymerization of D₄ onto HEMA (B-RH).

4.2.2 Particle size and morphology analysis

Particle sizes of siliconized and non-siliconized latexes were characterized by dynamic light scattering. Extra surfactant was added to prevent coagulation during polymerization along with initiator. However, addition of surfactant prolonged nucleation time. This resulted in all the latexes having a bimodal distribution. However, the advantage of having bimodal distributions is higher packing density and lower viscosity. The non-siliconized latex had the smallest particle size. Siloxane-grafting almost doubled size of larger latex particles as shown in Figure 4.1. The figure shows the intensity-average particle size, not the volume- or number-average particle size. The large particles were four times larger than the smaller particles.
Figure 4.1. Comparison of particle size and particle size distribution of non-siliconized (PA) with hybrid latexes via semi-continuous (SC-CS) and batch (B-MS, B-RH).

Transmission electron microscopy (TEM) was used to characterize phase-separated morphologies. Presence of polysiloxane can be designated easily due to a high electron cloud density. Hybrid latex synthesized with semi-continuous addition procedure (SC-CS) showed a core-shell structure as shown in Fig. 4.2. To illustrate a core-shell morphology, TEM pictures were taken with and without benzyl methacrylate replacing the acrylic core. Without the benzyl methacrylate, the polysiloxane formed a clearly distinguishable dark shell around the lighter acrylic core. Penetration of polysiloxane into polyacrylate core was not observed. It was presumed that miscibility between polyacrylate and polysiloxane was also enhanced by coupling agent (MATS) since the interfacial tension of polyacrylate decreased. When the core consisted 20 wt% of benzyl methacrylate, the darkness of core increased significantly after staining as
shown in Fig. 4.2 (b). The shell morphology was relatively brighter due to the higher electron diffraction of the core. This verified the proposed core-shell morphology.

Figure 4.2. TEM micrograph of hybrid latex with core-shell structure (a) without core staining. (b) with core (20 wt% benzyl methacrylate was copolymerized) staining.
Figure 4.3. TEM micrograph of hybrid latex with methacrylate-terminated polysiloxane in batch reactor (B-MS).

The TEM of the batch (B-MS) approach is shown in Fig. 4.3. The acrylic monomers (EHA, EA) and the methacrylate-terminated polysiloxane were copolymerized. Latex particles gave a relatively dark contrast due to presence of randomly distributed polysiloxane chains. Regardless of interpretation, the polysiloxane was observed to be almost randomly distributed throughout the latex. The largest particle size was around 400 nm.

A TEM micrograph of hybrid latex synthesized from ring opening polymerization of D₄ and an attachment onto HEMA (B-RH) is shown in Fig. 4.4. After the staining the
dark latex particles, grafting of polysiloxane onto polyacrylate was relatively uniform like the other batch process B-MS (see Fig. 4.3). In this hybrid latex, the polysiloxane was randomly attached to HEMA. The largest particle size observed was around 200 nm. Additionally, very broad particle size distribution was observed. Bimodal particle size distribution was also observed in the TEM micrographs.

Figure 4.4. TEM micrograph of hybrid latex synthesized from ring opening polymerization of D₄ and attachment onto HEMA (B-RH).
4.2.3 Contact angle and surface tension measurement

In contact angle measurements, dynamic angles give a better idea about surface energy since advancing and receding droplets on surface are assumed to contact with high and low energy portion of samples, respectively. Dynamic and static contact angles of each sample were measured. Surface tension components were solved by employing Youngs-Fowkes equation (1) for two different liquids:

\[
(1 + \cos \theta_1) \gamma_{L_1} = 2 \sqrt{\gamma_s^d \gamma_{L_1}^d} + 2 \sqrt{\gamma_s^p \gamma_{L_1}^p}
\]

\[
(1 + \cos \theta_2) \gamma_{L_2} = 2 \sqrt{\gamma_s^d \gamma_{L_2}^d} + 2 \sqrt{\gamma_s^p \gamma_{L_2}^p}
\]

where surface tension of solid and its dispersive and polar components were represented as \(\gamma_s, \gamma_s^d, \gamma_s^p\). \(\theta, \gamma_L, \gamma_L^d, \gamma_L^p\) represent angle between liquid and solid, surface tension of each liquid, dispersion, and polar components of surface tension of each liquid. After solving for \(\gamma_s^d, \gamma_s^p\) from eq. (1), eq. (2) is obtained:\(^{132}\)

\[
\gamma_s^d = \left( \frac{(1 + \cos \theta_1) \gamma_{L_1} \sqrt{\gamma_{L_2}^d} - (1 + \cos \theta_2) \gamma_{L_2} \sqrt{\gamma_{L_1}^d}}{2(\gamma_{L_1}^d \gamma_{L_2}^d - \sqrt{\gamma_{L_1}^p \gamma_{L_2}^p})} \right)^2
\]

\[
\gamma_s^p = \left( \frac{(1 + \cos \theta_1) \gamma_{L_1} \sqrt{\gamma_{L_2}^d} - (1 + \cos \theta_2) \gamma_{L_2} \sqrt{\gamma_{L_1}^d}}{2(\gamma_{L_1}^p \gamma_{L_2}^d - \sqrt{\gamma_{L_1}^p \gamma_{L_2}^d})} \right)^2
\]

The contact angle data for the films are shown in Table 4.1. After polysiloxane was grafted onto polyacrylates, contact angle of water increased. On the other hand, the films had almost same contact angles with ethylene glycol. This can be attributed to the almost identical dispersive forces of non-siloxane and siloxane-functionalized latexes. The siloxane-functionalized polyacrylates had lower surface energy than PA. Significant
differences in surface energy values were observed, especially dynamic contact angle measurements. The hybrid latex with methacrylate-terminated polysiloxane (B-MS) gave the lowest surface energy for dynamic and static angles. The polar component of surface tension ($\gamma^p$) for hybrid latex with methacrylate-terminated polysiloxane (B-MS) was also the lowest, indicating the most non-polar character among the four. The dispersive component of surface tension ($\gamma^d$) was almost same for all samples having almost equal dispersive forces, e.g. van der Waals forces.

Table 4.1. Dynamic and static contact angle and surface energy of samples.

<table>
<thead>
<tr>
<th>Contact Angle (deg)</th>
<th>Surface Free Energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water dynamic</td>
<td>Ethylene Glycol dynamic</td>
</tr>
<tr>
<td>SC-CS*</td>
<td>55.3±1.3</td>
</tr>
<tr>
<td>B-MS</td>
<td>64.7±3.5</td>
</tr>
<tr>
<td>B-RS</td>
<td>60.9±1.1</td>
</tr>
<tr>
<td>PA</td>
<td>44.7±1.9</td>
</tr>
</tbody>
</table>

* (a) Semi-continuous core-shell hybrid latex (SC-CS), (b) batch methacrylate-terminated polysiloxane (B-MS), (c) batch ring opening polymerization of D$_4$ on HEMA (B-RH).

† Dynamic angles were averaged out of advancing and receding contact angles.

Surface free energy ($\gamma$) of the films was calculated by the contact angles of water and ethylene glycol and the following values for the components of surface tension of the liquids (mN/m): $\gamma_{L1}$ 72.8; $\gamma^d_{L1}$ 21.8; $\gamma^p_{L1}$ 51 (water); $\gamma_{L2}$ 48; $\gamma^d_{L2}$ 29; $\gamma^p_{L2}$ 19 (ethylene glycol).

4.2.4 Differential scanning calorimetry (DSC) analysis

Thermograms obtained from DSC for the neat polyacrylate and polysiloxane-grafted polyacrylate hybrid latex films are shown in Fig. 4.5. A strong transition was observed at around -125 °C, which was attributed to polysiloxane. The polyacrylate
backbone for all samples had a glass transition temperature around -55 °C, which was in accordance with the Fox equation. In that transition, no shift to lower temperature was observed after polysiloxane modification. But the transition became less significant due to a decrease in the concentration in polyacrylate backbone per unit volume.

![Graph showing thermograms of neat and hybrid latex films](image)

**Figure 4.5.** Thermograms of neat and hybrid latex films for (a) semi-continuous core-shell hybrid latex (SC-CS). (b) methacrylate-terminated polysiloxane in batch (B-MS). (c) hybrid latex prepared via ring opening polymerization of D₄ on HEMA (B-RH).

### 4.2.5 Fourier Transform Infrared (FT-IR) analysis

Latex films were characterized by FT-IR with ATR apparatus to elucidate if stratification of polysiloxane occurs on either the film-air or film-substrate interface. In order to compare the film-air (F-A) and film-substrate (F-S) interfaces, the carbonyl peak (1740 cm⁻¹) from each spectrum was overlapped. Resonance between 1100 and 1000 cm⁻¹ was assigned to the asymmetric vibration of Si-O-Si. Symmetric deformation and
stretching vibrations of Si-CH₃ appear at 1260 and 800 cm⁻¹. The carbonyl (C=O) vibrations give a strong peak at 1740 cm⁻¹. Core-shell hybrid latex (SC-CS) prepared from D₄ ring-opening with alkoxy-silane coupling agent is shown in Fig. 4.6. The IR for hybrid latex with the methacrylate-terminated polysiloxane (B-MS), and hybrid latex prepared via ring opening polymerization of D₄ on HEMA (B-RH) are shown in Fig. 4.7 and Fig. 4.8, respectively. All three systems showed some differential in siloxane content. Polysiloxane favored F-S interface for SC-CS and B-RH. On the other hand, hybrid latex prepared via copolymerization of EHA, EA and methacrylate-terminated polysiloxane (B-MS) had relatively more polysiloxane at F-A interface (see Fig. 4.8). The distinction of polysiloxane distribution along F-A and F-S could be attributed to difference of molecular weight and incompatibility of polyacrylate and polysiloxane phases. Non-polysiloxane acrylic latex is shown in Fig. 4.9. The resonances in IR spectrum were assigned to functional groups such as carbonyl and alkyl.
Figure 4.6. ATR FT-IR of core-shell hybrid latex (SC-CS) film of film-air (F-A) and film-substrate (F-S) interfaces.
Figure 4.7. ATR FT-IR of hybrid latex film via copolymerization methacrylate-terminated polysiloxane, EHA and EA (B-MS) of film-air (F-A) and film-substrate (F-S) interfaces.
Figure 4.8. ATR FT-IR for ring-opening of D₄ with HEMA latex (B-RH) film of film-air (F-A) and film-substrate (F-S) interfaces.
4.2.6 Energy dispersive X-ray (EDX) analysis

The atomic composition of films was obtained using EDX attached on a scanning electron microscope (SEM). Silicon atom composition of the film-air and film-substrate interface by EDX is shown in Fig. 4.10. The EDX data was collaborated with the polysiloxane stratification found in the FT-IR. Core-shell hybrid latex (SC-CS) and hybrid latex which was prepared via ring-opening polymerization of D₄ on HEMA (BRH) showed higher Si content at the F-S interface than at the F-A interface. However, the Si content was higher at the F-A interface of B-MS than at the F-S interface. The weight % of Si atoms in B-MS oriented to F-A and F-S interfaces was higher than that of
other samples, probably due to lower $M_w$ of polysiloxane segment used. The least polysiloxane enrichment on interfaces was observed in SC-CS where a higher phase separation in core-shell morphology was expected than in other hybrid latexes. The polysiloxane with higher molecular weight led to higher degree of segregation at the F-A interface. However, polysiloxane with lower molecular weight formed sub-layers in bulk. From this conclusion, the polysiloxane of B-MS could be predicted as the highest molecular weight compared to other polysiloxane of SC-CS and B-RH.

![Figure 4.10. Silicon atom content of hybrid latex films via SEM-EDX for the film-air (F-A) and film-substrate (F-S) interface of (a) semi-continuous core-shell hybrid latex (SC-CS). (b) copolymerization of methacrylate-terminated polysiloxane with EHA and EA (B-MS). (c) ring-opening polymerization of $D_4$ with HEMA (B-RH).](image)

4.2.7 Atomic Force Microscopy (AFM)

Morphology of non-siliconized or hybrid latex films was investigated by atomic force microscopy (AFM) as shown in Fig. 4.11-14. Microphase separation was observed by AFM. Non-siliconized and hybrid latex particles did not form very continuous film
due to limited inter-diffusion. Continuity of micro-domains was lessened by polysiloxanes. Dark areas correspond to soft segments while hard segments are light in color.\textsuperscript{137} Core-shell hybrid latex (SC-CS) showed nano-scale indistinct interfaces without any differentiation of core and shell phases (see Fig. 4.11). The hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) did not have any clear phase separation (see Fig. 4.12) due to shorter polysiloxane segments. Hybrid latex prepared via ring-opening polymerization of D$_4$ on HEMA (B-RH) possessed uniformly distributed polysiloxane islands of 100 nm (see Fig. 4.13). The uniform distribution also pointed to successful polysiloxane grafting. The non-siliconized latex film had significant interfaces in AFM images as shown in Fig. 4.14. This was an indication that the minimum film forming temperature was higher before siloxane modification of latex particles.

Figure 4.11. AFM tapping mode height and phase images of core-shell hybrid latex (SC-CS).
Figure 4.12. AFM tapping mode height and phase images of hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS).

Figure 4.13. AFM tapping mode height and phase images of hybrid latex prepared via ring opening polymerization of D₄ on HEMA (B-RH).
Figure 4.14. AFM tapping mode height and phase images of non-siliconized latex (PA).

4.2.8 Dynamic mechanical analysis

Dynamic mechanical properties are summarized in Table 4.2. Storage modulus, loss modulus, and tan δ plots of non-siliconized and siliconized latex films are shown in Fig. 4.15-17, respectively. The storage modulus $G'$ was obtained from the rubbery region. Glass transition temperature ($T_g$) is specified by temperature at maximum transition of loss tangent. Hybrid latex prepared via ring-opening polymerization of D$_4$ on HEMA (B-RH) had the lowest $T_g$. Width of loss tangent transitions shows non-homogeneity of network. Wider $\alpha$-transition implied more phase-separated networks due to partial miscibility of polyacrylate and polysiloxane segment. Core-shell hybrid latex (SC-CS) had the most non-homogeneous network due to core-shell structure. The height of loss tangent transitions reflects the mobility of the chain segments between crosslinks in the glass transition temperature region. Therefore, hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) had
the highest chain mobility. Crosslink density ($\nu_e$) and molecular weight between crosslinks ($M_e$) were calculated from $G'$ at rubbery region. Crosslink density decreased after grafting of polysiloxane due to its low storage modulus.

A comparison of storage modulus ($G'$) of the latex films is shown in Fig. 4.15. Storage modulus ($G'$) decreased when polysiloxane-grafted onto polyacrylates since polysiloxanes have lower modulus than polyacrylates. A weak shoulder ($\beta$-transition) in $G'$ transition was observed due to side chains. Latex films showed rubbery plateau at 25 °C. Polysiloxane-functionalized latex films were less stiff than non-siliconized latex (PA) due to increase in free volume after polysiloxane-functionalization.

The comparison of loss modulus of latexes is shown in Fig. 4.16. Loss modulus transitions became noticeably broader by addition of flexible siloxane phase. Hybrid latex prepared via ring-opening polymerization of $D_4$ on HEMA (B-RH) had the broadest loss modulus transition, possibly due to the higher $M_w$ of polysiloxane. Polysiloxane-modification formed more flexible domains which had lower loss modulus than neat polyacrylate film (neat PA). Core-shell hybrid latex (SC-CS) and hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA, (B-MS), had almost same loss modulus ($G''$) in the rubbery region.

The tan δ transitions are shown in Fig. 4.17. Maximum tan δ transition increased after polysiloxane-functionalization of latexes since the presence of the polysiloxane had more effect on overall loss modulus. The tan δ of hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane (B-MS) was the highest due to more molecular rearrangements and internal frictions. Each film showed a weak shoulder ($\beta$-transition) that indicated secondary relaxation arisen from side groups such as
polysiloxane groups. The tan δ for hybrid latex films broadened indicating inhomogeneity of films. After polysiloxane modification, each tan δ transition shifted to lower temperatures due to decrease in $T_g$.

Table 4.2. Dynamic mechanical properties and crosslinked density for latex films.

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>Max. tan δ</th>
<th>transition width (°C)</th>
<th>$G'$ (MPa)</th>
<th>$v_e$ (mol/m$^3$)</th>
<th>$M_c$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-CS</td>
<td>-5.6</td>
<td>0.54</td>
<td>90.2</td>
<td>0.49</td>
<td>65.2</td>
<td>5622.1</td>
</tr>
<tr>
<td>B-MS</td>
<td>-9.2</td>
<td>0.64</td>
<td>74.2</td>
<td>0.61</td>
<td>81.9</td>
<td>4475.6</td>
</tr>
<tr>
<td>B-RH</td>
<td>-10.2</td>
<td>0.46</td>
<td>85.9</td>
<td>5.42</td>
<td>776.3</td>
<td>472.3</td>
</tr>
<tr>
<td>Neat polyacrylate (PA)</td>
<td>-2.1</td>
<td>0.50</td>
<td>86.1</td>
<td>4.11</td>
<td>543.2</td>
<td>674.9</td>
</tr>
</tbody>
</table>

* (a) Core-shell hybrid latex (SC-CS). (b) hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS). (c) hybrid latex prepared via ring-opening polymerization of D$_4$ on HEMA (B-RH).

Figure 4.15. Storage modulus comparison of non-siliconized and hybrid latex films (a) semi-continuous core-shell (SC-CS). (b) copolymerization of methacrylate-terminated poly-siloxane (B-MS). (c) ring-opening polymerization of D$_4$ with HEMA (B-RH) (d) non-siliconized polyacrylate latex (PA).
Figure 4.16. Loss modulus comparison of non-siliconized and hybrid latex films (a) semi-continuous core-shell (SC-CS). (b) copolymerization of methacrylate-terminated polysiloxane (B-MS). (c) ring-opening polymerization of D₄ with HEMA (B-RH) (d) non-siliconized polyacrylate latex (PA).
Figure 4.17. tan δ comparison of non-siliconized and hybrid latex films (a) semi-continuous core-shell (SC-CS), (b) copolymerization of methacrylate-terminated polysiloxane (B-MS), (c) ring-opening polymerization of D₄ with HEMA (B-RH), (d) non-siliconized polyacrylate latex (PA).

4.3 Discussion

Hybrid latex is one of the most active research fields in literature due to the wide variance in end properties.²,⁴ Acrylic polysiloxane latexes in particular bear several benefits like those of acrylic latexes such as low viscosity, lower VOC, and high UV-resistance. Different synthesis methodology led to a distinction in microstructure that influenced macroscopic properties. First difference in macroscopic property was observed in surface energy. Surface energy of polysiloxane-polyacrylate latexes was lower than that of neat polyacrylate due to low surface energy of polysiloxane (see Table 4.2). Interestingly, each polysiloxane-functionalized polyacrylate latex had different surface energy values even though the same amount of polysiloxane was reacted with
polyacrylate. Hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) had clearly lower surface tension than other siliconized latexes, probably due to increased randomness in grafting of polysiloxane.

Differences in microstructure of latexes were observed in analysis in AFM and TEM. In AFM, micro phase separation was observed. In B-RH, the domain size of each phase was very clear. Hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) yielded smoother films than non-siliconized latex due to a decrease in minimum film forming temperature. The proposed particle morphology of core-shell hybrid latex (SC-CS) with thin dark polysiloxane shell was observed. This morphology was also in agreement with the study by Cao et al.\textsuperscript{139} Hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane (B-MS) and hybrid latex prepared via ring-opening polymerization of D\textsubscript{4} on HEMA (B-RH) had a uniform dark morphology indicating uniformity of polysiloxane grafting onto polyacrylate backbone.

Siloxane-grafting onto polyacrylates affected dynamic mechanical properties. The storage modulus and width of tan \(\delta\) obtained in this study were in agreement with values reported by Kan et al.\textsuperscript{126} Storage modulus decreased as the amount of polysiloxane increased. However, the width of tan \(\delta\) broadened. Additionally, no polysiloxane transition was observed unless the amount of polysiloxane was increased to 30 wt\%. Storage modulus in the rubbery region decreased due to a decrease in cohesive energy density after siloxane grafting except in hybrid latex prepared via ring-opening polymerization of D\textsubscript{4} on HEMA (B-RH). Core-shell hybrid latex (SC-CS) and hybrid latex prepared via ring-opening polymerization of D\textsubscript{4} on HEMA (B-RH) had a weak
shoulder in tan δ indicating phase separation and an interpenetrating network. The elastic character of neat polyacrylate decreased after siloxane grafting as observed in the increase in tan δ. After polysiloxane grafting, α-transition broadened due to multiple secondary interactions between phases.

The Smith-Ewart theory proposed that initiation starts at the aqueous phase and monomers diffuse through aqueous phase into the particles where radicals are present. The D₄ has no significant water-solubility (~50 ppb). It is believed that mass transfer of D₄ mostly occurred via collisions between micelles and droplets in batch reactions (B-RH). This mechanism was more probable after some amount of acrylic monomers was polymerized where the surface area-to-volume ratio of droplets increased. At this moment, droplet nucleation cannot be neglected since all free micelles were presumably consumed. The polymerization of acrylic monomers was followed by polymerization of ring-opening polymerization of D₄ in aqueous phase similar to the mechanism reported before. The initiation of D₄ started in the aqueous phase where the active center of siloxane oligomer was probably associated with active group of surfactant (-SO₃⁻) at the particle-water interface. The growing siloxane oligomer at the interface was terminated by water. This termination reaction was reversible, which allowed the propagation reaction of D₄. The oligomer entry into particle probably occurred when the siloxane oligomers reached enough hydrophobicity where critical degree of polymerization was ~32. This was followed by condensation reactions between silanol oligomers in the particle, but no propagation reaction was observed. Based on this mechanism the coupling between HEMA and siloxane oligomer occurred in the particle. The coupling between HEMA and polysiloxane was proven by NMR where a peak that was observed
at 3.95 ppm belongs to the proton \((-CH_2-Si(-CH_3)-O)\) (see section 3.3.6). Scheme 4.4 shows the possible polymerization mechanism of D₄ for the hybrid latex (B-RH). A similar mechanism can be proposed for SC-CS where MATS and siloxane oligomer were coupled at the interface. The coupling between MATS and polysiloxane was proven by NMR where a peak that was observed at 1.30-1.60 ppm belongs to the proton \((CH_2-CH_2-Si-O)\). However, no ring opening occurred for B-MS (preformed methacrylate-terminated polysiloxane was used) polymerization but the polysiloxane diffusion probably occurred through collisions between monomer-swollen particles and droplets. The copolymerization of EHA, EA, and methacrylate-terminated polysiloxane was confirmed by NMR. A peak that was observed at 1.60-1.80 belongs to the proton \((CH-CH_2-Si(-CH_3)-O)\).
Possible morphologies of hybrid latexes obtained from different synthesis methodologies are shown in Scheme 4.5. The interpretation of latex particles is based on
Larger latex particles were obtained in hybrid latex synthesized via copolymerization of methacrylate-terminated polysiloxane (B-MS). The size of latex particles obtained in SC-CS and B-RH was almost same. However, semi-continuous core shell (SC-CS) hybrid latex showed a dark polysiloxane layer in shell without any diffusion into polyacrylate. Hybrid latex via ring-opening of D₄ with HEMA gave more dispersed polysiloxane into polyacrylate matrix than B-MS.

![Scheme 4.5. Morphology interpretation of hybrid latex particles based on TEM. (a) semi-continuous core-shell (SC-CS). (b) copolymerization of methacrylate-terminated polysiloxane (B-MS). (c) ring opening polymerization of D₄ with HEMA (B-RH).](image)

Preparation methodologies for hybrid latexes were reported. But the comparison of preparation methodologies was not previously published. It is believed that if preparation of polysiloxane-acrylic hybrid latexes is optimized in terms of polysiloxane-grafting efficiency, increasing solid content of latex, etc., then enhanced mechanical (toughness) and surface energy (low moisture absorption) can be obtained. In this study, optimum preparation methodology was found as hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) due to
less propensity of coagulum, higher uniformity of latex particles (tan δ transition), and the lowest free energy (contact angle measurements) among four latexes.

4.4 Conclusions

Polysiloxane functionalized acrylic latexes were synthesized by emulsion polymerization. Bimodal particle distribution was obtained for all the polymerization on the account of excess surfactant used. Dispersions were characterized after extraction in n-hexane. Surface energy of hybrid latex was significantly lower than that of polyacrylate. Two obvious glass transitions at -125 and -55 °C were assigned to polysiloxane and polyacrylate phases, respectively. Polysiloxane content of hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) was higher in the F-A interface than the F-S interface. Polysiloxane was observed on the F-S interface in SC-CS and B-RH. In hybrid lattices, micro-phase separation was observed in AFM. The presence of polysiloxane was also confirmed by transmission electron microscopy (TEM). Polysiloxane was randomly grafted in hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) and hybrid latex prepared via ring-opening polymerization of D₄ on HEMA (B-RH), whereas core-shell morphology was observed in core-shell hybrid latex (SC-CS).
CHAPTER V

INVESTIGATION OF THE ROLE OF HYDROPHILIC FUNCTIONAL MONOMER
AND SURFACTANT ON POLYMERIZATION KINETICS OF COMPOSITE
LATEXES

5.1 Introduction

Latexes are prepared by emulsion polymerization\(^{31}\), in which monomers are
emulsified in droplets (monomer reservoir) and polymerized through free radical
polymerization in an aqueous medium. Initiation predominantly occurs in the aqueous
phase. Particle nucleation occurs either by micellar nucleation (entry of radicals into
micelles) or homogeneous nucleation (stabilization of precipitated oligomeric radicals by
surfactants).\(^{145}\) Since radical species are separated into different particles, bimolecular
termination can be reduced and molecular weight, thus, is increased. Even though the
nucleation interval is short, particle size and particle size distribution (PSD) can be
determined during nucleation.\(^{146}\) Particle size and particle size distribution (PSD) depend
on many factors such as initiator, surfactant\(^{96}\), feeding rate, and hydrophilicity of
monomers\(^{100}\), etc. Particle size determines the interfacial area between particle and
continuous phase and surface to volume ratio of particles.

Emulsion polymerization can be accomplished in a batch, semi-batch, or
continuous reactor. Each reactor has its own advantages and disadvantages. Semi-batch
reactors are commonly used due to the flexibility of latex synthesis, resulting in defined particle morphology, copolymer composition, and conversion. The copolymer composition and rate of polymerization can be controlled by adjusting the rate of monomer addition in semi-batch reactor. The homogeneity of copolymers can be adjusted in a semi-batch feeding by the type of monomer, initiator feeding, and the composition of initial reactor charge. On the other hand, in batch emulsion polymerization, monomer composition changes during polymerization due to different reactivity ratios of the monomers. Continuous reactors, however, cannot provide the same degree of control as semi-batch reactors. As a consequence, continuous polymerization has application only for large-scale production of homopolymers such as poly(vinyl chloride).

Semi-batch polymerization usually starts with the synthesis of seed. Seeds can be synthesized in another reactor and can be used to control the number of particles. If the amount of seed is very low or the amount of surfactant is too high, secondary nucleation might occur which causes a broad particle size of distribution. Also, non-uniform polymerization kinetics has been shown to lead to bimodal particle size distribution due to differences in the growing rate of particles. The monomer addition procedure also affects particle size distribution. The monomer can be charged either as a pre-emulsion or neat monomer. However, the mass transfer from aqueous phase to the particles is slower when neat monomer is added into reactor. When a pre-emulsion is charged, particle size distribution (PSD) can be broader due to secondary nucleation. However, neat monomer addition leads to smaller particles. The particle size also decreases when the amount of surfactant is increased in the initial charge.
Secondary nucleation can be correlated with the kinetics of polymerization.\textsuperscript{146} Secondary nucleation occurs when growth rate of the particles in Interval III is not high enough to prevent new particle nucleation.\textsuperscript{157} In one study, secondary nucleation occurred when relatively water-soluble vinyl acetate was polymerized in the presence of large polystyrene seeds. The authors attributed this to the fast polymerization of vinyl acetate in the aqueous phase and low surface area of the seeds.\textsuperscript{145} Secondary nucleation can be avoided in seeded emulsion polymerization if these conditions are ensured: 1) high surface area of seeds is formed, 2) high concentration of radical species per polymer particle, i.e. monomer starved conditions, and 3) entry and exit of radical species from particles has to be controlled to prevent initiation or termination in aqueous phase. As a rule of thumb, polymer volume per active growing radical is required to be within the particle for 1 s.\textsuperscript{158}

The type and amount of surfactant are the important parameters to determine the polymerization kinetics. A mixture of anionic and nonionic surfactants increases the rate of polymerization since there is less nonionic surfactant to partition to the oil phase.\textsuperscript{96} When the polyacrylic acid is used as a stabilizer, the surface coverage of the stabilizer plays an important role.\textsuperscript{159} As the pH of the media increases at high surface coverage, the entry rate of \( z \)-mers into the particles decreases, resulting in secondary nucleation. On the other hand, low coverage does not affect entry rate of \( z \)-mers at higher pH. Another study compared the effect of anionic, polymeric anionic, and polymeric nonionic surfactants on polymerization kinetics.\textsuperscript{160} The type and amount of surfactant had no effect on the overall polymerization rate. However, secondary nucleation was observed when the concentration of anionic surfactant was increased in the pre-emulsion feed. In another
study, however, a narrower particle size distribution with a larger particle size was obtained when the ratio of anionic surfactant to nonionic surfactant increased.\textsuperscript{161}

The polarity of monomers has also a great influence on the polymerization kinetics. As the amount of methacrylic acid increased in styrene and butadiene pre-emulsion, the rate of polymerization increased.\textsuperscript{15} Another study showed that a higher rate of polymerization was obtained in a batch reactor when the concentration of methacrylic acid increased.\textsuperscript{162} Chen and Chang showed that nucleation was dominated by persulfate initiator in an emulsifier-free system when HEMA was used as comonomer.\textsuperscript{163} For the copolymerization of styrene with HEMA, most of the HEMA was consumed in the first stage and located around the particle surface.\textsuperscript{164} The addition of more HEMA into mini-emulsion polymerization increased the rate of polymerization, which was attributed to a higher interfacial area.\textsuperscript{14}

Pedraza and Soucek\textsuperscript{11} obtained latexes with a bimodal particle size distribution (PSD) when a very high concentration (21 wt\%) of functional monomers such as HEMA and MAA was used. As the concentration of HEMA and MAA was increased, the water solubility of monomer composition also increased. Therefore, it was concluded that colloidal stability decreased, resulting in homogeneous nucleation and secondary particle formation. In the present study, the possible critical factors leading to formation of secondary particles were investigated using similar formulations\textsuperscript{11} but with the addition of neat monomer. Sixteen latexes were synthesized with combinations of high and low levels of HEMA and MAA (in weight \%), and four surfactants (anionic, non-ionic). The effects of three variables—the amount of HEMA, MAA, and type of surfactant (anionic, nonionic)—on polymerization kinetics were investigated.
5.2 Results

The kinetics of emulsion polymerization was studied and the details of results were given in the following sections.

5.2.1 Kinetic during seed synthesis

Seeds were synthesized in a batch reactor. Time evolution of overall conversion ($x$) and volume-average diameter of particles are shown in Figure 5.1. Overall conversion, not instantaneous conversion, was calculated since the polymerization was run in a batch reactor in which all components were available in the reactor. Overall conversion and particle size increased during seed synthesis. The rate of polymerization ($R_p$) and number of particles ($N_p$) as a function of time are shown in Figure 5.2. The rate of polymerization ($R_p$) increased very quickly and decreased slowly, indicating that an Interval II had not occurred. This could be attributed to the surfactant concentration above CMC (>10000 ppm), which increased the rate of disappearance of droplets. The rate of polymerization ($R_p$) and number of particles ($N_p$) were much higher than the results obtained from the semi-batch polymerization, which could be attributed to high monomer and initiator concentration in the media. The number of particles decreased as conversion increased. The decrease in the number of particles could be ascribed to coagulative nucleation in which flocculation of unstable particles with high monomer/polymer volume ratio occurred probably due to some partition of the surfactant in oil phase. The size of particles also shrank as the conversion of monomer to polymer increased.
Figure 5.1. Evolution of total conversion and volume-average particle diameter ($d_v$) during seed synthesis in a batch reactor.

Figure 5.2. Rate of polymerization and number of particles as a function of time during seed synthesis in a batch reactor.
5.2.2 Effect of Type of Surfactant

The effect of the type of surfactant on polymerization kinetics was studied. Four surfactants were used. Table 5.1 shows the critical micelle concentration of the surfactants. Critical micelle concentration (CMC) depends on chemical structure of the surfactant. For anionic surfactants, CMC diminishes 75% with the addition of two methylene (-CH₂) groups. Nonionic surfactants having the same chain length with the ionic surfactant have much lower CMC. The addition of two methylene groups decreases the CMC of nonionic surfactant only by 10%. However, branching or carrying an ionic group in the center of surfactant, e.g. Aerosol MA, has been shown to increase the CMC.¹⁶⁷

A core (BA, MMA, and HEMA) was synthesized with the four surfactants. Figure 5.3 shows the instantaneous conversion and volume-average diameter as a function of time during core synthesis (H18, formulation with 18 wt% of HEMA). The volume-average diameter with error bars as a function of time is shown in section 5.5. As previously reported, the instantaneous conversion at the beginning of reaction was standardized at unity since no monomer was present in the reactor.¹⁵³ After monomer feeding started, the monomers’ concentration accumulated in the reactor for the first 15 min. After 45 min of feeding, the instantaneous conversion reached 90%. All surfactants showed very high (> 95%) instantaneous conversion. This indicated that polymerization had performed under monomer-starved conditions. The anionic surfactant, Aerosol MA-80, showed a discernibly slower start than other surfactants, indicating a longer nucleation time. Evolution of volume-average particle diameter was also obtained as a function of time during polymerization. Latexes synthesized with Triton X-200 had
smaller particles, which resulted in a slightly higher rate of polymerization due to the higher ratio of amount of surfactant to CMC. Additionally, some fluctuations in volume-average particle diameter were also observed when Triton X-200 was used as surfactant.

Table 5.1. Chemical names and critical micelle concentrations (CMC) for the surfactants used in this study.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical name</th>
<th>Molecular Weight (g/mol)</th>
<th>Critical micelle concentration (CMC), ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton X-200</td>
<td>Sodium octyl phenoxy tetraethoxy sulfonate</td>
<td>490</td>
<td>230</td>
</tr>
<tr>
<td>Aerosol MA-80</td>
<td>Sodium dihexyl sulfosuccinate</td>
<td>388</td>
<td>14000\textsuperscript{172}</td>
</tr>
<tr>
<td>Tergitol NX</td>
<td>Ethylene oxide/propylene oxide copolymer</td>
<td>2550</td>
<td>0.5</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>Polyethylene glycol \textit{tert}-octylphenyl ether</td>
<td>650</td>
<td>135\textsuperscript{172}</td>
</tr>
</tbody>
</table>
Figure 5.3. Instantaneous conversion ($x$) and volume-average diameter ($d_v$) as a function of time during core synthesis (H18) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.

The instantaneous rate of polymerization of core (H18, formulation with 18 wt% of HEMA) was evaluated as a function of time when four surfactants were used. Figure 5.4 shows the evolution of instantaneous rate of polymerization (g/L.min) and number of particles (1/dm$^3$) during core (H18, formulation with 18 wt% of HEMA) synthesis. The number of particles with error bars as a function of time is shown in Section 5.5. Neat monomer mixture including BA, MMA, and HEMA was fed into reactor where the seeds and surfactant were already present. Three surfactants (Tergitol XJ, Triton X-100, and Triton X-200) showed almost the same overall instantaneous rate of polymerization; very fast nucleation was followed by a decrease in the instantaneous rate of polymerization. This was an interesting observation since the mass transfer is slower when neat monomer is fed into the reactor. Interval II was very short in all the types of surfactants due to
minimal accumulation of monomers in the reactor. The number of particles for the latexes with three surfactants (Tergitol XJ, Triton X-100, and Aerosol MA-80) remained constant after 30 min. This indicated some new particles were formed at the beginning of polymerization even though 20 wt% latex seed (based on total monomer amount) was used in the reactor. This was attributed to the micellar nucleation in the remaining micelles.\textsuperscript{177}

![Graph showing the rate of polymerization (Rp) and number of particles (Np) as a function of time.](image)

**Figure 5.4.** Rate of polymerization ($R_p$, g/L.min) and number of particles ($N_p$, 1/dm$^3$) as a function of time during core synthesis (H18) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.

The instantaneous conversion of core (H25, formulation with 25 wt% of HEMA) was evaluated as a function of time when four surfactants were used. Figure 5.5 shows the evolution of instantaneous conversion ($\chi$) and volume-average diameter as a function
of time during the core synthesis (H25, formulation with 25 wt% of HEMA) with surfactants as aforementioned (Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80). Instantaneous conversion \( (x) \) was slow at the beginning of the synthesis for all surfactants due to accumulation of monomers similar to Figure 5.5. Latex prepared with Triton X-200 showed a slower start than other surfactants presumably due to the longer particle nucleation period. After 45 min, the instantaneous conversion \( (x) \) reached 90% conversion. Smaller particle size was obtained when Triton X-200 was used as surfactant than the other three. However, particle size remained almost constant with the nonionic surfactants (Tergitol XJ, Triton X-100) on the account of smaller CMC values of the nonionic surfactants in comparison with anionic surfactants (see Table 5.1).
Figure 5.5. Instantaneous conversion ($\chi$) and volume-average diameter ($d_v$) as a function of time during core synthesis (H25) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.

Figure 5.6 shows the evolution of instantaneous rate of polymerization ($R_p$, g/L.min) and number of particles during core synthesis (H25, formulation with 25 wt% of HEMA) as a function of time. The highest instantaneous rate of polymerization was observed for the latex synthesized with Triton X-100, and the slowest instantaneous rate of polymerization was obtained when Triton X-200 was used. The difference in rate of polymerization with anionic and nonionic surfactants was attributed to the higher number of radicals available in nonionic surfactant micelles compared to anionic surfactant micelles.$^{169}$
In contrast to the other three surfactants, a large amount of secondary nucleation was observed when the Triton X-200 was used (see Figure 5.4). The fluctuation in the number of particles can be attributed to the equilibrium between secondary nucleation and limited coagulation. This explanation was in agreement with the previous report in which the oscillations in a number of particles were profoundly observed when only anionic or nonionic surfactant was used. After secondary particles were formed, the particles started to coagulate until a smaller number of particles was formed with higher surface charge and stability. Additionally, the slowest instantaneous rate of polymerization was observed when Triton X-200 was used in some experiments (see
Figure 5.6). This could be attributed to viscous surfactant layer\textsuperscript{172} or electrostatic repulsion\textsuperscript{173} between persulfate initiator and head of surfactants (-SO$_3$-).

5.2.3 Effect of concentration of HEMA on the rate of polymerization of core

The concentration of HEMA in the core composition was varied to investigate the effect of concentration of HEMA on polymerization kinetics and particle size. Figure 5.7 shows the instantaneous conversion ($x$) and volume-average diameter as a function of time during the core synthesis (H18 and H25, formulation with 18 and 25 wt% of HEMA) with nonionic surfactants (Tergitol XJ, Triton X-100). As the concentration of the HEMA increased, the instantaneous conversion decreased for the first 15 min. The critical chain length of oligomers increased as the concentration of HEMA increased due to higher water solubility.\textsuperscript{174} Therefore, the monomers were mostly consumed in aqueous phase, which resulted in a decrease in the initial rate of conversion. Particle size was not significantly affected by change in the concentration of HEMA during core synthesis. When Triton X-100 was used, the volume-average particle size was almost 250 nm at the end of polymerization. However, the particle size was almost 320 nm when Tergitol XJ was used to synthesize core (H25, formulation with 25 wt% of HEMA), likely due to the limited coagulation of particles.
Figure 5.7. Comparison of instantaneous conversion (x) and volume-average diameter ($d_v$) as a function of time during core synthesis (H18, and H25, formulation with 18 and 25 wt% of HEMA) with surfactants, Tergitol XJ, and Triton X-100.

Figure 5.8 shows the evolution of instantaneous rate of polymerization ($R_p$, g/L.min) and number of particles during core synthesis (H18 and H25, formulation with 18 and 25 wt% of HEMA) with nonionic surfactants. The time period of interval II was very short, implying that all monomers charged into the reactor were swollen into the seeds present in the reactor. The highest instantaneous rate of polymerization was observed for the core synthesis (H25, formulation with 25 wt% of HEMA) with Tergitol XJ. When the concentration of HEMA increased from 18 wt% to 25 wt% in core composition, the rate of polymerization slightly decreased, indicating the presence of a prolonged nucleation time. The instantaneous rate of polymerization was higher when
Tergitol XJ was used. This can be attributed to higher radical capture by Tergitol XJ micelles than by Triton X-100 micelles. This statement was also confirmed by the number of particles. Less particles were obtained at the end of first 60 min when Tergitol XJ was surfactant. The number of particles for three latex syntheses (Tergitol H18, Triton X-100 H18, and Triton X-100 H25) was almost equal. On the other hand, a lesser number of particles were obtained for the latex (Tergitol H25). Additionally, the number of particles increased presumably by secondary nucleation especially at the beginning of polymerization. This was followed by a decrease in the number of particles.

Figure 5.8. Comparison of rate of polymerization ($R_p$, g/L.min) and number of particles ($N_p$, 1/dm$^3$) as a function of time during core synthesis (H18, and H25) with surfactants, Tergitol XJ, and Triton X-100.
The effect of HEMA concentration in core on polymerization kinetics of the shell was investigated by using anionic surfactants (Triton X-200 and Aerosol MA-80). Figure 5.9 shows the evolution of instantaneous conversion ($x$) and volume-average diameter during the shell synthesis (12 wt% MAA in H18M12 or H25M12). The highest instantaneous conversion was observed for the formulation of Aerosol H18M12. As the concentration of HEMA in the core increased from 18 to 25 wt%, the instantaneous conversion decreased when the anionic surfactant (Aerosol MA-80) was used as surfactant. However, the opposite was observed for the oligomeric anionic surfactant, Triton X-200. The volume-average particle size increased as the concentration of HEMA increased when Triton X-200 was used. The largest particle size obtained for the latex, Aerosol H25M12, likely due to the reduced surface coverage provided by Aerosol MA-80.\textsuperscript{153, 155}
Figure 5.9. Comparison of instantaneous conversion ($x$) and volume-average diameter ($d_v$) as a function of time during shell synthesis (H18M12 and H25M12) with surfactants, Triton X-200, and Aerosol MA-80.

The effect of the hydrophilicity of core formulation (H18 and H25) on the polymerization kinetics of shell was investigated when anionic surfactants were used. Figure 5.10 shows the evolution of instantaneous rate of polymerization ($R_p$, g/L.min) and number of particles during shell synthesis on core with varying hydrophilicity (H18M12 and H25M12) with anionic surfactants (Triton X-200 and Aerosol MA-80). The highest instantaneous rate of polymerization was observed for the latex H18M12 with Aerosol MA-80. The lowest rate of polymerization was observed for the latex, H18M12 with Triton X-200. After the core synthesis, the number of particles did not change significantly during shell synthesis.
Figure 5.10. Comparison of rate of polymerization ($R_p$, g/L.min) and number of particles ($N_p$, 1/dm$^3$) as a function of time during shell synthesis (H18M12, and H25M12) with surfactants, Triton X-200, and Aerosol MA-80.

The lowest rate of polymerization was observed for the latex, H18M12 with Triton X-200 (see Figure 5.10). This indicated that higher microscopic viscosity of oligomeric surfactants (Triton X-200) blocked the oligomeric radical entry into particles during the shell synthesis.$^{175}$ The instantaneous rate of polymerization decreased as the HEMA concentration increased in the core (see Figure 5.10) when Aerosol MA-80 was used. The poly(HEMA)-rich particles can absorb water and as a consequence can decrease the interfacial tension between particle and water.$^{163}$ If the volume-average diameter of the particles is smaller, then the degree of swelling of the particles by water
should be more pronounced. Hydrophilic monomers such as HEMA occupy a larger surface area that retards the diffusion of oligomeric radicals or relatively hydrophobic monomers such as BA, MMA into particles.\textsuperscript{176} This might be the reason why the instantaneous rate of polymerization decreased when the concentration of HEMA in the core increased from 18 wt\% to 25 wt\% for the latexes with Aerosol MA-80.

5.2.4 Effect of concentration of MAA on the rate of polymerization of shell

The concentration of MAA in shell formulation was changed to investigate whether there is any effect of the concentration of MAA on the conversion of shell monomer composition. No additional surfactant was added during shell polymerization. Figure 5.11 shows the evolution of instantaneous conversion ($\alpha$) and volume-average diameter as a function of time during the shell synthesis (H25M12 and H25M17) with nonionic surfactants (Tergitol XJ and Triton X-100). The volume-average particle size of the latexes was almost the same (296.6 nm) at the end of the polymerization. However, larger particle size (331.8 nm) was observed for the latex Tergitol H25M12.
Figure 5.11. Comparison of instantaneous conversion ($x$) and volume-average diameter ($d_v$) as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Tergitol XJ, and Triton X-100.

The concentration of MAA in shell formulation was changed to investigate whether there is any effect of the concentration of MAA on rate of polymerization of shell. Figure 5.12 shows the evolution of instantaneous rate of polymerization ($R_p$, g/L.min) and number of particles during shell synthesis with varying shell formulation (H25M12 and H25M17) with nonionic surfactants (Tergitol XJ and Triton X-100). The higher concentration of MAA in monomer composition decreased the rate of polymerization at the beginning of the polymerization. Additionally, nucleation time was prolonged, presumably due to retardation in radical entry when more MAA was used. The number of particles increased for the first 240 min and then decreased.
Figure 5.12. Comparison of rate of polymerization ($R_p$, g/L.min) and number of particles ($N_p$, 1/dm$^3$) as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Tergitol XJ, and Triton X-100.

The concentration of MAA in shell formulation was varied to investigate whether there is any effect of the concentration of MAA on rate of polymerization of shell when anionic surfactants were used. Figure 5.13 shows evolution of instantaneous conversion ($x$) and volume-average diameter as a function of time during the shell synthesis (H25M12 and H25M17) with anionic surfactants (Triton X-200 and Aerosol MA-80). The instantaneous conversion was lower when Aerosol MA-80 was used than when Triton X-200 was used. Smaller particle size was obtained when Triton X-200 was used due to lower CMC (see Table 5.1). The particles with smaller size increased radical capture and resulted in monomer-starved conditions whereas some monomer accumulated in reactor when Aerosol MA-80 was used. Poor surface coverage of
particles by Aerosol MA-80 led to larger particle size due to some limited coagulation and slower induction time.\textsuperscript{153}

Figure 5.13. Comparison of instantaneous conversion ($x$) (filled symbols, primary axis) and volume-average diameter ($d_v$) (unfilled symbols, secondary axis) as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Triton X-200 and Aerosol MA-80.

The concentration of MAA in shell formulation was varied to investigate whether there is any effect on rate of polymerization of shell when anionic surfactants are used. Figure 5.14 shows the evolution of the instantaneous rate of polymerization ($R_p$, g/L.min) and number of particles during shell synthesis with varying shell formulation (H25M12 and H25M17) with anionic surfactants (Triton X-200 and Aerosol MA-80). Oligomeric surfactants have poorer radical capture ability than surfactants with low molecular weight due to the hairy layer.\textsuperscript{169} However, the rate of polymerization was slightly higher when
Triton X-200 was used since Triton X-200 has much lower CMC than Aerosol MA-80. Interestingly, an increase in the MAA content in the shell from 12 wt% to 17 wt% led to a higher rate of polymerization. The number of particles increased for the first 45 min even though the seed particles were present.

![Comparison of rate of polymerization (Rp, g/L.min) and number of particles (Np, 1/dm³) as a function of time during shell synthesis (H25M12, and H25M17) with surfactants Triton X-200 and Aerosol MA-80.](image)

As the concentration of MAA in the feed increased, the instantaneous conversion decreased (see Figure 5.11). This indicated \( j \)-mers rich in MAA retarded the entry rate of radicals into existing particles due to their hydrophilic nature. This could be attributed to the Coulombic repulsions and the hydrophilicity of MAA rich \( j \)-mers which prevented the penetration of \( j \)-mers into the particles. In addition to this, some oscillations in the
instantaneous rate of polymerization for Tergitol H25M12 (see Figure 5.12) could be attributed to fluctuations of the surface tension of the media.\textsuperscript{155} This was observed as the formation of secondary nuclei, which were formed by coagulative nucleation of precursors in the aqueous phase due to emulsifier-starved conditions.\textsuperscript{156} This was followed by the decrease in the number of particles, which was also clearly observed, especially when the MAA concentration was higher (H25M17). It was postulated that secondary nucleation and limited coagulation was induced in the presence of hydrophilic monomers.\textsuperscript{170, 176} An increase in the concentration of MAA led to a decrease in the instantaneous rate of polymerization when Aerosol MA-80 was used (see Figure 5.14). This could be attributed to the larger particle size where bimolecular termination of the radicals was more possible. On the other hand, higher MAA concentration increased the instantaneous rate of polymerization when Triton X-200 was used due to compartmentalization effects.\textsuperscript{177}

5.3 Discussion

Studies about polymerization kinetics have been extensively reported.\textsuperscript{18-21} However, controlling factors of latex stability leading to bimodal PSD are not well understood. Controlling PSD is important since better film formation and rheology characteristics can be obtained via bimodal PSD.\textsuperscript{10} This study showed polymerization kinetics was dependent on the type of surfactant and the ratio of hydrophilic monomer. Although seeded polymerizations were employed, the number of particles oscillated significantly when anionic surfactant (Triton X-200) was employed. Longer nucleation times were observed when Triton X-200 was used (see Fig. 5.6). This observation was in
agreement with Feeney’s report.178 If the concentration of surfactant was high, nucleation time was very long, which caused the formation of higher number of particles than in the precursors, i.e. secondary nuclei. In this case, the collision between secondary nuclei and primary particles become more frequent. This resulted in an increase in coagulation and a decrease in the number of particles. Aerosol MA-80 (anionic surfactant) generally showed a low radical capture efficiency compared to other anionic and nonionic surfactants, especially at the beginning of the reaction. This result opposed the report by Wu and Schork. In their study, anionic surfactant (sodium lauryl sulfate) showed a higher rate of polymerization than nonionic surfactant (Brij-35) when the same amount of surfactant was used.169

Mostly monomodal particle size distribution (PSD) was obtained since neat monomer was fed into reactor previously charged with surfactant and seed in this study. This produced a similar observation to that of the study reported by Gerrens.152 However, PSD was affected by the concentration of hydrophilic monomers (HEMA and MAA). A conventional Smith-Ewart model is not applicable to hydrophilic monomers. Hydrophilic monomers undergo homopolymerization in continuous phase until precipitation occurs. As the concentration of HEMA and MAA increased, secondary nucleation was observed and generally followed by limited coagulation. This phenomenon was observed for a different system by Sajjadi.153 When the surface coverage of particles by surfactant was very low, secondary nucleation occurred. However, the amount of surfactant was not enough (reduced surface coverage) to stabilize particles; consequently, secondary nuclei were coagulated on primary particles.
As the concentration of HEMA and MAA increased, the instantaneous rate of polymerization decreased. This observation was in agreement with a previous report.\textsuperscript{17} Water-soluble monomers (HEMA and MAA) were mostly nucleated homogenously in the aqueous phase. Oligomers rich in HEMA (core) and MAA (shell) remained in aqueous phase while hydrophobic oligomers entered micelles and polymerize faster. Homogeneous nucleation and oligomer growth of HEMA and MAA also induced secondary nucleation. Gaboyard et al. also observed secondary nucleation when water-soluble monomer was used greater than 5 wt\%.\textsuperscript{176}

The polymerization kinetics was affected by the type of surfactant. Scheme 5.1 shows the schematic representation of oligomeric radical entry into the monomer-swollen particles when anionic (Triton X-200) and nonionic (Tergitol XJ) surfactants were used. The use of anionic surfactant caused a severe new particle formation. This was observed as fluctuations in the number of particles during the course of polymerization. This could be attributed to much higher microscopic viscosity of Triton X-200 compared to Tergitol XJ. The viscous hairy layer and Coulombic repulsion of Triton X-200 retarded the entry of oligomeric radicals, which resulted in a slow increase in the number of free radicals in the particles. Therefore, entry ($k_{\text{entry}}$) and exit ($k_{\text{des}}$) rates should be lower when Triton X-200 was used compared to Tergitol XJ (see Scheme 5.1). This was observed as longer nucleation time when Triton X-200 was used (see Figure 5.6). The average number of radicals in the particles reaches a maximum when the viscosity of hairy layer is low.\textsuperscript{169} This probably caused the presence of higher amount of polymer chains in the particles when Tergitol XJ was used. The retardation of the entry of oligomeric radicals in the aqueous phase induces the formation of $j$-mers with higher molecular weight and
consequently coagulative nucleation.\textsuperscript{177} This conclusion was clearly observed (see Figure 5.6) where the larger number of particles was formed with a sluggish rate of polymerization when Triton X-200 was used.
Scheme 5.1. Schematic representation of oligomeric radical entry to the monomer-swollen particles or new particle formation through homogeneous nucleation in the presence of a) anionic (Triton X-200) surfactant, b) nonionic (Tergitol XJ) surfactants.
The use of Triton X-200 as surfactant caused severe fluctuations in the number of particles (see Fig. 5.4). Piirma proposed there was a dynamic equilibrium between particle nucleation and limited coagulation during polymerization.\textsuperscript{170} As the particles grow, there is a need of surfactant to keep the particles stable. If the concentration of surfactant is not sufficient, coagulation of particles occurs until particles attain enough stability. After coagulation, surfactants are released to the aqueous medium since the particle area/volume ratio is smaller. The release of surfactants causes the formation of new particles. This mechanism continues until all particles are stable.

The results from this study have direct implications to the controlled incorporation of functional monomers in the latex particles. If the particle size and particle size distribution are controlled, this would have effects on the mechanical and rheological properties of latexes. It was anticipated that Triton X-200 would show better mechanical properties than the other surfactants due to combination of smaller and bigger particles. The higher amount of functional monomers (HEMA and MAA) decelerated the conversion, implying that hydrophilic monomers showed a lower nucleating ability.

5.4 Conclusions

Functional two-stage latexes were synthesized through seeded semi-batch polymerization. The effect of three parameters, amount of functional monomers (HEMA, MAA) and type of surfactant (anionic, non-ionic), on conversion, particle diameter, and particle size distribution (PSD) were investigated. Polymerization kinetics of sixteen latexes in terms of instantaneous rate of polymerization ($R_p$) and number of particles ($N_p$) were evaluated. Critical micelle concentration played an important role in
polymerization kinetics. The type of surfactant did not profoundly influence the rate of polymerization during core synthesis. However, the lowest rate of polymerization was obtained during the shell synthesis when Aerosol MA-80 was used due to very its high CMC. The particle size and particle size distribution were strongly dependent on the type of surfactant. Although a seeded emulsion polymerization was used, there was an increase in the number of particles. There were severe oscillations in the number of particles when viscous anionic surfactant (Triton X-200) was used. Higher fractions of functional monomers (HEMA and MAA) yielded more homogeneous nucleation observed through extended Rp curves (longer nucleation time). The Rp decreased when the amount of hydrophilic monomer increased. The polymerizations run under monomer-starved conditions after 45 min, which caused a very short interval II.

5.5 Supplementary Data

The volume-average diameter and number of particles of latex aliquots with error bars as a function of time are shown in Supplementary Figure 5.1-12.
Figure 5.15. The volume-average diameter ($d_v$) with error bars as a function of time during core synthesis (H18) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.
Figure 5.16. The number of particles (Np, 1/dm3) with error bars as a function of time during core synthesis (H18) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.
Figure 5.17. The volume-average diameter ($d_v$) with error bars as a function of time during core synthesis (H25) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.
Figure 5.18. The number of particles ($N_p$, 1/dm$^3$) with error bars as a function of time during core synthesis (H25) with surfactants, Tergitol XJ, Triton X-100, Triton X-200, and Aerosol MA-80.
Figure 5.19. The volume-average diameter ($d_v$) with error bars as a function of time during core synthesis (H18, and H25, formulation with 18 and 25 wt% of HEMA) with surfactants, Tergitol XJ, and Triton X-100.
Figure 5.20. The number of particles ($N_p$, 1/dm$^3$) with error bars as a function of time during core synthesis (H18, and H25) with surfactants, Tergitol XJ, and Triton X-100.
Figure 5.21. The volume-average diameter ($d_v$) with error bars as a function of time during shell synthesis (H18M12, and H25M12) with surfactants, Triton X-200, and Aerosol MA-80.
Figure 5.22. The number of particles ($N_p$, 1/dm$^3$) with error bars as a function of time during shell synthesis (H18M12, and H25M12) with surfactants, Triton X-200, and Aerosol MA-80.
Figure 5.23. The volume-average diameter ($d_v$) with error bars as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Tergitol XJ, and Triton X-100.
Figure 5.24. The number of particles \( (N_p, \text{1/dm}^3) \) as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Tergitol XJ, and Triton X-100.
Figure 5.25. The volume-average diameter ($d_v$) with error bars as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Triton X-200 and Aerosol MA-80.
Figure 5.26. The number of particles (Nₚ, 1/dm³) with error bars as a function of time during shell synthesis (H25M12, and H25M17) with surfactants, Triton X-200 and Aerosol MA-80.
6.1 Introduction

Latexes having at least two different polymers in the core and shell are called as core-shell latexes. Core-shell latexes have applications in coatings, inks, and paints. Desired physical properties such as modulus and stiffness are attainable in core-shell latexes, and this cannot be obtained by just blending of two polymers. Core-shell latexes with hydrophilic comonomers were used in outdoor paint applications since hydrophilic monomers were beneficial for protection against oily contaminants and provided good adhesion onto substrate.\textsuperscript{179} Emulsion polymers with hydroxyl and carboxylic acid functional groups are used for two-package water-borne polyurethane applications.\textsuperscript{180} Carboxylated styrene-butadiene latexes were used as binder in paper industry.\textsuperscript{18} By alternating core and shell composition in the core-shell latexes, different morphologies can be obtained by phase separation.\textsuperscript{181} These include core-shell, inverted core-shell, hemispheres, etc.\textsuperscript{182}
Morphology development is a result of interaction between thermodynamic and kinetic parameters. Thermodynamic factors determine morphology when the diffusion of polymer chains is faster than the polymerization rate. On the other hand, kinetic factors such as viscosity of polymerization loci and monomer addition mode play key roles in the formation rate of morphology. In a composite latex, the final morphology is determined through diffusion of at least two species in which interfacial tension is the controlling factor.\textsuperscript{183} Monomer amount and polarity, surfactants, and initiators are also important parameters affecting the composite latex morphology.\textsuperscript{184} The equilibrium morphology can be reached if the interfacial tension between the phases is high and the phases are immiscible. New interface formation between polymer/water and each polymer during diffusions of the phases is the most important parameter determining Gibbs free energy.

The morphology is dependent on the interfacial tension of each polymer.\textsuperscript{185} A core-shell morphology can be kinetically obtained when the viscosity of first stage polymer is sufficiently high or crosslinked so that penetration of the second stage polymer is blocked. If the polarity of polymer in core is higher than the polarity of the shell polymer, an inverted core-shell morphology is formed.\textsuperscript{186} In order to form individual particles of the first and second stage polymers, interfacial tension between polymers has to be higher than the interfacial tensions of each polymer and water. When the individual particles are formed, the contribution to the formation of new interfaces is higher than in other cases.\textsuperscript{187} Interfacial tension of phases also depends on monomer addition mode.

The addition of reactants into the reactor also influences the polymer structure and morphology of latex particles. In batch emulsion polymerization, low viscosity is
obtained which favors the chain diffusion into different domains. On the other hand, a very viscous barrier of first stage polymer blocks the chain migration into different domains in a semi-batch addition mode. This results in a lower degree of phase separation. Therefore, controlling particle morphology is easier for a semi-batch emulsion polymerization than in a batch emulsion polymerization. In addition, homogeneous polymer composition was obtained in a semi-batch polymerization when the rate of monomer feeding is slower than the rate of polymerization (monomer-starved conditions). Vinyl acetate and butyl acrylate were homogeneously copolymerized in semi-batch reactor under monomer-starved conditions.

In order to control specific physical properties, not only the morphology but also the heterogeneities on morphology of the core-shell latexes have to be tuned. The investigation of these small domains requires very powerful characterization tools such as solid state NMR, DSC, etc. The inter-phase region is important in order to prepare impact modifiers. Solid state NMR analysis showed the thickness of inter-phase between core and shell increased in poly(butyl acrylate)/poly(methyl methacrylate) core-shell latex when the PMMA macromonomer was used as compatibilizing agent. Poly(divinylbenzene)/poly(n-butyl acrylate) core/shell latexes were prepared and characterized by solid state NMR. The inter-phase region was thicker when polymerization was performed under monomer-starved conditions other than monomer-flooded conditions. In the DSC analysis of poly(methyl methacrylate)/poly(vinyl acetate) core-shell latex, the interfacial thickness decreased when the annealing time was increased due to higher extent of phase separation.
Analysis of core-shell latexes which have varying hydrophilicity in the phases is important to have an insight on the microstructure. Better understanding of phase separation of the core and shell phases was sought in this study. The poly(BA-MMA) seeds were used to prepare two-stage latexes with 2-hydroxyethyl methacrylate in core and methacrylic acid in shell in a semi-batch reactor. The amount of hydrophilic monomers was varied in the core (HEMA) from 9 wt% to 25 wt% and shell (MAA) from 6 wt% to 17 wt%. The polymerization kinetics and particle morphology were investigated. Interfacial tension between core and shell phases was also calculated via contact angle measurements. The amount of core, shell, and diffused phases was determined by using DSC. The solid state 2D NMR was used to investigate the dynamic heterogeneity of the latex.

6.2 Results

Preparation of two-stage latexes was conducted in the presence of poly(BA-MMA) seeds to investigate the effect of concentration of functional hydrophilic monomers (HEMA and MAA) on polymerization kinetics and particle morphology. It was anticipated that a change in hydrophilicity of monomer composition in core or shell would influence polymerization kinetics, interfacial tension, and morphology of latex particles. Latexes with varying core and shell composition were synthesized based on the previous report.\textsuperscript{11} Previously, morphology investigation of latex particles was reported for PMMA/poly(styrene-co-butyl acrylate) core-shell latexes by using several characterization tools such as TEM, NMR, and DSC, etc.\textsuperscript{194} The morphology of core-shell latexes was investigated as a function of pH of the core composition with varying
The coverage of core phase as a function of macromonomer chain length was determined by using solid state NMR. But no study has been reported on the investigation of morphology when the concentration of hydrophilic monomers in the core or shell was varied. This study is important to learn the detailed knowledge about morphology of core-shell latexes with hydroxyl and carboxylic functional groups. The internal structure and entire morphology was expected to influence different physical properties of the latexes such as mechanical and rheological properties.

6.2.1 Polymerization kinetics

The poly(BA-MMA) seeds were synthesized in a batch reactor. The overall rate of polymerization was calculated since the polymerization was run in a batch reactor where all components were present in the reactor. Figure 6.1 shows the overall rate of polymerization ($R_p$) and number of particles ($N_p$) as a function of time. The instantaneous rate of polymerization ($R_{ip}$) increased very fast and decreased slowly indicating that the interval II was very short. This could be attributed to the surfactant concentration above CMC, which increased the rate of disappearance of droplets. Instantaneous rate of polymerization ($R_{ip}$) and number of particles ($N_{ip}$) were much higher than results obtained in semi-batch polymerization due to high monomer and initiator concentration in the medium (see Figure 6.3). The number of particles decreased as conversion increased. The number of particles decreased to a constant to reach stable surface coverage of particles by surfactants. The decrease in the number of particles could be ascribed to coagulative nucleation. The flocculation of unstable particles with high monomer/polymer volume ratio occurred probably due to some partition of the surfactant in oil phase. The
particles also shrank in size as the conversion of monomer to polymer increased due to the higher density.

![Graph](image)

Figure 6.1. Time evolution of instantaneous rate of polymerization ($R_p$, g/min.L) and number of particles ($N_p$, 1/L) during polymerization of seed.

Figure 6.2 shows the evolution of overall conversion and volume-average particle size of core polymerization (H9 and H25) as a function of time. A linear overall conversion was observed until monomer feeding was ended. This linear overall conversion versus time indicated the polymerization ran under pseudo-steady state, i.e. monomer-starved conditions, where monomer amount in the reactor remained constant. After the addition of the monomers for the core composition, a steady overall conversion was observed. As the concentration of HEMA increased, overall conversion also increased. Volume-average particle size of core composition with 9 wt% HEMA
(H9) was almost constant during polymerization. In contrast, particle diameter for core composition with 25 wt% HEMA (H25) increased showing that unstable oligomers were extensively formed due to homogeneous nucleation. These precursors underwent the coagulation with primary particles during polymerization likely due to the high surface area of seeds.\textsuperscript{166} The formation of larger particles led to higher overall conversion due to the higher number of radicals.

![Graph showing time evolution of overall conversion (x\textsubscript{tot}) and volume-average particle size (nm) for core polymerizations (H9, H25).](image)

Figure 6.2. Time evolution of overall conversion ($x_{\text{tot}}$) and volume-average particle size (nm) for core polymerizations (H9, H25).

Figure 6.3 shows the instantaneous rate of polymerization and number of particles during core formation (H9 and H25). When the concentration of HEMA was increased from 9 wt% to 25 wt%, the instantaneous rate of polymerization was higher. A similar result has previously been reported.\textsuperscript{12} However, fewer particles were obtained at the end
of polymerization. Nucleation of new particles was observed even though seeds were used. The nucleation stage of H9 was shorter than that of H25. The number of particles increased in the first 90 min in H9, whereas the number of particles remained constant in H25. This could be attributed to the very fast consumption of HEMA in the first stage. Under monomer-starved conditions, secondary nucleation was prevented. However, relatively hydrophobic feed (9 wt% HEMA) seemed to extend the nucleation period. This could be attributed to the tendency to micellar nucleation by hydrophobic monomer mixture (H9). Additionally, interval II was longer for H9. Li and Brooks found the relation that the ratio of rate of polymerization ($R_p$) to the rate of feeding ($R_f$) gave volume fraction of polymer ($\Phi_p$) in particle at steady-state in semi-batch polymerization under monomer-starved conditions.\textsuperscript{199} In our study, the instantaneous rate of polymerization in steady-state was \(~2\) g/min.L (0.40 g/min) for H9 and \(~3\) g/min.L (0.42 g/min) for H25. The rate of feeding for the core composition was 0.44 g/min. By using this relation, $\Phi_p$ was calculated as 0.91 for H9 and 0.95 for H25.
Figure 6.3. Time evolution of instantaneous rate of polymerization ($R_p$, g/min.L) and number of particles ($N_p$, g/min.L) for core polymerizations (H9, H25).

Figure 6.4 shows the overall conversion and volume-average particle size during shell polymerization of H9M6 and H9M17 as a function of time. A linear overall conversion was observed when core composition with 9 wt% HEMA was used for the shell formulation with 6 wt% and 17 wt% MAA. The overall conversion for shell composition with lower fraction of MAA (H9M6) reached 98% whereas overall conversion for H9M17 was almost 92%. The volume-average particle size fluctuated significantly during polymerization. The fluctuation in the number of particles could be attributed to the equilibrium between secondary nucleation and limited coagulation. This was in agreement with the previous report. The oscillations in the number of particles were profoundly observed when only anionic or nonionic surfactant was used. The
number of particles started to coagulate after secondary particles were formed until fewer particles were formed with higher surface charge and stability. Another reason of fluctuations in particle size could be attributed to shrinking of monomer-swollen particles after the polymerization of monomers.

![Graph showing time evolution of overall conversion and particle size](image)

Figure 6.4. Time evolution of overall conversion ($x_{\text{tot}}$) and volume-average particle size (nm) for shell polymerizations (H9M6, H9M17).

Figure 6.5 shows the instantaneous rate of polymerization during shell polymerization for H9M6 and H9M17. As the concentration of MAA increased from 6 wt% to 17 wt%, the instantaneous rate of polymerization was lower. This indicated that oligomers containing MAA retards the entry rate of radicals into existing particles. This could be attributed to the hydrophilicity of MAA, which had lowered the entry rate of
Figure 6.5. Time evolution of instantaneous rate of polymerization ($R_p$, g/min.L) and number of particles ($N_p$, 1/L) for shell polymerizations over H9 (H9M6, H9M17).

Figure 6.6 shows the instantaneous conversion against overall conversion during core (H9, H25) and shell (H9M6, H9M17) polymerization. Core polymerization (H9, H25) was run under almost monomer-starved conditions due to very high instantaneous conversion. Some oscillations were observed in instantaneous conversion of core polymerization, when 9 wt% and 25 wt% HEMA was used. The oscillations in the instantaneous conversion can be attributed to accumulation of monomer in reactor. Conversely, shell polymerization started at low conversion, and then increased to 90% instantaneous conversion. Sajjadi and Brooks proposed that transition time for steady-state condition of instantaneous conversion was related to load of seed weight under
monomer-starved conditions. As the weight of seed decreased, instantaneous conversion reached equilibrium faster. Short transition time of H9 and H25 polymerization was attributed to the small amount of seed. However, transition time was much longer for the shell polymerization of H9M6 and H9M17 due to the presence of a high amount of core, H9.

![Instantaneous conversion vs overall conversion](image)

Figure 6.6. Instantaneous conversion ($x_{\text{int}}$) versus overall conversion ($x_{\text{tot}}$) for core (H9, H25) and shell (H9M6, H9M17) polymerizations.

The instantaneous rate of polymerization as a function of time for shell polymerization of H9M6, H9M17, H25M6 and H25M17 is shown in Figure 6.7. The highest instantaneous rate of polymerization was observed for H9M6 with very short intervals I and II due to absorption of monomers by particles. However, intervals I and II were longer when the concentration of HEMA in the core was increased from 9 wt% to
25 wt%. The HEMA oligomers were mostly located in outer surface particle. This caused latex particles to be swollen in the presence of water during polymerization. This could increase absorption and desorption rate of oligoradicals resulting in longer intervals I and II. The monomer fed into the reactor was absorbed by the particles in the reactor. The monomers diffused into new particles while the monomer-swollen particles shrank. The diffusion process and new particle formation prolonged intervals I and II, especially when the concentration of MAA increased.

Figure 6.7. Time evolution of instantaneous rate of polymerization ($R_p$, g/min.L) for the shell polymerization in H9M6, H9M17, H25M6, and H25M17.
6.2.2 Effect of neat monomer and pre-emulsion addition on polymerization kinetics

The effect of monomer and pre-emulsion addition on polymerization kinetics of core formulation with 25 wt% HEMA (H25) was studied. This formulation was selected since the highest instantaneous rate of polymerization was obtained (see Figure 6.3). A previous study showed that conversion was slower when neat monomer was fed into the reactor compared to pre-emulsion addition. This was attributed to mass-transfer limitations. Figure 6.8 shows the comparison of rate of polymerization and number of particles for the neat monomer and pre-emulsion feeding procedures during core (H25) polymerization. The neat monomer mixture was fed into the reactor having seed, water, and surfactant (Triton X-200 or Tergitol XJ). The pre-emulsion feeding was performed after monomers were pre-emulsified with the mixture of surfactants (Triton X-200 and Tergitol XJ) and water. The feeding of pre-emulsion yielded a rate of polymerization almost twice as high as that of the feeding of neat monomer mixture. This could be attributed to the higher decomposition rate of initiator in the presence of surfactant at the CMC level. Sajjadi reported that the saturation of aqueous phase with surfactant was the highest when no surfactant was used in the initial charge. Therefore, continuous surfactant addition could enhance the rate of initiator dissociation, resulting in faster formation of radicals. Fewer particles were obtained throughout the reaction when pre-emulsion feeding was performed. The number of particles showed fewer oscillations when the mixture of surfactants in pre-emulsion and Tergitol XJ were used. The surfactant, Triton X-200, caused severe secondary nucleation.
Figure 6.8. Time evolution of instantaneous rate of polymerization ($R_p$, g/min.L) and number of particles ($N_p$, 1/L) for the core, H25, with neat monomer with anionic (Triton X-200) or nonionic surfactant (Tergitol XJ) and pre-emulsion (mixture of surfactants, Triton X-200 and Tergitol XJ) feeding.

The time evolution of instantaneous rate of polymerization and number of particles during the formation of shell with neat monomer and pre-emulsion feeding is shown in Figure 6.9. Higher instantaneous rate of polymerization was obtained when the pre-emulsion was fed. Fewer particles were obtained in pre-emulsion feeding than neat monomer feeding. In all feeding procedures, secondary nucleation occurred. In neat monomer feeding, secondary nucleation was followed by a limited coagulation. On the other hand, formation of secondary nuclei continued until end of the polymerization. Chu and Piirma reported that fluctuations in the number of particles were more profound when only one type of surfactant (anionic or non-ionic) was used.\textsuperscript{170} The number of
particles started to decrease after secondary nucleation occurred. The decrease in the number of particles continued until particles reached higher surface charge and sufficient stability.\textsuperscript{171} This result was in agreement with our study since the number of particles had significant fluctuations when Triton X-200 was used. However, there was a smaller tendency towards fluctuations in the number of particles when the mixture of surfactants was used. Similarly, the number of particles showed less fluctuation when Triton X-200 and Tergitol XJ were used together. The decrease in the number of particles was attributed to the coagulation of low molecular weight primary particles after monomer feeding was completed. Poor radical capturing of low molecular weight primary particles by monomer-swollen micelles could also lead to the decrease in the number of particles.\textsuperscript{202}
6.2.3 Interfacial Surface Tension

Surface tension is the inward force acting on boundaries and decreasing the surface area of interface. \(^\text{205}\) Quantity of surface tension is directly related to contact angle of the liquid. Contact angle is lower for polar surfaces since polar surfaces absorb polar solvents better. Therefore, the polar component of surface energy will be higher with increase in polar bonds, i.e. H-bonding. Interfacial tensions for polymers in the core or in the shell were determined. Surface tension components were solved by employing Youngs-Fowkes equation (5) for two different liquids:

---

**Figure 6.9.** Time evolution of instantaneous rate of polymerization \((R_p, \text{g/min.L})\) and number of particles \((N_p, \text{1/L})\) for the shell, H25M17, with neat monomer with anionic (Triton X-200) or nonionic surfactant (Tergitol XJ) and pre-emulsion (mixture of surfactants, Triton X-200 and Tergitol XJ) feeding.
where surface tension of the solid and its dispersive and polar components were represented as $\gamma_S$, $\gamma_d^S$, $\gamma_p^S$. $\theta$, $\gamma_L$, $\gamma_d^L$, $\gamma_p^L$ represent the angle between liquid and solid, surface tension of each liquid, dispersion and polar components of surface tension of each liquid. After taking out $\gamma_d^S$, $\gamma_p^S$ from eq. (5), eq. (6) is obtained:

\[
(1 + \cos \theta_1)\gamma_L^1 = 2\sqrt{\gamma_s^d \gamma_{L1}^d} + 2\sqrt{\gamma_s^p \gamma_{L1}^p} \\
(1 + \cos \theta_2)\gamma_L^2 = 2\sqrt{\gamma_s^d \gamma_{L2}^d} + 2\sqrt{\gamma_s^p \gamma_{L2}^p}
\]

Contact angle and surface tension for core and shell polymers are shown in Table 6.1.

### Table 6.1. Static contact angle (in degrees) and surface energy of core and shell polymers synthesized separately.

<table>
<thead>
<tr>
<th></th>
<th>Contact angle (water)</th>
<th>Contact angle (EG)</th>
<th>$\gamma^p$ (mN/m)</th>
<th>$\gamma^d$ (mN/m)</th>
<th>$\gamma^f$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H9</td>
<td>54±4.3</td>
<td>48.8±4.5</td>
<td>47.9</td>
<td>3.2</td>
<td>51.1</td>
</tr>
<tr>
<td>H25</td>
<td>44±3.6</td>
<td>37±2.9</td>
<td>56.1</td>
<td>3.8</td>
<td>59.9</td>
</tr>
<tr>
<td>M6</td>
<td>49±3.5</td>
<td>39±3.7</td>
<td>48</td>
<td>5.3</td>
<td>53.3</td>
</tr>
<tr>
<td>M17</td>
<td>44±2.5</td>
<td>36.7±3.2</td>
<td>55.7</td>
<td>4</td>
<td>59.7</td>
</tr>
</tbody>
</table>

† Static angles were averaged out of five contact angle measurements.

Surface free energy of samples was calculated by contact angles of water and ethylene glycol and the following values for the components of surface tension of the liquids (mN/m): $\gamma_{L1}$, 72.8; $\gamma_{d1}^L$, 21.8; $\gamma_{p1}^L$, 51 (water); $\gamma_{L2}$, 48; $\gamma_{d2}^L$, 29; $\gamma_{p2}^L$, 19 (ethylene glycol).
Interfacial surface tensions between core and shell compositions were also calculated for four polymers by substituting polar and dispersive surface tension components into a harmonic mean equation\textsuperscript{206}, eq. (7):

\[ \gamma_{12} = \gamma_1 + \gamma_2 - \frac{4 \gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4 \gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \]  

where $\gamma_{12}$ is the interfacial tension between components 1 and 2, $\gamma_1^d$, $\gamma_2^d$ is dispersive fraction of surface tension of polymer 1 and 2, and $\gamma_1^p$, $\gamma_2^p$ are polar fractions of surface tension of polymer 1 and 2, respectively. Interfacial tensions for the latexes are shown in Table 6.2. The highest interfacial tension was obtained for H25M6 due to the very hydrophilic nature of core with 25 wt% HEMA. However, interfacial tension was the lowest for H25M17 due to the very hydrophilic nature of both core and shell compositions.

Table 6.2. Interfacial tension between core and shell polymers determined from surface energy of core and shell polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\gamma_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H9M6</td>
<td>0.52</td>
</tr>
<tr>
<td>H9M17</td>
<td>0.68</td>
</tr>
<tr>
<td>H25M6</td>
<td>0.88</td>
</tr>
<tr>
<td>H25M17</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
6.2.4 Differential Scanning Calorimetry (DSC) Analysis

The extent of phase separation was analyzed by using DSC. Figure 6.10 shows the thermograms of the core-shell latexes. In all latexes, multiple transitions were observed due to significant phase separation. These transitions were closer in H9M6 and H25M17, where an equivalent amount of polar monomers was used in the both core and shell. Additionally, very broad transitions were observed in H25M17 due to more heterogeneous morphology, indicating a better inter-diffusion of core and shell. In latex, H25M6, the transitions were narrow and distant indicating a higher phase-separated morphology.

Figure 6.10. The thermograms of core-shell latexes, H9M6, H9M17, H25M6, and H25M17.
Figure 6.11 shows the differential of heat capacity versus temperature ($dC_p/dT$) signal for core-shell latexes H9M6, H9M17, H25M6, and H25M17. In $dC_p/dT$ plots, main peaks represent the core and shell phases whereas intermediate transition between two peaks represents inter-phase. The theoretical glass transition temperature for core and shell was calculated as -5 °C by Fox equation.\textsuperscript{134} The latex (H9M6) showed two glass transitions at -58.5 and 7.0 °C. However, the soft segment did not have significant transition (-58.5 °C), indicating presence of a lower fraction of soft segment. The glass transition temperatures of the latex (H25M17) were observed at -48.2 °C and 24.1 °C due to higher concentration of HEMA and MAA. The latex (H9M17) showed a significant phase separation with two glass transitions. One of the glass transition temperatures was very broad due to phase separation in hard domain. The latex (H25M6) showed two significant transitions with lower intermediate transition. This suggested a better phase separation. The difference between experimental and theoretical glass transitions could be attributed to phase separation of hard (e.g., polymethyl methacrylate) and soft (e.g., polybutyl acrylate) polymer segments.

Weight fractions of core, shell, and inter-phase were calculated based on the fraction of main and intermediate peaks.\textsuperscript{207} Table 6.3 shows the calculated weight fractions for latexes H9M6, H9M17, H25M6, and H25M17. The lowest inter-phase fraction (diffused phase) was observed in latex H25M6. This result suggested that the extent of phase separation was the highest in H25M6. In all latex particles, a very high weight fraction of diffused phase was observed indicating that a gradient phase or partially phase separated morphology\textsuperscript{208} was obtained due to very close glass transition temperatures of core and shell.
Figure 6.11. Differential of heat capacity (d\(C_p/dT\)) for core-shell latexes H9M6, H9M17, H25M6, and H25M17.

Table 6.3. Weight fractions of core-shell latexes for 1\(^{st}\), 2\(^{nd}\) and diffused phases, calculation based on the ratio of the d\(C_p/dT\) for main and intermediate transitions.

<table>
<thead>
<tr>
<th>Latex sample</th>
<th>1(^{st}) phase</th>
<th>Diffused phase</th>
<th>2(^{nd}) phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>H9M6</td>
<td>0.27</td>
<td>0.18</td>
<td>0.55</td>
</tr>
<tr>
<td>H9M17</td>
<td>0.40</td>
<td>0.23</td>
<td>0.38</td>
</tr>
<tr>
<td>H25M6</td>
<td>0.28</td>
<td>0.17</td>
<td>0.55</td>
</tr>
<tr>
<td>H25M17</td>
<td>0.32</td>
<td>0.20</td>
<td>0.48</td>
</tr>
</tbody>
</table>
6.2.5 Solid State NMR

Solid state NMR with wide-line separation (WISE) technique was used to study dynamic heterogeneities in the latex (H9M17). Latex film cast from H9M17 was selected since it had the highest diffused phase (see Table 6.3). If this sample shows a motion contrast between core and shell phases, other latex particles are believed to have some motion contrast between core and shell. Figure 6.12 shows 2D WISE spectrum of core-shell latex (H9M17). The axis F1 designates the 1H-NMR whereas F2 belongs to 13C-NMR. The small size of heterogeneities was observed in 2D WISE spectrum. The wider peaks along F1-axis reveal the presence of hard segments in the system. The widest peak belongs to methyl (-CH₃), at around 15 ppm from butyl acrylate. However, the narrowest peak was observed at 177 ppm corresponding to carbonyl (-C=O) groups. Peaks for carbonyl (-C=O) groups did not show a significant motional averaging or fast relaxation for 1H-NMR width. Motion contrast was observed by the difference in width of 1H-NMR for the MAA peak at 45 ppm and the HEMA peak at 65 ppm, even though theoretical glass transition temperatures of core and shell are very close. The 1H-NMR linewidth for HEMA was narrower than 1H-NMR linewidth for MAA since the shell of the latex was harder. However, this motion contrast was lost when the mixing time was increased to 1000 μs as shown in Fig. 6.13. The narrow HEMA peak broadened and equilibrated with the MAA peak indicating that dynamic heterogeneity of the system decreased.
Figure 6.12. 2D WISE NMR spectrum of core-shell latex, H9M17, with a core-shell latex ratio 1/1 when the mixing time was 100 μs.

Figure 6.13. 2D WISE NMR spectrum of core-shell latex H9M17, with a core-shell latex ratio 1/1 when the mixing time was 1000 μs.
A stacked plot of $^{13}$C-NMR of core-shell latex for H9M17 as a function of mixing time is shown in Fig. 6.14. At a higher relaxation time, the intensity of peaks at 13.4 ppm belongs to –CH$_3$ in butyl acrylate increased. Other peaks can be assigned to functional groups in polymer backbone as followed: methyl (-CH$_3$) in methacrylates at 17-21 ppm, quaternary carbon (C$_\alpha$) in MMA and MAA at 45 ppm, methoxy (-OCH$_3$) in MMA at 51, methylene carbon (-CH$_2$-) from polymer backbone at 53 ppm, quaternary carbon (C$_\alpha$) in HEMA at 65 ppm, carbonyl carbon at 175 ppm. No motion contrast was observed for the core and shell due to their close glass transition temperatures. The spin-latex relaxation time was measured as 0.71 s for -CH$_3$ of butyl acrylate, 1.19 s for quaternary carbon (C$_\alpha$) in HEMA, 0.80 s for carbonyl carbon at 175 ppm, 0.96 s for methylene carbon (-CH$_2$-) from polymer backbone at 53 ppm, 0.74 s for quaternary carbon (C$_\alpha$) in MMA and MAA at 45 ppm. This result suggested that hard segments such as α-transition in HEMA had longer relaxation time whereas methyl groups in butyl acrylate showed the shortest relaxation time.

Figure 6.14. Stacked plot of 13C-NMR spectra of core-shell latex, H9M17, with a core-shell latex ratio 1/1 as a function of relaxation time.
6.2.6 Transmission Electron Microscopy (TEM) Analysis

The morphology between core and shell of core-shell latexes was observed by TEM analysis. Figure 6.15 shows the morphology of particles and contrast between core and shell of the core-shell latexes after staining the core with benzyl methacrylate. The darkness of the core is an indication of the inter-diffusion of core and shell. As the inter-diffusion of core into shell increases, the darkness of the core supposedly decreases. The lowest darkness in the core was observed for the latex (H9M17). This observation was in agreement with the calculation of the highest diffused phase determined by DSC. The highest contrast was observed in H25M6, as expected from the calculation of diffused phase by DSC. The latex (H9M6) also showed core-shell morphology. However, very thin shell was observed in H9M6. A gradient morphology where the darker core gradually turned into the lighter shell was observed in H25M17.
6.3 Discussion

Polymerization kinetics is important to optimize the particle nucleation and growth of particles in emulsion polymerization. Several studies have been reported on kinetics of emulsion polymerization. Polymerization kinetics is one of the factors determining the particle morphology. In this study, the effect of hydrophilicity of core and shell was studied on particle morphology and polymerization kinetics. The approach was to prepare core and shell compositions with low and high amounts of monomers.
Core with 9 and 25 wt. % HEMA and shell with 6 and 17 wt. % MAA were copolymerized in different combinations such as H9M6, H9M17, H25M6, and H25M17.

The effect of monomer composition on kinetics and morphology control of latex particles has been extensively studied. Li et al. prepared polyurethane (PU)/poly (butyl methacrylate) (PBMA) hybrids via miniemulsion process. They obtained a faster polymerization rate when PU was used as seed since a larger surface area (more polymerization loci) was provided by hydrophilic smaller particles than by hydrophobic PBMA droplets.209 As the hydrophilicity of monomer composition increased, the rate of polymerization decreased due to lower entry of hydrophilic oligoradicals into particles.210 This result was not in agreement with our study. The maximum instantaneous rate of polymerization increased when the concentration of MAA increased during shell formation. However, in the present study, the nucleation period was prolonged for the higher concentration of MAA, which was in agreement with previous study.210

The effect of the HEMA fraction on polymerization kinetics was significant. During the synthesis of core phase, a higher rate of polymerization was observed as the fraction of HEMA increased. As the amount of HEMA increased, homogeneous nucleation occurred extensively resulting in limited coagulation as proposed by previous report.211 This led to fewer particles with larger size, while the larger particles had more radicals. Therefore, the instantaneous rate of polymerization increased.

The fraction of MAA also influenced polymerization kinetics. As the fraction of MAA increased, the instantaneous rate of polymerization also increased. The rate of polymerization for higher MAA fraction surpassed the rate for lower fraction of MAA after 45 min. This result was in agreement with the previous report17 up to first 45 min
during shell formation, where the lower rate of polymerization was attributed to radical desorption from particles in the presence of MAA. The number of particles increased in H9M6 and H9M17 for the first 120 min. This could be attributed to two factors. Probably, the concentration of the surfactant was still above the critical micelle concentration (CMC). Additionally, the surface area of core particles was not sufficient to capture oligoradicals in the aqueous phase. Sajjadi proposed a mechanism for the particle formation in interval III in the presence of seeds. The particle formation in interval III involved the monomer diffusion from monomer-swollen particles to the new particles. This caused the depletion of emulsifiers and prolonged the nucleation period. This was followed by the increase in the number of particles.

The rate of polymerization was almost twice as high when a pre-emulsion addition was performed. This result was in agreement with previous report in which pre-emulsion feeding yielded faster instantaneous conversion than neat monomer addition. This was attributed to higher mass transfer rates due to larger interfacial area of monomer droplets. However, there was no difference in particle size as the monomer addition procedure was changed. As opposed to this study, there were fewer particles formed when a pre-emulsion was fed into reactor in this study.

The hydrophilicity of comonomers played an important role in development of morphology. As the hydrophilicity of either core or shell composition increased, interfacial tension between core and shell also increased. This is the parameter that influences which polymer migrates to the outermost layer of particle and final particle morphology. But core-shell morphology was observed for all latex samples in this study observed by TEM (see Figure 6.15). A gradient morphology was observed where an
interface was observed between core and shell phases. This could be attributed to the almost identical solubility parameters and Tg of the core and shell phases. Interestingly, Kan et al. observed a deviation from perfect core-shell morphology (polyacrylate/polysiloxane) when polyacrylate core was not crosslinked. The interpenetration of core and shell was observed even though there is a big difference in the solubility and Tg of core and shell phases. The highest phase separation was observed for the latex (H25M6) on TEM (see Figure 6.15). The latex (H25M6) showed the highest interfacial tension (see Table 6.3). This was a similar observation to a previous report in which the highest phase separation was observed when the interfacial tension was increased between polymer 1 (PS) and polymer 2 (PMMA).

6.4 Conclusions

Latexes with varied concentrations of HEMA and MAA were synthesized. The effect of the concentration of HEMA and MAA on polymerization kinetics and particle morphology was studied. Polymerizations were run under monomer-starved conditions in which the polymer amount in particles was estimated over 90%. The number of particles increased in some cases even though seeded emulsion polymerization was conducted. The instantaneous rate of polymerization for the shell was lower than that of the core polymerization. Polymerization with pre-emulsion feeding showed a higher instantaneous rate of polymerization than the polymerization with neat monomer addition. Interfacial surface tension increased when the polarity difference between core and shell increased. The extent of diffused phase decreased when the polarity between core and shell was higher (see Table 6.3). The motion contrast between hard and soft segments was
observed for H9M17 when the mixing time was shorter (100 µs) in 2D WISE NMR analysis. In the TEM analysis, particles having a gradient phase were observed.
7.1 Introduction

Thermosetting latexes have the advantages of higher solvent, moisture, abrasion resistance, and cohesive energy density. Shear and tensile moduli of thermosetting polymers are also higher than those of thermoplastic polymers over thermoplastic latexes. However, elasticity of polymer decreases as the extent of crosslinking increases. High concentration of crosslinkable functional groups in polymer chains leads to a reduction of the shelf life of latex. Therefore, crosslinking has to be controlled during film formation. Otherwise, the film might have cracks and brittle character. Additionally, the film might form some craters. In order to have effectively crosslinked film, functional groups must have regular spacing along the chain to enhance collision rates of functional groups. Thus, polymerization with gradual feeding might solve this problem. Curing at higher temperature than minimum film formation temperature (MFFT) is also important to have coherent and strong film. Extent of crosslinking is enhanced at temperature higher than MFFT. Catalysts are typically used to aid in crosslinking. To trigger crosslinking after application, volatile ammonium salts can be employed. Several types of crosslinker
have been proposed in the literature, including melamine, aziridine, zinc, polycarbodiimide, oxirane, and oxazoline.

Cycloaliphatic diepoxide has been used effectively to crosslink carboxyl and hydroxyl functional latexes. Crosslinking of hydroxyl functionality required acid catalyst whereas crosslinking of carboxylic acid functionality was completed without need of any catalyst. As concentration of carboxylic acid functionality increased in latex composition, hardness and gel content also increased. Additionally, films crosslinked through carboxylic acid functionality had higher water resistance than the film crosslinked through hydroxyl functionality. In addition to improvement of water resistance, pencil hardness, solvent resistance, and adhesion of the coatings significantly improved after crosslinking with cycloaliphatic diepoxide. Reactivity of cycloaliphatic diepoxides with carboxylic acid and hydroxyl functionality increased in acidic medium due to the lower activation energy of epoxy ring. Carboxylic acids showed higher reactivity towards model compound, styrene oxides, than towards alcohols.

Polyisocyanates such as uretdiones and isocyanurates can be used as formaldehyde-free crosslinkers for acrylic polymers. Several two-pot (2K) systems were prepared with polyisocyanates and acrylic polymers to improve the physical properties of coatings. Polymeric polyisocyanates were used as crosslinker for wood coatings to improve strength and water resistance. Abrasion resistance of latex film with hydroxyl groups increased when HDI isocyanurate was used as crosslinker. Hydrophilically modified HDI crosslinkers resulted in coatings with good clarity. Two-pot (2K) waterborne transparent coatings were formulated with HDI isocyanates. Isocyanurate crosslinker improved water, solvent and abrasion resistance of acrylic-
Isocyanates showed better reactivity with latexes than solvent-borne coatings due to acceleration of carboxylic acids in water. \(^{225}\)

Aqueous dispersions with carboxylic acid can also be formulated with polycarbodiimides to be used in roof, hardboard, coil and plastic coatings. \(^{226}\) Urea or N-acylurea is obtained when polycarbodiimides react with carboxylic acids. \(^{227}\) There is no by-product after crosslinking reactions to contaminate coating and contribute VOC. Carboxylic acid functionalized acrylic resin was crosslinked with polycarbodiimide to improve peel strength. \(^{228}\) Crosslinking between polycarbodiimide and carboxylic acid not only increased crosslinking density, but also increased the moisture resistance of the coating. Tensile properties and solvent resistance of coatings increased after polycarbodiimide crosslinking. \(^{229}\)

One pack (1K) stable self-crosslinkable latex can be prepared via zinc crosslinkers. Zinc crosslinking is based on reaction between \(\text{Zn}^{2+}\) ions with pendant carboxylate groups in latex particles upon removal of ammonia. Curing can be fulfilled at room temperatures limited by the evaporation rate of ammonia, resulting in hard and water resistance films. Tough and continuous film was developed for floor polish applications. \(^{42}\) Zinc ammonium carbonate was used for crosslinker of styrene-maleic anhydride latexes for thermally stable inks. \(^{230}\) In addition, corrosion-resistant coatings were developed by employing zinc ammonium carbonate as crosslinker for latexes onto metallic substrates. \(^{231}\)

The molecular weight of network is increased after crosslinking. The solid content of latex formulation can be increased by virtue of keeping the molecular weight
of polymer chains to a minimum. Melamine-formaldehyde (MF) resin is used in the automotive industry as crosslinker for acrylic or polyester binders. Melamine-formaldehyde (MF) is synthesized through condensation of melamine, formaldehyde and alcohol. Latex formulation including melamine-formaldehyde (MF) resin has been utilized as can coatings. Inclusion of MF resin in latex formulation increased the coating speed from 400 cans per minute to 1200 cans per minute due to faster curing. Process resistance, such as temperature and pH, was also enhanced after melamine-formaldehyde curing. Curing of melamine-formaldehyde resin also improved water and organic solvent resistance of coating for hardboard clear coating applications. When water-soluble MF resin was used, several properties of latex film were enhanced, such as low blister, better gloss as opposed to that produced by other crosslinkers, and films with no mottling.

In this study, composite latexes with varying concentrations of hydrophilic functional monomers (HEMA, MAA) and type of surfactant were synthesized. Only core with hydroxyl functionality, shell with carboxylic acid functionality, and core-shell of these latexes were respectively crosslinked with melamine-formaldehyde (hexamethoxymethyl melamine), zinc ammonium carbonate, cycloaliphatic diepoxide (3, 4-epoxycyclohexyl methyl-3,4-epoxycyclohexane carboxylate), N,N'-dicyclohexyl-carbodiimide, and HDI isocyanurate (Desmodur N3300A). The mechanical properties of thermosetting latex films were evaluated by tensile testing, dynamic mechanical properties, pull-off adhesion, pencil hardness, impact resistance, gloss of crosslinked latex films, and cross-hatch adhesion for each system.
7.2 Results

Varied crosslinking mechanisms of latexes have been proposed by several authors. However, quantitative comparison of mechanical properties of thermoset latexes has not been reported. Therefore, the amount of functional monomers (HEMA, MAA) and type of crosslinker were investigated with respect to the mechanical properties of thermoset latex films. A 2-level factorial design of experiment as a function of HEMA, MAA and type of surfactant (Tergitol XJ, Triton X-200) was performed. Core, shell or both core-shell was crosslinked with MF, zinc, N,N'-dicyclohexylcarbodiimide, HDI isocyanurate and cycloaliphatic diepoxide. These crosslinkers were chosen according to the reactivity of functional groups with hydroxyl and carboxylic functionalities. Additionally, crosslinkers used in this study can react selectively or non-selectively with hydroxyl and carboxylic groups.

Cycloaliphatic diepoxides are frequently used as crosslinkers in coating formulations for carboxylic and hydroxyl functionalities.236 A schematic representation of crosslinking reaction of cycloaliphatic diepoxide is shown in Scheme 7.1. Isocyanurates can be used to crosslink functional groups such as hydroxyl, carboxylic acid, and amine. A schematic representation of the crosslinking reaction of HDI isocyanurate is shown in Scheme 7.2. Zinc salts are effective crosslinkers for carboxylic-functionalized latexes due to Coulombic interaction. Curing of carboxylic-functionalized polymer chains with zinc ammonium carbonate occurs at the interface of particles as shown in Scheme 7.3. Crosslinking reaction between N, N'-dicyclohexylcarbodiimide and carboxylic groups in latex shell is shown in Scheme 7.4. Melamine-formaldehyde crosslinkers are used for hydroxyl-functionalized water-borne polymers. Melamine-formaldehyde resin, such as
hexamethoxymethylmelamine (HMMM), is a significant plasticizer that improves polymer chain inter-diffusion and gel fraction. A schematic representation of the crosslinking reaction of melamine-formaldehyde (MF) resin is shown in Scheme 7.5.

Scheme 7.1. Schematic representation of curing mechanism of hydroxyl and carboxylic acid functionalized latex particles with cycloaliphatic diepoxide.
Scheme 7.2. Schematic representation of curing mechanism of hydroxyl and carboxylic acid functionalized latex particles with HDI isocyanurate.
Scheme 7.3. Schematic representation of curing mechanism of carboxylic acid functionalized latex particles with zinc ammonium carbonate.
Scheme 7.4. Schematic representation of curing mechanism of carboxylic acid functionalized latex particles with N, N'-dicyclohexylcarbodiimide.
Scheme 7.5. Schematic representation of curing mechanism of hydroxyl functionalized latex particles with MF resin.

7.2.1 Dynamic Mechanical Analysis

Figure 7.1 shows the comparison of storage modulus for the thermoplastic (non-crosslinked) and the thermoset (crosslinked) latex films. Storage modulus was the highest when latex particles were crosslinked with MF resin. Latexes synthesized with anionic surfactant (Triton X-200) showed a higher storage modulus than when the nonionic surfactant (Tergitol XJ) was used. Zinc crosslinking was not as effective as MF crosslinking in terms of storage modulus. The lowest storage modulus was observed in latex films crosslinked with carbodiimide. This implied that the carbodiimide crosslinker was not as an effective crosslinker as MF resins. The crosslink density of thermoplastic and thermoset latex films is shown in Fig. 7.2. The crosslink density showed a similar trend to storage modulus. As storage modulus decreased, crosslink density also decreased.
The latexes synthesized with Triton X-200 surfactant showed a higher storage modulus and crosslink density than the latexes with Tergitol XJ. This can be attributed to smaller particle size and bimodal particle size distribution of latexes synthesized with Triton X-200. Figure 7.3 shows the storage modulus of non-crosslinked and crosslinked films at room temperature where MF crosslinked films mostly showed lower modulus compared to films crosslinked with HDI isocyanurate and zinc.

![Figure 7.1. Storage modulus films (rubbery plateau) from non-crosslinked and crosslinked latexes with cycloaliphatic diepoxide, MF, zinc, carbodiimide and HDI isocyanurate.](image-url)
Figure 7.2. Crosslink density of films from non-crosslinked and crosslinked latexes with cycloaliphatic diepoxide, MF, zinc, carbodiimide and HDI isocyanurate.

Figure 7.3. Storage modulus of films (at room temperature) from non-crosslinked and crosslinked latexes with cycloaliphatic diepoxide, MF, zinc, carbodiimide and HDI isocyanurate.
The storage modulus of MF crosslinked films was analyzed in response surface methodology. Figure 7.4 shows the response surface of storage modulus when melamine-formaldehyde (MF) resin was used as crosslinker. The storage modulus of the crosslinked films increased with the increase in concentration of HEMA. However, the storage modulus was almost independent of the concentration of MAA. This was expected since MF resin crosslinked predominantly with hydroxyl groups (HEMA) and the reaction with the acid was sluggish at best. Storage modulus was almost two-times higher when the latexes prepared with Triton X-200 were used. This could be attributed to smaller particle size latexes obtained when Triton X-200 was used as surfactant.

Figure 7.4. Response surface graphs of storage modulus of MF crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
Table 7.1 shows the tan δ of non-crosslinked and crosslinked latex films. Concerning the thermoplastic (non-crosslinked), most of the thermoset latex films crosslinked with carbodiimide and MF resin showed two-transitions. This indicated a distinct phase separation. This could be attributed to varying compositions at the latex interfaces creating a boundary between domains.\textsuperscript{116} When zinc ammonium carbonate was used as crosslinker, a single glass transition (Tg) was observed for six of the films. This observation indicated zinc was a better crosslinker than carbodiimide and MF resin since more homogenous crosslinking was obtained resulting in disappearance of the secondary transition. A similar result was obtained for the films crosslinked with HDI isocyanurate. Cycloaliphatic diepoxide also had single Tg for six of the films. There was a slight increase in Tg crosslinked with cycloaliphatic diepoxide relative to Tg for non-crosslinked film due to partial crosslinking of hydroxyl and carboxylic acid groups. The height and width of tan δ represents the homogeneity and crosslink density of the polymer film. The height of tan δ was almost one for the non-crosslinked latex films. When the cycloaliphatic diepoxide was used as crosslinker, maximum tan δ increased for some samples. This could be attributed to improvement of the homogeneity of the film. When other crosslinkers were used, the α-transition was significantly lower due to the broader molecular weight distribution.\textsuperscript{116} The narrowest width of α-transition was observed when carbodiimide was used as a crosslinker. This could be attributed to narrow molecular weight distribution of polymers between crosslink points.\textsuperscript{116} Other crosslinkers yielded a very broad molecular weight distribution between crosslink junctions.
Table 7.1. Glass transition temperatures obtained from DMA.

<table>
<thead>
<tr>
<th>Film</th>
<th>H18M12 tergitol</th>
<th>H18M17 triton</th>
<th>H25M12 tergitol</th>
<th>H25M17 triton</th>
<th>H31M12 tergitol</th>
<th>H31M17 triton</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-crosslinked</td>
<td>21.6</td>
<td>44.9</td>
<td>22.3</td>
<td>43.8</td>
<td>3.8</td>
<td>-9.7</td>
<td>-5.8</td>
</tr>
<tr>
<td>Cyclo diepoxide</td>
<td>7.9</td>
<td>4.3</td>
<td>17.6</td>
<td>37.9</td>
<td>29.1</td>
<td>46.3</td>
<td>-5.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>-4.8</td>
<td>86.2</td>
<td>47.6</td>
<td>104.9</td>
<td>60.7</td>
<td>92.1</td>
<td>62.4</td>
</tr>
<tr>
<td>MF</td>
<td>1.2</td>
<td>-7.9</td>
<td>-10.6</td>
<td>37.8</td>
<td>45.2</td>
<td>4.7</td>
<td>3.6</td>
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<tr>
<td>Carbdodiimide</td>
<td>48.2</td>
<td>64.4</td>
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<td>72.2</td>
<td>46.8</td>
<td>68.7</td>
<td>35.1</td>
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<td>HDI isocyanurate</td>
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<td>93.9</td>
<td>65.5</td>
<td>80.4</td>
<td>83.9</td>
<td>67.6</td>
<td>60.7</td>
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<table>
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<tr>
<th>Film</th>
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<th>H18M17 triton</th>
<th>H25M12 tergitol</th>
<th>H25M17 triton</th>
<th>H31M12 tergitol</th>
<th>H31M17 triton</th>
<th>Tg (°C)</th>
</tr>
</thead>
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<tr>
<td>Non-crosslinked</td>
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<td>153.9</td>
<td>112.4</td>
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<td>140.8</td>
<td>141.4</td>
<td>144.8</td>
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<td>Cyclo diepoxide</td>
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<td>-</td>
<td>157.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Zinc</td>
<td>198.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MF</td>
<td>198.3</td>
<td>200.1</td>
<td>215.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>196.1</td>
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<td>Carbdodiimide</td>
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<td>160.4</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>107.2</td>
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<table>
<thead>
<tr>
<th>Film</th>
<th>H18M12 tergitol</th>
<th>H18M17 triton</th>
<th>H25M12 tergitol</th>
<th>H25M17 triton</th>
<th>H31M12 tergitol</th>
<th>H31M17 triton</th>
<th>(\tan\delta) Width (°C) (width for the (\alpha)-transition)</th>
</tr>
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<tr>
<td>Non-crosslinked</td>
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<td>235.4</td>
<td>215.8</td>
<td>219.5</td>
<td>199.5</td>
<td>221.2</td>
<td>208.4</td>
</tr>
<tr>
<td>Cyclo diepoxide</td>
<td>196.8</td>
<td>356.6</td>
<td>316.5</td>
<td>181.7</td>
<td>288.9</td>
<td>264.7</td>
<td>356.4</td>
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<tr>
<td>Zinc</td>
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<td>223.8</td>
<td>206.4</td>
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<td>219.4</td>
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<tr>
<td>MF</td>
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<td>143.8</td>
<td>139.4</td>
<td>277.2</td>
<td>184.4</td>
</tr>
<tr>
<td>Carbdodiimide</td>
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<td>159.4</td>
<td>120.3</td>
<td>90.9</td>
<td>110.3</td>
<td>144.6</td>
</tr>
<tr>
<td>HDI isocyanurate</td>
<td>216.2</td>
<td>205.2</td>
<td>206.8</td>
<td>214.9</td>
<td>214.2</td>
<td>212.5</td>
<td>213.2</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Film</th>
<th>H18M12 tergitol</th>
<th>H18M17 triton</th>
<th>H25M12 tergitol</th>
<th>H25M17 triton</th>
<th>H31M12 tergitol</th>
<th>H31M17 triton</th>
<th>(\tan\delta) Height (Maximum) °C</th>
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<tr>
<td>Non-crosslinked</td>
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<td>0.95</td>
<td>0.77</td>
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<td>0.79</td>
<td>0.92</td>
<td>0.95</td>
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<tr>
<td>Cyclo diepoxide</td>
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<td>1.1</td>
<td>1.2</td>
<td>0.72</td>
<td>0.89</td>
<td>0.78</td>
<td>1.1</td>
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<tr>
<td>Zinc</td>
<td>0.49</td>
<td>0.37</td>
<td>0.40</td>
<td>0.39</td>
<td>0.40</td>
<td>0.30</td>
<td>0.53</td>
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<tr>
<td>MF</td>
<td>0.51</td>
<td>0.75</td>
<td>0.35</td>
<td>0.53</td>
<td>0.43</td>
<td>0.78</td>
<td>0.37</td>
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<tr>
<td>Carbdodiimide</td>
<td>0.80</td>
<td>0.78</td>
<td>0.79</td>
<td>0.71</td>
<td>0.81</td>
<td>0.94</td>
<td>0.65</td>
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<tr>
<td>HDI isocyanurate</td>
<td>0.82</td>
<td>0.51</td>
<td>0.66</td>
<td>0.44</td>
<td>0.49</td>
<td>0.45</td>
<td>0.54</td>
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</tbody>
</table>

7.2.2 Tensile Testing

Figure 7.5 shows the analysis of the tensile properties of non-crosslinked and crosslinked films. The highest tensile modulus was observed in thermoset films crosslinked with carbdodiimide. This was probably due to extra hardness by cyclohexyl groups on N, N'-dicyclohexylcarbdodiimide. Latexes crosslinked with HDI isocyanurate also showed a very high modulus due to tri-functionality of HDI isocyanurate and
flexible isocyanate groups (-NCO) on primary carbons. The MF crosslinked films exhibited very high modulus when the HEMA concentration increased from 18 wt% to 25 wt%. Some of the zinc crosslinked films had higher modulus than the films crosslinked with cycloaliphatic diepoxide and MF resin. However, an increase in the amount of HEMA and MAA led to brittle behavior in zinc crosslinked films. Cycloaliphatic diepoxide crosslinked thermoset films mostly showed lower modulus due to the plasticizing effect of unreacted cycloaliphatic diepoxide in the medium. Young’s modulus of crosslinked films was analyzed in response surface methodology. Figure 7.6 shows response surface graphs for Young’s modulus of zinc crosslinked latex films. Young’s modulus increased when the amount of HEMA and MAA increased. Glassy behavior gradually increased when the amount of HEMA and MAA increased. Therefore, the films were stiffer but more brittle. The type of surfactant had no significant effect on Young’s modulus.
Figure 7.5. Young’s modulus of crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate.

Figure 7.6. Response surface graphs of Young’s modulus of zinc crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
Tensile strength of the latexes crosslinked with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate is shown in Fig. 7.7. After crosslinking, there was an improvement in tensile strength except in films crosslinked with cycloaliphatic diepoxide. The latex films (H18M17) crosslinked with HDI isocyanurate showed the highest tensile strength for some films. Zinc crosslinked latexes (H25M17) showed very small tensile strength (~ 0.1 MPa) due to their higher concentration of electrostatic interactions (increase in brittle nature). The very low tensile strength (~ 2 MPa) of latexes crosslinked with cycloaliphatic diepoxide could be attributed to some plasticization by unreacted cycloaliphatic diepoxide and also to poor miscibility of cycloaliphatic diepoxide and acrylic polymer chains. Tensile strength of crosslinked films was analyzed in response surface methodology. Figure 7.8 shows response surface graphs for tensile strength of MF crosslinked latex films. The highest tensile strength (7.20 MPa) was observed when the amount of HEMA and MAA was maximized. The tensile strength of MF crosslinked film was dependent on the concentration of HEMA. Tensile strength of crosslinked films increased as the concentration of functional monomers (HEMA, MAA) increased. The tensile strength was also higher when Triton X-200 was used as surfactant.
Figure 7.7. Tensile strength of crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate.

Figure 7.8. Response surface graphs of tensile strength of MF crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
Elongation % for non-crosslinked and crosslinked latex films was determined. Figure 7.9 shows elongation % for the crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide or HDI isocyanurate. Cycloaliphatic diepoxide and MF crosslinked films showed high elongation % (over 400%) due to low crosslink density and the plasticizing effect of crosslinkers. On the contrary, films crosslinked with zinc showed smaller elongation % due to brittle character of film. Carbodiimide crosslinked films showed a better elongation % (~150%) than the zinc (30%) or HDI isocyanurate (~100%) crosslinked films. Elongation % of MF crosslinked films was analyzed in response surface methodology. Figure 7.10 shows response surface graphs for elongation % of latex films crosslinked with MF resin. Elongation % increased as the amount of HEMA decreased. This observation was more significant when Tergitol XJ was used as surfactant. However, elongation % was much higher when Triton X-200 was used. Amount of MAA did not have a much of an effect on the response of elongation %.
Figure 7.9. Elongation % of crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate.

Figure 7.10. Response surface graphs of elongation % of MF crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
Toughness of crosslinked films is shown in Fig. 7.11. Toughness of crosslinked films with cycloaliphatic diepoxide was comparable to that of MF crosslinked films when the amount of functional groups was maximized. Additionally, the toughness of the films for all latexes was higher when MF resin was used due to plasticization by MF resin. This improved the interdiffusion and therefore toughness. Toughness of zinc crosslinked films decreased as the amount of MAA increased and films displayed brittle behavior. A similar trend was observed in latexes crosslinked with isocyanates. No correlation was found between toughness and surfactant type. Toughness of cycloaliphatic diepoxide crosslinked films was analyzed in response surface methodology. Figure 7.12 shows response surface graphs of toughness of the latex films when cycloaliphatic diepoxide was used as crosslinker. Toughness of films crosslinked with cycloaliphatic diepoxide increased as the concentration of HEMA increased when Tergitol XJ was used as surfactant. However, toughness increased with increase in the concentration of MAA when Triton X-200 was used as surfactant. When Triton X-200 was used as surfactant, the toughness of films crosslinked with cycloaliphatic diepoxide was 3 times higher than latexes with Tergitol XJ, probably due to the bimodal particle size distribution and relatively smaller particle size.
Figure 7.11. Toughness of crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate.

Figure 7.12. Response surface graphs of toughness of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
7.2.3 Cross-hatch adhesion, Pencil Hardness and MEK Rubs

Cross-hatch adhesion and pencil hardness of crosslinked hydroxyl and carboxylic functional latexes are shown in Table 7.2. Crosslinked and non-crosslinked latexes did not show any significant flake-off except zinc crosslinked latexes in a cross-hatch adhesion test. Some of zinc crosslinked films were very brittle since complete film formation was inhibited by the crosslinking of shell by the zinc crosslinker. Cycloaliphatic diepoxide crosslinked films exhibited higher pencil hardness than other films due to complete crosslinking of core and shell. Zinc crosslinked films displayed very poor pencil hardness since rapid gelation in zinc crosslinked latexes stopped polymer chain diffusion before it was completed. As the amount of functional monomers increased, pencil hardness of coatings increased in coatings cured with MF resin. However, the opposite was observed in coatings cured with cycloaliphatic diepoxide since there was possibly unreacted cycloaliphatic diepoxide remaining in the coating. Very good pencil hardness values were obtained in thermoset latex films crosslinked with N,N'-dicyclohexylcarbodiimide. Even though HDI isocyanurate crosslinked latex films gave smaller pencil hardness than films crosslinked with N,N'-dicyclohexylcarbodiimide, pencil hardness was still higher than in the non-crosslinked latex films.

A strong solvent such as methyl ethyl ketone (MEK) provides a fast way to measure the chemical resistance of a coating. Methyl ethyl ketone resistance was studied for non-crosslinked and crosslinked latex films. After films were crosslinked, MEK resistance increased as shown in Table 7.3. This result indicated that curing of latex films had occurred. Cycloaliphatic diepoxide and MF resin showed a better MEK resistance than zinc crosslinked films. Carbodiimide and HDI isocyanurate crosslinkers in
formulation showed very fast drying due to fast network formation. However, carbodiimide and HDI isocyanurate crosslinked thermoset films showed very poor MEK resistance. This can be attributed to poor cohesive strength development in thermoset films due to slow polymer chain inter-diffusion in the presence of branched external crosslinkers (N, N'-dicyclohexylcarbodiimide, HDI isocyanurate). Additionally, very high network molecular weight can also cause poor MEK resistance. No correlation was found between type of surfactant and MEK resistance.

Table 7.2. Cross-hatch adhesion and pencil hardness properties of non-crosslinked and crosslinked latex films.

<table>
<thead>
<tr>
<th></th>
<th>Cross-hatch adhesion</th>
<th>Pencil Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-cros</td>
<td>Epoxide</td>
</tr>
<tr>
<td></td>
<td>linked</td>
<td></td>
</tr>
<tr>
<td>H18M12-tergiol</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>H18M17-trition</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>H25M12-trition</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>H25M17-tergiol</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>H25M17-trition</td>
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</tr>
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</tr>
<tr>
<td>H38M12-tergiol</td>
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Table 7.3. Methyl ethyl ketone (MEK) resistance of non-crosslinked and crosslinked latex films.

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</tr>
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<tr>
<td>H25M12-triton</td>
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<tr>
<td>H25M17-tergitol</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>H18M12-triton</td>
<td>60</td>
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</tbody>
</table>

7.2.4 Impact test

Figure 7.13 shows the impact resistance of non-crosslinked and crosslinked latex films. Films crosslinked with cycloaliphatic diepoxide showed higher impact resistance. Some of zinc crosslinked films had very low impact resistance. However, most of the films had comparable impact resistance. Increase in amount of functional groups did not cause any significant difference as to impact resistance in cycloaliphatic diepoxide and MF crosslinked latex films, but lower impact resistance was obtained for zinc crosslinked films when the amount of functional groups increased. Impact resistance of latex films crosslinked with zinc was statistically analyzed to screen response in design space. Figure 7.14 shows response surface graphs for forward impact resistance of latex films crosslinked with zinc. Forward impact resistance increased when the amount of MAA decreased. However, forward impact test increased or decreased by the change of surfactant. The minimum forward impact resistance observed for the film was higher when Triton X-200 was used as surfactant.
Figure 7.13. Impact resistance of non-crosslinked and crosslinked latex films with cyclo-epoxide, zinc, MF, carbodiimide and HDI isocyanurate.
7.2.5 Pull-off Adhesion

A comparison of pull-off adhesion for the non-crosslinked and crosslinked films is shown in Fig. 7.15. Cycloaliphatic diepoxide and MF crosslinked resins had higher pull-off adhesion than non-crosslinked latex films. This can be attributed not only to crosslinking but also to the plasticizing effects of these crosslinkers. As the amount of functional groups increased, pull-off adhesion decreased due to blocked polymer chain diffusion. Development of high internal stress, due to limited diffusion of polymer chains with zinc crosslinker, caused very low adhesion strength and brittle failure. Lower pull-off adhesion values were observed for thermoset latex films crosslinked with carbodiimide and HDI isocyanurate. Very low pull-off adhesion values for thermoset latex films crosslinked with carbodiimide and HDI isocyanurate can be attributed to weak
adhesion interface between coating and substrate. Pull-off adhesion force of non-crosslinked and crosslinked films was statistically analyzed to screen response in design space. Figure 7.16 shows response surface graphs for pull-off adhesion of latex films crosslinked with cycloaliphatic diepoxide. Pull-off adhesion values decreased as the amount of MAA increased. Therefore, a smaller amount of crosslink density in crosslinked films was more desired to increase pull-off adhesion. Cycloaliphatic diepoxide (1 eq. mole) was used for 2 moles of functional groups (HEMA, MAA). When the added amount of cycloaliphatic diepoxide is very high, an unreacted amount of cycloaliphatic diepoxide remains in film. This plasticized coating and resulted in softer films.\(^{239}\)

![Figure 7.15. Pull-off adhesion force of non-crosslinked and crosslinked latex films with cyclo-aliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate.](image-url)
Figure 7.16. Response surface graphs of pull-off adhesion of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

7.2.6 Gloss

Figure 7.17 shows gloss % measured at 20° for the non-crosslinked and crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate. Cycloaliphatic diepoxide crosslinked films gave comparable or better gloss % at 20° than other thermoset latex films. However, crosslinking with zinc and MF resin was so fast that polymer chain diffusion across particle interfaces was inhibited. Much less gloss % was obtained for latex films crosslinked with carbodiimide and HDI isocyanurate. This phenomenon was clearly observed in latexes having a high amount of functional monomers such as H25M17-tri, probably due to rough surfaces. Latexes with anionic surfactant (Triton X-200) generally gave a better gloss since all latexes with Triton X-200 had bimodal particle size distribution. Bimodal particle size distribution
induced smooth film formation. Gloss % of non-crosslinked and crosslinked films was statistically analyzed to screen response in design space. Figure 7.18 shows response surface graphs for gloss % of latex films crosslinked with cycloaliphatic diepoxide. Gloss is mainly related to the extent of crosslinking since film becomes smoother. Gloss % increased as the amount of HEMA decreased due to decrease in the roughness of film. On the other hand, gloss % was maximized when both HEMA and MAA concentration was maximized or minimized. The nonionic surfactant (Tergitol XJ) showed a higher gloss % than anionic surfactant (Triton X-200).

Figure 7.17. Gloss % (20°) of non-crosslinked and crosslinked latex films with cycloaliphatic diepoxide, zinc, MF, carbodiimide and HDI isocyanurate.
7.3 Discussion

Optimization of mechanical properties of thermoset films is important for different applications. It was assumed that increase in functional monomer concentration and change in type of crosslinker affect the mechanical characteristics of thermoset latex films. Higher crosslinking density is needed when stiff latex films are required. Crosslink density can be adjusted by copolymerizing more functional monomers. Wu et al. found an increase in the functionality of the latexes resulted in thermoset films with enhanced water resistance, solvent resistance, and film hardness of the coatings. Teng and Soucek studied mode of addition of hydroxyl functionality to latex particles. Latex having hydroxyl functionality in core gave the highest Tukon hardness and tensile modulus due to better chain interdiffusion and developed mechanical properties. This observation was similar to the results of this study. When MF resin was used as
crosslinker, the mechanical properties improved significantly. Very high storage modulus, toughness, and elongation % was observed when latexes were crosslinked with MF resin.

Methacrylic acid (MAA) in shell has been previously reported as a barrier to chains which limits the extent of polymer chain interdiffusion. This result was in agreement with results in this study. When zinc ammonium carbonate was used as crosslinker, very poor Young’s modulus, toughness, and elongation % values were obtained compared to other crosslinkers in this study. However, latex films crosslinked with carbodiimide only by the shell showed better tensile properties than films crosslinked with zinc. From this observation, it can be concluded that every crosslinker had different effects on film even if it crosslinked the same phase, e.g. shell. Coulombic interactions resulted in coating with very poor mechanical properties.

Zinc salt crosslinked latexes showed brittle character and very poor adhesion to substrate due to fast crosslinking of zinc salt and limited chain inter-diffusion. This result was in agreement with a previous report in which ammonium zirconium carbonate was used as crosslinker. As the amount of ammonium zirconium carbonate increased, the adhesion of coating onto substrate decreased. In our study, poor inter-diffusion in latex film crosslinked with zinc was also confirmed by gloss % measurements where higher gloss % indicates better chain inter-diffusion and leveling off for latex particles. Gloss % of latex crosslinked with zinc salt was clearly lower than non-crosslinked and crosslinked thermoset latex films. Scheme 7.6 shows the difference between the rupture behavior of weak and tough thermoset latex films. In order to develop better mechanical properties and solvent resistance, the rate of polymer chain interdiffusion across interfaces has to be followed by the rate of crosslinking. Zinc crosslinked the polymer chains at the interfaces
and probably retarded chain interdiffusion across interfaces. This led to breakage through the interfaces of films and poor toughness. However, MF resins diffused into the core phase of latexes. Crosslinking reaction between hydroxyl functionality and MF resin was slower than polymer chain interdiffusion. Therefore, a higher extent of chain interdiffusion was more likely. The higher chain interdiffusion led to tougher films with no clear interfaces.

Scheme 7.6. Schematic representation of rupturing of polymer films crosslinked with (a) zinc. (b) MF resin under stress.

The improvement on the mechanical properties of the coatings depends not only on the reactivity between crosslinker and functional groups in the latex, but also on the solubility of crosslinker in water. As the solubility of crosslinker increases in aqueous phase, the miscibility of the two components (acrylic polymer and crosslinker) increases. The MF resin used in this study was water-soluble. This could be another reason why MF resin yielded very good mechanical properties beside the plasticizing effects. Latex films crosslinked with carbodiimide also yielded good toughness probably due to allowance of
better entanglement. This could be attributed to the reduction of columbic charge density as carbodiimide reacted with carboxylic acid functionalities. This effect also improved chain inter-diffusion. Zinc ammonium carbonate did not lead to the expected results as MF resin did. This might originate from the significant polarity of zinc ions that were only miscible in carboxylic acid domains. HDI isocyanurate has a close solubility parameter to that of acrylic resin, which improved the miscibility between crosslinker and polymer. This resulted in high Young’s modulus and tensile strength.

Statistical design of the mechanical and coating properties of crosslinked latex films was performed to have an insight of experimental variables. Some of the surface response graphs did not have enough signal due to the small, number of input data for each experiment. The very low signal to noise ratio observed in some of the experiments could also be because the variables did not have a significant effect on the response. This result was in agreement with this study. Some of the surface response graphs are shown in the results. The rest of the surface responses are shown in the supplementary data.

7.4 Conclusions

Composite latexes with varying hydrophilic functional monomers (HEMA, MAA) and different types of surfactant (anionic or nonionic) were synthesized by a two-stage emulsion polymerization. The toughest films were obtained when melamine-formaldehyde (MF) resins were used due to the plasticizing effect of MF resin. Films crosslinked with HDI isocyanurate and carbodiimide had poor toughness. However, carbodiimide and HDI isocyanurate showed very high Young’s modulus. Zinc
crosslinked latex films resulted in the highest Young’s modulus due to high electrostatic interactions. Increase in the concentration of functional monomers decreased pencil hardness of zinc crosslinked thermoset films due to limited chain diffusion across interfaces. Crosslinking of latex having high functionality with zinc salt yielded poor gloss.

7.5 Supplementary Data

The bestfit mathematical model for storage modulus of MF crosslinked latex films (see Fig. 7.3) in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

**Surfactant Triton**

Storage Modulus (MF) = -10.53+0.91 ×[H] +0.58×[M]- 0.046×[H] ×[M]

**Surfactant Tergitol**

Storage Modulus (MF) = -12.58+0.91×[H] +0.58×[M]- 0.046×[H] ×[M]

The "Model F-value" of 1.39 implies the model is not significant relative to the noise. There is a 41.01% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 3.37 indicates an inadequate signal, and we should not use this model to navigate the design space.

Figure 7.19 shows the response surface graphs of storage modulus of cycloaliphatic diepoxide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for storage modulus of cycloaliphatic diepoxide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:
Surfactant Triton

Storage Modulus (Epoxy) = +2.073 -0.146 × [H] -0.198 × [M] +0.015 × [H] × [M]

Surfactant Tergitol

Storage Modulus (Epoxy) = +2.538 -0.146 × [H] -0.235 × [M] +0.015 × [H] × [M]

The Model F-value of 22.25 implies the model is significant. There is only a 4.36% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 11.809 indicates an adequate signal. This model can be used to navigate the design space.

![Figure 7.19](image1)

**Figure 7.19.** Response surface graphs of storage modulus of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.20 shows the response surface graphs of storage modulus of zinc crosslinked films as a function of HEMA or MAA. The best fit mathematical model for
storage modulus of zinc crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

**Surfactant Triton**

Storage Modulus (zinc) = -4.394 + 0.302 × [H] + 0.251 × [M] - 0.011 × [H] × [M]

**Surfactant Tergitol**

Storage Modulus (zinc) = -2.139 + 0.136 × [H] + 0.251 × [M] - 0.011 × [H] × [M]

The "Model F-value" of 5.38 implies the model is not significant relative to the noise. There is a 16.41% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 6.052 indicates an adequate signal. This model can be used to navigate the design space.

![Response Surface Graphs](image_url)

Figure 7.20. Response surface graphs of storage modulus of zinc crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
Figure 7.21 shows the response surface graphs of storage modulus of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for storage modulus of carbodiimide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Storage Modulus (carbodiimide) = -0.685 + 0.047 × [H] + 0.045 × [M] - 2.728E-003 × [H] × [M]

Surfactant Tergitol
Storage Modulus (carbodiimide) = -0.617 + 0.047 × [H] + 0.045 × [M] - 2.728E-003 × [H] × [M]

The "Model F-value" of 4.61 implies the model is not significant relative to the noise. There is a 11.98% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 6.142 indicates an adequate signal. This model can be used to navigate the design space.
Figure 7.21. Response surface graphs of storage modulus of carbodiimide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.22 shows the response surface graphs of storage modulus of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for storage modulus of isocyanurate crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Storage Modulus (HDI) = -3.716 +0.097 ×[H] +0.399 × [M] -9.424E-003 × [H] × [M]

Surfactant Tergitol
Storage Modulus (HDI) = -3.841 +0.097 ×[H] +0.399 × [M] -9.424E-003 × [H] × [M]

The Model F-value of 11.55 implies the model is significant. There is only a 3.63% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision"
measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 7.502 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.22. Response surface graphs of storage modulus of isocyanurate crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

The best fit mathematical model for Young’s modulus of zinc crosslinked latex films (see Fig. 7.6) in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
E’ (Zn) = -1815.106 + 107.891 × [H] + 177.532 × [M] - 10.146 × [H] × [M]

Surfactant Tergitol
E’ (Zn) = -1916.498 + 106.118 × [H] + 187.272 × [M] - 10.146 × [H] × [M]

The "Model F-value" of 10.90 implies the model is not significant relative to the noise. There is a 22.78% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 7.935 was obtained indicating an adequate signal to navigate the design space.

Figure 7.23 shows the response surface graphs of Young’s modulus of cycloaliphatic diepoxide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Young’s modulus of cycloaliphatic diepoxide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

\[
E'(Epoxy) = +64.018 -5.128 \times [H] -6.916 \times [M] +0.556 \times [H] \times [M]
\]

Surfactant Tergitol

\[
E'(Epoxy) = +100.468 -5.128 \times [H] -9.917\times [M] +0.556 \times [H] \times [M]
\]

The "Model F-value" of 2.00 implies the model is not significant relative to the noise. There is a 36.64% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 3.71 indicates an inadequate signal to navigate the design space.
Figure 7.23. Response surface graphs of Young’s modulus of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.24 shows the response surface graphs of Young’s modulus of MF crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Young’s modulus of MF crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, \([H]\), MAA, \([M]\), and type of surfactant, \([S]\) was:

Surfactant Triton

\[
E' \text{ (MF)} = +140.413 -4.991 \times [H] -24.230 \times [M] +1.339 \times [H] \times [M]
\]

Surfactant Tergitol

\[
E' \text{ (MF)} = +151.663 -4.991 \times [H] -24.230 \times [M] +1.339 \times [H] \times [M]
\]

The Model F-value of 9.24 implies the model is significant. There is only a 4.91% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 7.419 indicates an adequate signal. This model can be used to navigate the design space.
Figure 7.24. Response surface graphs of Young’s modulus of MF crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.25 shows the response surface graphs of Young’s modulus of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Young’s modulus of carbodiimide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

\[ E'(\text{carbodiimide}) = -2911.960 + 141.714 \times [H] + 273.839 \times [M] - 12.202 \times [H] \times [M] \]

Surfactant Tergitol

\[ E'(\text{carbodiimide}) = -2907.510 + 141.714 \times [H] + 273.839 \times [M] - 12.202 \times [H] \times [M] \]

The "Model F-value" of 5.06 implies the model is not significant relative to the noise. There is a 10.71% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A
ratio of 5.502 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.25. Response surface graphs of Young’s modulus of carbodiimide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.26 shows the response surface graphs of Young’s modulus of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Young’s modulus of isocyanurate crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, $[H]$, MAA, $[M]$, and type of surfactant, $[S]$ was:

Surfactant Triton

\[
E' (HDI) = -71.154 + 4.803 \times [H] + 7.536 \times [M] - 0.472 \times [H] \times [M]
\]

Surfactant Tergitol

\[
E' (HDI) = -76.988 + 4.803 \times [H] + 8.070 \times [M] - 0.472 \times [H] \times [M]
\]
The Model F-value of 26.17 implies the model is significant. There is only a 3.72% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 14.464 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.26. Response surface graphs of Young’s modulus of isocyanurate crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

The best fit mathematical model for tensile strength of MF crosslinked latex films (see Fig. 7.8) in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Tens. St. (MF) = +2.131+5.952E-003×[H] -0.319×[M] +0.035×[H]×[M]
Surfactant Tergitol

Tens. St. (MF) = +1.231 +5.952E-003×[H] -0.319×[M] +0.035×[H]×[M]

The "Model F-value" of 2.57 implies the model is not significant relative to the noise. There is a 23.25% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 4.496 was obtained, indicating an adequate signal to navigate the design space.

Figure 7.27 shows the response surface graphs of tensile strength of cycloaliphatic diepoxide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for tensile strength of cycloaliphatic diepoxide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Tens. St. (Epoxy) = -7.777 +0.152 ×[H] +0.653 × [M]

Surfactant Tergitol

Tens. St. (Epoxy) = +2.039 +0.152 ×[H] -0.208 × [M]

The "Model F-value" of 2.31 implies the model is not significant relative to the noise. There is a 32.94% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 4.574 indicates an adequate signal. This model can be used to navigate the design space.
Figure 7.27. Response surface graphs of tensile strength of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.28 shows the response surface graphs of tensile strength of zinc crosslinked films as a function of HEMA or MAA. The best fit mathematical model for tensile strength of zinc crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

\[
\text{Tens. St. (zinc)} = -71.155 + 4.804 \times [H] + 7.536 \times [M] - 0.472 \times [H] \times [M]
\]

Surfactant Tergitol

\[
\text{Tens. St. (zinc)} = -76.988 + 4.803 \times [H] + 8.071 \times [M] - 0.472 \times [H] \times [M]
\]

The Model F-value of 26.17 implies the model is significant. There is only a 3.72% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision"
measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 14.464 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.28. Response surface graphs of tensile strength of zinc crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.29 shows the response surface graphs of tensile strength of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for tensile strength of carbodiimide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

\[
\text{Tens. St. (carbodiimide)} = -7.058 +0.271 \times [H] +1.049 \times [M] -0.019 \times [H] \times [M]
\]

Surfactant Tergitol

\[
\text{Tens. St. (carbodiimide)} = +1.492 +0.271 \times [H] +0.299 \times [M] -0.019 \times [H] \times [M]
\]
The "Model F-value" of 2.63 implies the model is not significant relative to the noise. There is a 29.84% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 4.516 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.29. Response surface graphs of tensile strength of carbodiimide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.30 shows the response surface graphs of tensile strength of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for tensile strength of isocyanurate crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:
Surfactant Triton

\[
\text{Tens. St. (HDI)} = -16.765 + 0.799 \times [H] + 2.192 \times [M] - 0.082 \times [H] \times [M]
\]

Surfactant Tergitol

\[
\text{Tens. St. (HDI)} = -10.015 + 0.362 \times [H] + 2.192 \times [M] - 0.082 \times [H] \times [M]
\]

The Model F-value of 9.67 implies there is a 9.63\% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 8.935 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.30. Response surface graphs of tensile strength of isocyanurate crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

The best-fit mathematical model for elongation % of MF crosslinked latex films (see Fig. 7.10) in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:
Surfactant Triton

Elongation % (MF) = +994.312 -21.488 \times [H] +12.111 \times [M] -2.222 \times [H] \times [M]

Surfactant Tergitol

Elongation % (MF) = +234.874 +0.065 \times [H] +42.805 \times [M] -2.222 \times [H] \times [M]

The Model F-value of 94.08 implies the model is significant. There is only a 7.88% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 28.343 was obtained, indicating an adequate signal to navigate the design space.

Figure 7.31 shows the response surface graphs of elongation % of cycloaliphatic diepoxide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for elongation % of cycloaliphatic diepoxide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Elongation % (Epoxy) = -1155.752 +85.818 \times [H] +166.379 \times [M] -9.385 \times [H] \times [M]

Surfactant Tergitol

Elongation % (Epoxy) = -1386.152 +85.818 \times [H] +166.379 \times [M] -9.385 \times [H] \times [M]

The Model F-value of 6.09 implies there is a 8.48% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 7.085 indicates an adequate signal. This model can be used to navigate the design space.
Figure 7.31. Response surface graphs of elongation % of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.32 shows the response surface graphs of elongation % of zinc crosslinked films as a function of HEMA or MAA. The best fit mathematical model for elongation % of zinc crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Elongation % (zinc) = +1044.929 -39.449 ×[H] -68.329 × [M] +2.490 × [H] × [M]

Surfactant Tergitol
Elongation % (zinc) = +1063.679 -39.449 ×[H] -68.329 × [M] +2.490 × [H] × [M]

The "Model F-value" of 3.64 implies the model is not significant relative to the noise. There is a 15.83% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A
ratio of 5.117 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.32. Response surface graphs of elongation % of zinc crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.33 shows the response surface graphs of elongation % of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for elongation % of isocyanurate crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Elongation % (HDI) = +240.332 +3.199 ×[H] -16.682 × [M] -0.325 × [H] × [M]

Surfactant Tergitol
Elongation % (HDI) = +281.457 +3.199 ×[H] -16.682 × [M] -0.325 × [H] × [M]

The "Model F-value" of 4.02 implies the model is not significant relative to the noise. There is a 14.10% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 4.956 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.33. Response surface graphs of elongation % of isocyanurate crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.34 shows the response surface graphs of elongation % of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for elongation % of carbodiimide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Elongation % (carbodiimide) = +903.289 -25.015×[H] -66.673 × [M] +2.168 × [H] × [M]

Surfactant Tergitol
Elongation % (carbodiimide) = +888.839 -25.015 ×[H] -66.673× [M] +2.168 × [H] × [M]

The "Model F-value" of 2.12 implies the model is not significant relative to the noise. There is a 28.18% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 3.39 indicates an inadequate signal to navigate the design space.

Figure 7.34. Response surface graphs of elongation % of carbodiimide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

The best fit mathematical model for cycloaliphatic diepoxide crosslinked latex films (see Fig. 7.12) in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Toughness (Epoxy) = -17.869+0.464 ×[H] +1.519 ×[M] -0.015×[H] × [M]
Surfactant Tergitol

Toughness (Epoxy) = \(-1.897 + 0.286 \times [H] + 0.186 \times [M] - 0.015 \times [H] \times [M]\)

The Model F-value of 1.28 implies the model is significant. There is a 58.94% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 3.12 was obtained indicating an inadequate signal to navigate the design space.

Figure 7.35 shows the response surface graphs of toughness of MF crosslinked films as a function of HEMA or MAA. The best fit mathematical model for toughness of MF crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Toughness (MF) = \(-1.463 + 1.199 \times [H] + 1.013 \times [M] - 0.102 \times [H] \times [M]\)

Surfactant Tergitol

Toughness (MF) = \(-11.913 + 1.199 \times [H] + 1.805 \times [M] - 0.102 \times [H] \times [M]\)

The Model F-value of 13.58 implies there is a 7.00% chance that a "Model F-Value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 10.687 indicates an adequate signal. This model can be used to navigate the design space.
Figure 7.35. Response surface graphs of toughness of MF crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.36 shows the response surface graphs of toughness of zinc crosslinked films as a function of HEMA or MAA. The best fit mathematical model for toughness of zinc crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, \([H]\), MAA, \([M]\), and type of surfactant, \([S]\) was:

Surfactant Triton

\[
\text{Toughness (zinc)} = +10.445 +0.114 \times [H] +0.137 \times [M] -0.049 \times [H] \times [M]
\]

Surfactant Tergitol

\[
\text{Toughness (zinc)} = +10.510 +0.114 \times [H] +0.137 \times [M] -0.049 \times [H] \times [M]
\]

The "Model F-value" of 0.67 implies the model is not significant relative to the noise. There is a 65.77% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 2.07 indicates an inadequate signal and we should not use this model to navigate the design space.
Figure 7.36. Response surface graphs of toughness of zinc crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.37 shows the response surface graphs of toughness of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for toughness of carbodiimide crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, \([H]\), MAA, \([M]\), and type of surfactant, \([S]\) was:

Surfactant Triton
Toughness (carbodiimide) = +19.229 -0.395 \times [H] -1.259 \times [M] +0.042 \times [H] \times [M]

Surfactant Tergitol
Toughness (carbodiimide) = +18.704 -0.396 \times [H] -1.259 \times [M] +0.042 \times [H] \times [M]

The "Model F-value" of 0.19 implies the model is not significant relative to the noise. There is a 92.81% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 1.09 indicates an inadequate signal and we should not use this model to navigate the design space.
Figure 7.37. Response surface graphs of toughness of carbodiimide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.38 shows the response surface graphs of toughness of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for toughness of isocyanurate crosslinked films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Toughness (HDI) = +19.229 -0.395 × [H] -1.259 × [M] +0.042 × [H] × [M]

Surfactant Tergitol
Toughness (HDI) = +18.704 -0.396 × [H] -1.259× [M] +0.042 × [H] × [M]

The "Model F-value" of 0.19 implies the model is not significant relative to the noise. There is a 92.81% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 1.09 indicates an inadequate signal and we should not use this model to navigate the design space.
Impact resistance results were statistically analyzed to screen response of non-crosslinked and crosslinked films in design space. The best fit mathematical model for forward impact test of zinc crosslinked latex films (see Fig. 7.14) in terms of actual factors for the response and variables, concentrations of HEMA, \([H]\), MAA, \([M]\), and type of surfactant, \([S]\) was:

**Surfactant Triton**

\[ \text{F. Imp. Test (Zn)} = +99.458 - 1.354 \times [H] - 4.871 \times [M] + 0.025 \times [H] \times [M] \]

**Surfactant Tergitol**

\[ \text{F. Imp. Test (Zn)} = +37.351 + 0.164 \times [H] - 1.121 \times [M] + 0.025 \times [H] \times [M] \]

The "Model F-value" of 58.63 implies the model is not significant relative to the noise. There is a 9.96% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable.
The ratio of 22.174 indicates an adequate signal to navigate the design space.

Figure 7.39 shows the response surface graphs of forward impact test of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA. The best fit mathematical model for forward impact test of cycloaliphatic diepoxide crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

F. Imp. Test (Epoxy) = -37.702 + 4.047 \times [H] + 6.528 \times [M] - 0.347 \times [H] \times [M]

Surfactant Tergitol

F. Imp. Test (Epoxy) = -39.202 + 6.528 \times [H] + \times [M] - 0.347 \times [H] \times [M]

The "Model F-value" of 6.25 implies the model is not significant relative to the noise.
There is a 8.20% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable.
The ratio of 7.230 indicates an adequate signal to navigate the design space.
Figure 7.39. Response surface graphs of forward impact test of cycloaliphatic diepoxide crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

Figure 7.40 shows the response surface graphs of forward impact test of MF crosslinked latex films as a function of HEMA or MAA. The best fit mathematical model for forward impact test of MF crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

\[ F. \text{ Imp. Test (MF)} = -1.244 + 2.589 \times [H] + 2.936 \times [M] - 0.223 \times [H] \times [M] \]

Surfactant Tergitol

\[ F. \text{ Imp. Test (MF)} = 5.952 \times 10^{-3} + 2.589 \times [H] + 2.936 \times [M] - 0.223 \times [H] \times [M] \]

The "Model F-value" of 1.11 implies the model is not significant relative to the noise. There is a 48.6% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio of 3.06 indicates an inadequate signal and we should not use this model to navigate the design space.

Figure 7.40. Response surface graphs of forward impact test of MF crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

Figure 7.41 shows the response surface graphs of forward impact test of carbodiimide crosslinked latex films as a function of HEMA or MAA. The best fit mathematical model for forward impact test of carbodiimide crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

**Surfactant Triton**

F. Imp. Test (carbodiimide) = -4.375+2.291×[H]+2.917×[M]-0.174×[H]×[M]

**Surfactant Tergitol**

F. Imp. Test (carbodiimide) = -2.625+2.292×[H]+2.917×[M]-0.174×[H]×[M]
The "Model F-value" of 2.18 implies the model is not significant relative to the noise. There is a 27.45% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 4.556 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.41. Response surface graphs of forward impact test of carbodiimide crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

Figure 7.42 shows the response surface graphs of forward impact test of isocyanurate crosslinked latex films as a function of HEMA or MAA. The best fit mathematical model for forward impact test of isocyanurate crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:
Surfactant Triton

F. Imp. Test (HDI) = +67.994 -1.860×[H]-2.550×[M] + 0.124×[H]×[M]

Surfactant Tergitol

F. Imp. Test (HDI) = +37.768 -0.877×[H]- 1.577×[M] + 0.124×[H]×[M]

The "Model F-value" of 37.00 implies the model is not significant relative to the noise. There is a 12.52% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 17.386 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.42. Response surface graphs of forward impact test of isocyanurate crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.
The best fit mathematical model for pull-off adhesion of cycloaliphatic diepoxide
crosslinked latex films (see Fig. 7.16) in terms of actual factors for the response and
variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Pull-off Adhesion (Epoxy) = +4.869 - 0.117 × [H] - 0.178 × [M] + 7.688E-003 × [H] × [M]

Surfactant Tergitol

Pull-off Adhesion (Epoxy) = +5.184 + -0.079 × [H] - 0.266 × [M] + 7.688E-003 × [H] × [M]

The "Model F-value" of 4.76 implies the model is not significant relative to the noise.
There is a 33.71% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A
ratio of 5.813 was obtained, indicating an adequate signal to navigate the design space.

Figure 7.43 shows the response surface graphs of pull-off adhesion of MF
crosslinked films as a function of HEMA or MAA. The best fit mathematical model for
pull-off adhesion of MF crosslinked latex films in terms of actual factors for the response
and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Pull-off Adh. (MF) = +3.398 - 0.046 × [H] - 2.778E-003 × [M] - 1.736E-003 × [H] × [M]

Surfactant Tergitol

Pull-off Adh. (MF) = +0.107 + 0.138 × [H] - 2.778E-003 × [M] + 1.736E-003 × [H] × [M]

The "Model F-value" of 0.78 implies the model is not significant relative to the noise.
There is a 64.45% chance that a "Model F-value" this large could occur due to noise.
"Adeq Precision" measures the signal to noise ratio. A ratio of 2.24 indicates an
inadequate signal and we should not use this model to navigate the design space.
Figure 7.43. Response surface graphs of pull-off adhesion of MF crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

Figure 7.44 shows the response surface graphs of pull-off adhesion of zinc crosslinked films as a function of HEMA or MAA. The best fit mathematical model for pull-off adhesion of zinc crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

**Surfactant Triton**

Pull-off Adh. (zinc) = +3.842 -2.976E-003×[H] -0.078× [M] -7.688E-003×[H]×[M]

**Surfactant Tergitol**

Pull-off Adh. (zinc) = +3.699 -2.976E-003×[H] -0.078×[M] -7.688E-003×[H]×[M]

The "Model F-value" of 1.68 implies the model is not significant relative to the noise. There is a 34.93% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 3.52 indicates an inadequate signal to navigate the design space.
Figure 7.44. Response surface graphs of pull-off adhesion of zinc crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

Figure 7.45 shows the response surface graphs of pull-off adhesion of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for pull-off adhesion of carbodiimide crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

**Surfactant Triton**

Pull-off Adh. (carbodiimide) = -9.179 +0.515 ×[H] +0.983 × [M] -0.051 ×[H] ×[M]

**Surfactant Tergitol**

Pull-off Adh. (carbodiimide) = -8.626 +0.515 ×[H] +0.983 × [M] -0.051 ×[H] ×[M]

The "Model F-value" of 2.62 implies the model is not significant relative to the noise. There is a 22.77% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A
ratio of 4.565 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.45. Response surface graphs of pull-off adhesion of carbodiimide crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

Figure 7.46 shows the response surface graphs of pull-off adhesion of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for pull-off adhesion of isocyanurate crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Pull-off Adh. (HDI) = +2.682 +2.083E-003 ×[H] -0.111 × [M] -3.472E-003 ×[H] ×[M]

Surfactant Tergitol

Pull-off Adh. (HDI) = +1.900 + 0.068×[H] - 0.111× [M] -3.472E -003 ×[H] ×[M]
The "Model F-value" of 8.91 implies the model is not significant relative to the noise. There is a 10.39% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 8.824 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.46. Response surface graphs of pull-off adhesion of isocyanurate crosslinked latex films as a function of HEMA or MAA (a) Tergitol XJ. (b) Triton X-200.

The best fit mathematical model for gloss % of epoxy crosslinked latex films (see Fig. 7.18) in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Gloss % (Epoxy) = +150.386 - 7.059[H] - 7.980[M] + 0.523[H][M]

Surfactant Tergitol
Gloss % (Epoxy) = +156.661 - 7.059[H] - 7.980[M] + 0.523[H][M]
The "Model F-value" of 4.11 implies the model is not significant relative to the noise. There is a 13.74% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 5.898 was obtained, indicating an adequate signal to navigate the design space.

Figure 7.47 shows the response surface graphs of Gloss % of MF crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Gloss % of MF crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Gloss % (MF) = +10.173 +2.637 ×[H] +2.993 × [M] -0.268 ×[H] ×[M]

Surfactant Tergitol
Gloss % (MF) = -53.640 +2.637 ×[H] +8.865 × [M] -0.268 ×[H] ×[M]

The "Model F-value" of 0.60 implies the model is not significant relative to the noise. There is a 72.05% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. "Adeq Precision" measures the signal to noise ratio. A ratio of 2.12 indicates an inadequate signal to navigate the design space.
Figure 7.47. Response surface graphs of Gloss % of MF crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.48 shows the response surface graphs of Gloss % of zinc crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Gloss % of zinc crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, \([H]\), MAA, \([M]\), and type of surfactant, \([S]\) was:

Surfactant Triton
Gloss \% (zinc) = +233.211 -10.902 \times [H] -12.470 \times [M] +0.655 \times [H] \times [M]

Surfactant Tergitol
Gloss \% (zinc) = +167.446 -7.241 \times [H] -12.470 \times [M] +0.655 \times [H] \times [M]

The "Model F-value" of 0.55 implies the model is not significant relative to the noise. There is a 74.35% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 2.19 indicates an inadequate signal to navigate the design space.
Figure 7.48. Response surface graphs of Gloss % of zinc crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.49 shows the response surface graphs of Gloss % of carbodiimide crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Gloss % of carbodiimide crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton
Gloss % (carbodiimide) = +45.332 -0.826 × [H] -3.109 × [M] +0.0871×[H] ×[M]

Surfactant Tergitol
Gloss % (carbodiimide) = +77.867 -2.705 × [H] -3.109 × [M] + 0.0870 ×[H] ×[M]

The "Model F-value" of 4.92 implies the model is not significant relative to the noise. There is a 17.77% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable.
A ratio of 6.927 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7.49. Response surface graphs of Gloss % of carbodiimide crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.

Figure 7.50 shows the response surface graphs of Gloss % of isocyanurate crosslinked films as a function of HEMA or MAA. The best fit mathematical model for Gloss % of isocyanurate crosslinked latex films in terms of actual factors for the response and variables, concentrations of HEMA, [H], MAA, [M], and type of surfactant, [S] was:

Surfactant Triton

Gloss % (HDI) = -82.404 + 6.105 × [H] +10.305 × [M] -0.607 × [H] × [M]

Surfactant Tergitol

Gloss % (HDI) = -108.547 +7.650 × [H] +10.305 × [M] -0.607 × [H] × [M]
The "Model F-value" of 1.08 implies the model is not significant relative to the noise. There is a 54.59% chance that a "Model F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio of 2.87 indicates an inadequate signal to navigate the design space.

Figure 7.50. Response surface graphs of Gloss % of isocyanurate crosslinked latex films as a function of HEMA or MAA with surfactants (a) Tergitol XJ. (b) Triton X-200.
CHAPTER VIII
PREPARATION OF AMIDE- AND ACRYLATE-FUNCTIONALIZED LATEXES
FOR DUAL-CURE COATINGS

8.1 Introduction

Thermoset latex films have enhanced mechanical properties and chemical resistance compared to thermoplastic latex films.\textsuperscript{23, 242} The mechanical properties of the latex films depend on the balance between chain inter-diffusion and crosslinking. The chain inter-diffusion is a dominant factor when the molecular weight of polymer is high. The type of crosslinker and method of crosslinking determines the chain inter-diffusion.\textsuperscript{2} The crosslinking mode of latex particles can be described as homogeneous, interfacial, and interstitial or combination where a three-dimensional network with a higher molecular weight is obtained with controlled physical properties.\textsuperscript{25, 243} Several kinds of crosslinkers were studied including amino resins, isocyanates, carbodiimides, aziridines, oxazolines, aromatic epoxides, zinc salts, and silanes.\textsuperscript{27}

Physical properties of films improved after the latexes were crosslinked. Films cured by melamine-formaldehyde resin had better water and organic solvent resistance for hardboard clear coating applications.\textsuperscript{234} When water-soluble MF resin was used as crosslinker, latex films with low blister, better gloss, and no mottles were obtained.\textsuperscript{235}
Abrasion resistance of latex film with hydroxyl groups increased when HDI isocyanurate was used as crosslinker.\textsuperscript{221} Zinc ammonium carbonate was used to crosslink styrene-maleic anhydride latexes for thermally stable inks.\textsuperscript{230} Tensile properties and solvent resistance of film increased after polycarbodiimide crosslinking.\textsuperscript{229} Solvent resistance and tensile strength of the film markedly increased when one-pack acetoacetoxy functionalized latex with a diamine as crosslinker was used.\textsuperscript{64}

Radiation curing is another option to crosslink emulsion polymers rapidly.\textsuperscript{244} Radiation curing offers economic (low energy and space requirement) and environmental advantages over thermal curing.\textsuperscript{245} Volatile organic compounds (VOCs) can be decreased when radiation curing is applied. Heat sensitive substrates such as plastics can be coated through radiation curing. Tough and scratch resistance coatings can be obtained after radiation curing. Additionally, radiation curable coatings have very long pot-life when stored in the absence of radiation. Increase in viscosity during curing is one of the problems in radiation curing. Therefore, reactive diluents were used in several studies,\textsuperscript{246, 247} but reactive diluents especially acrylic monomers increase volatile organic compounds (VOCs) of coating formulations. Additionally, working areas have to be ventilated to eliminate odor of acrylic monomers. An alternative way to eliminate reactive diluents is to use waterborne coatings of which the viscosity of coating formulation is appreciably small.

Waterborne coatings for exterior coating applications can be cured by visible light ambient conditions.\textsuperscript{248} Camphorquinone (CQ) was the most effective photoinitiator for waterborne coatings among several photoinitiators such as acenaphtoquinone, $\alpha$-dicetodibenzosuberane, indole-2, 3-dione, and 1-Phenyl-1, 2-propanedione. In the
presence of oxygen, 100% conversion was obtained within 1 min. Camphorquinone functionalized polymer chains were crosslinked with amide-functionalized polymers. Camphorquinone absorbs light in the UV region (200-300 nm) and the visible region (400-500 nm). The absorption coefficient ($\epsilon$) is 10000 in UV region compared to just 40 in visible region. In order to improve efficiency of CQ in visible light range, coinitiator such as amine and peroxide compounds was used.

Visible light curing bears the same disadvantages as radiation curing. Curing is limited to only a few micrometers of the coating from the top of surface where the oxygen blocks curing. The curing rate is decelerated in the presence of pigments and moisture. Through curing of 3-D objects is very hard. In order to have a through cure, an additional curing mechanism is needed. Pressure sensitive adhesive formulations that have acrylic polymer chains with benzophenone and 2-hydroxyethyl methacrylate as comonomers were cured by UV radiation and polyisocyanates. Through-cure was obtained in thick coatings (75 μm). Additionally, high viscosity built during UV curing can be decreased by thermal curing. By the aid of heat, 100% conversion of double bonds can be obtained in radiation cure formulations. Several thermal curing chemistries have been studied. Acetoacetoxy-functionalized polymers can be cured by amine, amide, isocyanate and melamine functionalities. One-pack (1K) waterborne coating formulations with acetoacetoxy functionality were prepared and cured at room temperature. Corrosion resistance increased when the acetoacetoxy-functionalized emulsion polymers were crosslinked with poly(alkylenimine).

Functional groups have to be compartmentalized into separate latex particles in order to increase pot-life. Therefore, in this study, amide- and acrylate-functionalized
latexes with acetoacetoxy functionality were prepared in separate reactors. Two latexes were blended in different ratios (50/50, 40/60, 60/40 wt/wt). After, the best formulation (50/50 wt/wt amide- and acrylate-functionalized latexes) was found in terms of the highest tensile properties. The best formulation was mixed with methanolic camphorquinone and t-butyl hydroperoxide at different ratios (1, 2, 4, 6 wt% of triacrylate amount). Tensile, dynamic mechanical and thermal properties were studied for all formulations.

8.2 Results

The mechanical properties of dual-cure latexes were studied and the details of results were given in the following sections.

8.2.1 Synthesis of Dual-cure Latexes

Scheme 8.1 shows synthesis of amide-functionalized latexes by seeded two-stage polymerization. In the first stage, the mixture of 2-ethylhexyl acrylate, methyl methacrylate, ethylene glycol dimethacrylate, and acrylonitrile were copolymerized. In the second stage, the mixture of 2-ethylhexyl acrylate and acrylamide were copolymerized. Acrylate-functionalized latex was synthesized in another batch. This synthesis is illustrated in Scheme 8.2. In the first stage, the mixture of 2-ethylhexyl acrylate, ethyl acrylate, methyl methacrylate, acrylonitrile and acetoacetoxyethyl methacrylate was copolymerized. This was followed by the polymerization of trimethylolpropane triacrylate by the redox initiation at room temperature.
Dual-cure waterborne latexes were synthesized. Functional latexes (amide- and acrylate-functionalized latex) were mixed in different fractions (50/50, 40/60, 60/40) to study the effects of blend ratio and the concentration of photosensitizer (camphorquinone) on the mechanical and thermal properties. The presence of double bonds in acrylate-functionalized latex was confirmed by NMR as shown in Fig. 8.1. The resonances at 5.8 and 6.4 ppm were assigned to double bonds (\(-\text{CH}_2=\text{CH}-\)). The formulation was cast onto glass substrate after the mixing the acrylate- and amide-functionalized latexes with photosensitizer (CQ) and coinitiator (\(\tau\)-butyl hydroperoxide). The sample was taken after 15 minutes and analyzed in NMR. The double bonds of acrylate-functionalized latex on the NMR spectrum disappeared. This observation suggested that the curing occurred very rapidly.

Scheme 8.1. Schematic representation of synthesis of amide-functionalized latex.
Scheme 8.2. Schematic representation of synthesis of acrylate-functionalized latex with acetoacetoxy methacrylate in core.
Figure 8.1. $^1$H-NMR spectra for (a) acrylate-functionalized latex (b) mixture of acrylate- and amide-functionalized latex (50/50 wt/wt) (NMR sample was taken after blending latexes with CQ and $t$-butyl hydroperoxide for 15 min.)
8.2.2 Differential Scanning Calorimetry (DSC) Analysis of Dual-cure Latexes

Acrylate- and amide-functionalized latexes were mixed at different ratios (50/50, 40/60, 60/40 wt). Methanolic camphorquinone and \( t \)-butyl hydroperoxide (1 wt% of triacrylate amount in the blend) was added into the formulation. The latex blends were dried at ambient conditions. Figure 8.2 shows the differential scanning calorimetry (DSC) thermograms of latex blends (50acr50tri, 40acr60tri, 60acr40tri). Two glass transition temperatures were obtained for latex blends as broad endotherms. This observation indicated the presence of a loosely crosslinked polymer network.\(^{255}\) The latex films (50acr50tri, 40acr60tri, 60acr40tri) had the first glass transition temperature values as -23.5, -20.6, -29.7 °C, respectively. The second glass transition temperatures were observed at 2.9, 3.2, 18.1 °C. Even though amide-functionalized latex had supposedly lower glass transition temperature than acrylate-functionalized latex according to the Fox equation\(^ {134} \), 60acr40tri had the highest glass transition temperature (Tg). This could be attributed to better thermal curing between amide- and acetoacetoxy-functionalities.
Figure 8.2. Differential scanning calorimetry (DSC) thermograms of latex blends at different fractions (50/50, 40/60, 60/40 wt/wt) cured at ambient conditions with camphorquinone and t-butyl hydroperoxide (1 wt% of triacrylate amount in blend).

The effect of the concentration of photosensitizer (CQ) and coinitiator (t-butyl hydroperoxide) was also studied. The latex (50acr50tri) was selected as a model blend since it showed the best tensile properties among 50acr50tri, 40acr60tri, 60acr40tri. The latex (50acr50tri) was cured by camphorquinone and t-butyl hydroperoxide at different concentrations relative to triacrylate amount (1, 2, 4, and 6 wt% of triacrylate amount). Figure 8.3 shows the differential scanning calorimetry (DSC) thermograms of latex films (50acr50triCQ1, 50acr50triCQ2, 50acr50triCQ4, and 50acr50triCQ6). All latex films showed two glass transition temperatures. First transitions of 1a (50acr50triCQ1), 2a (50acr50triCQ2), 3a (50acr50triCQ4), and 4a (50acr50triCQ6) were observed around -26.7, -25.4, -23.5 and -22.8 °C, respectively. Second transitions of 1b (50acr50triCQ1),
2b (50acr50triCQ2), 3b (50acr50triCQ4), and 4b (50acr50triCQ6) were observed around 2.9, 6.7, 19.4 and 19.5 °C, respectively. The presence of two glass transitions can be attributed to the immiscibility of phases, which was more obvious as the photoinitiator concentration increased. The curing extent of acrylate-functionalized latexes significantly increased with the higher concentration of photoinitiator. As the photoinitiator concentration increased, glass transition broadened, implying that the formation of multiple domains occurred.

Figure 8.3. Differential scanning calorimetry (DSC) analysis of 50 wt% acrylamide- and 50 wt% acrylate-functionalized latex (50acr50tri) as a function of photosensitizer (1 wt%, 2 wt%, 4 wt%, and 6 wt% relative to amount of TMPTA).
8.3.3 Tensile Testing of Dual-cure Latex Films

Tensile properties of dual-cure latex films were tested. Mixtures of amide- and acrylate-functionalized latexes were cured with 1 wt% of camphorquinone and \( t \)-butyl hydroperoxide (the amount of photoinitiator determined in the basis of triacrylate amount in latex). Tensile modulus, tensile strength and elongation % of individual latexes (amide- and acrylate-functionalized latexes) and dual cure latex films are shown in Fig. 8.4. The individual amide- and acrylate-functionalized latexes showed less elongation % than the dual cure latex blends. However, tensile strength was higher for these latex films than that of dual-cure latex film, likely due to a better chain inter-diffusion in the absence of crosslinkable functional groups. If the curing reaction is faster than the chain inter-diffusion, this results in very low toughness.\(^{23}\) Therefore, the mechanical properties of latexes depend on inter-diffusion as well as chemical composition. The highest modulus and elongation % was observed for the latex film (50acr50tri). This could be attributed to better chain inter-diffusion across the interfaces during film formation of latex than other latex films (40acr60tri and 60acr40tri). As the amount of acrylate- or amide-functionalized latexes (40acr60tri and 60acr40tri) increased, modulus and elongation % decreased. This could be attributed to a better adhesion and/or reaction between latex particles, which prevents a complete chain inter-diffusion resulting in lower elongation %.\(^{256}\) Similarly, a better adhesion and/or reaction between acrylate- or amide-functionalized latexes (40acr60tri and 60acr40tri) yielded higher tensile strength than the latex film (50acr50tri).

The effect of photoinitiator concentration on tensile properties was also investigated. Methanolic camphorquinone and \( t \)-butyl hydroperoxide (1, 2, 4, and 6 wt%
of the amount of triacrylate) were mixed with amide- and acrylate-functionalized latex (50/50 wt/wt). Interestingly, the tensile strength of the latex films decreased whereas elongation % increased as the concentration of photoinitiator increased even though functional groups were expected to crosslink at the latex particle interfaces. This could be attributed to the plasticization effect of the photoinitiator. Visible light curing mostly occurred on the top of the surface. Therefore, most of the unreacted photoinitiator and its fragments remained in the film and behaved as a plasticizer.

Figure 8.4. Tensile properties of films obtained from amide- (Acr) and acrylate functionalized (Tri) latexes and from amide- and acrylate-functionalized latexes blended in different ratios (50/50, 40/60, and 60/40 wt/wt.).
Figure 8.4. Tensile properties of films obtained from amide- (Acr) and acrylate functionalized (Tri) latexes and from amide- and acrylate-functionalized latexes blended in different ratios (50/50, 40/60, and 60/40 wt/wt.) (continued).
Figure 8.5. Tensile properties of films obtained from amide- and acrylate-functionalized latexes (50/50 wt/wt) as a function of photosensitizer amount (1, 2, 4, and 6 wt%).
8.2.4 Dynamic Mechanical Analysis of Latex Films

Dynamic mechanical properties of dual-cure latex films were studied. Effects of blending ratio of amide- and acrylate-functionalized latexes (50/50, 40/60, 60/40 wt/wt) and photoinitiator concentration (1, 2, 3, 4, and 6 wt% camphorquinone and \( t \)-butyl hydroperoxide) on storage modulus, crosslink density and glass transition temperature of dual-cure latex films were investigated. Dynamic mechanical values of dual-cure latex films were tabulated in Table 8.1. Mixtures of amide- and acrylate-functionalized latexes (50/50, 40/60, 60/40 wt/wt.) were cured with 1 wt% of camphorquinone and \( t \)-butyl hydroperoxide. Figure 8.6 shows the storage modulus plots of thermoset latex films (50acr50tri, 40acr60tri, 60acr40tri) where almost the same storage modulus was observed.

Figure 8.5. Tensile properties of films obtained from amide- and acrylate-functionalized latexes (50/50 wt/wt) as a function of photosensitizer amount (1, 2, 4, and 6 wt%) (continued).
at rubbery plateau. The highest storage modulus was observed for 50acr50tri at room temperature (25 °C). This latex film (50acr50tri) also yielded the highest tensile modulus among latexes with different blending ratios (50acr50tri, 40acr60tri, 60acr40tri) (see Fig. 8.4). Tan δ of amide- and acrylate-functionalized latex films (50acr50tri, 40acr60tri, 60acr40tri) is shown in Figure 8.7. Two glass transition temperatures were observed. These two transitions could be assigned to uncured and cured domains in latex films. The latex film (50acr50tri) showed the highest glass transition temperature, indicating a better cure. The magnitude of tan δ for the latex film (50acr50tri) was lower than that of latexes (40acr60tri and 60acr40tri) at around 90 °C. The latex films were expected to show cocontinuous phase morphology due to large area under the tan δ plot. The continuous phase had lower Tg whereas discontinuous phase (platelet-like domains) had high Tg. The highest area under the tan δ plot was observed for the latex film (60acr40tri) indicating a better miscibility relative to the other two latex films (50acr50tri and 40acr60tri).

Amide- and acrylate-functionalized latex (50/50 wt/wt) was selected as a model blend to study the effect of photoinitiator concentration on dynamic mechanical properties since film of this blend showed the highest storage modulus at 25 °C. The methanolic camphorquinone and t-butyl hydroperoxide (1, 2, 4, and 6 wt% relative to the amount of triacrylate) was mixed with amide- and acrylate-functionalized latex (50/50 wt/wt). Figure 8.8 shows the storage modulus plots for the latex blends cured with varying photoinitiator concentration (50acr50triCQ1, 50acr50triCQ2, 50acr50triCQ4, and 50acr50triCQ6). As the photoinitiator concentration increased, storage modulus and crosslink density of latex films increased. Figure 8.9 shows the tan δ plots of the latex
films (50acr50triCQ1, 50acr50triCQ2, 50acr50triCQ4, and 50acr50triCQ6). Glass transition temperature that belongs to the uncured region of latex films also increased from -15.6 to -8.1 °C. The latex film (50acr50triCQ6) showed the poorest miscibility. This could be attributed to the higher solubility difference between hard and soft domains as the crosslink density increased.258

Table 8.1. Dynamic mechanical properties and crosslink density for thermoset latex films.

<table>
<thead>
<tr>
<th></th>
<th>Storage Modulus, $E'$, (Pa)</th>
<th>$n_s$ (mol/m$^3$)</th>
<th>$T_g1$ (°C)</th>
<th>$T_g2$ (°C)</th>
<th>Max tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>50acr50tri</td>
<td>9.4E+4</td>
<td>10.0</td>
<td>-15.6</td>
<td>95.6</td>
<td>1.27</td>
</tr>
<tr>
<td>40acr60tri</td>
<td>8.8E+4</td>
<td>10.5</td>
<td>-16.6</td>
<td>88.9</td>
<td>1.27</td>
</tr>
<tr>
<td>60acr40tri</td>
<td>9.4E+4</td>
<td>10.5</td>
<td>-13.2</td>
<td>91.6</td>
<td>1.20</td>
</tr>
<tr>
<td>50acr50triCQ1</td>
<td>9.4E+4</td>
<td>10.0</td>
<td>-15.6</td>
<td>95.6</td>
<td>1.27</td>
</tr>
<tr>
<td>50acr50triCQ2</td>
<td>7.9E+4</td>
<td>8.7</td>
<td>-14.6</td>
<td>84.9</td>
<td>1.38</td>
</tr>
<tr>
<td>50acr50triCQ4</td>
<td>1.6E+5</td>
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<td>-11.6</td>
<td>94.8</td>
<td>1.32</td>
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<tr>
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<td>2.2E+5</td>
<td>22.9</td>
<td>-8.1</td>
<td>95.7</td>
<td>1.27</td>
</tr>
</tbody>
</table>
Figure 8.6. Storage modulus of films obtained from amide- and acrylate-functionalized latexes blended in different ratios (50/50, 40/60, and 60/40 wt/wt.).

Figure 8.7. tan δ of films obtained from amide- and acrylate-functionalized latexes blended in different ratios (50/50, 40/60, and 60/40 wt/wt.).
Figure 8.8. Storage modulus of films obtained from amide- and acrylate-functionalized latexes (50/50 wt/wt) as a function of photosensitizer (1, 2, 4, and 6 wt%).
8.3 Discussion

Higher cohesive strength is required for most of the coating applications to obtain desired properties such as good scratch resistance and stiffness since physical entanglement of polymer chains (thermoplastics) is not an adequate alone. The cohesive strength of film can be increased by chemical crosslinking of the functional groups in polymer backbone. Radiation curing is one of the methodologies used to obtain crosslinked coatings. Visible light curing is desired for exterior coatings since the intensity of UV light is less than visible light in sunlight. Additionally, visible light is not blocked by UV absorbing pigments such as titanium oxide in formulation. However, one of the limitations of radiation curing is that it is very difficult to obtain through cure.
Therefore, another curing mechanism is needed for coating formulations. In order to overcome these insufficiencies, dual-cure systems combining thermal and visible light curing were developed in this study.

One of the aims of this study was to find the optimum blend ratio that yields the highest modulus. Modulus of the latex formulation was studied as a function of blend ratio. The latex blend (50acr50tri) gave the highest tensile modulus and storage modulus value at 25 °C. On the other hand, the tensile strength of the 40acr60tri and 60acr40tri was higher than that of 50acr50tri. For the latex film (40acr60tri), this was consisted with the previous study in which crosslinkable functional groups on the shell showed a higher tensile strength than the functional groups buried in the seeds.65 This blend (50acr50tri) was picked to study the effect of the photoinitiator concentration on mechanical properties. As the photoinitiator concentration increased, elongation % also increased.

The latex films (40acr60tri and 60acr40tri) showed higher storage modulus than 50acr50tri at the rubbery plateau. This was attributed to optimal packing of the blends in the previous report.259 The formation of hexagonal closed-packed unit cell was proposed, resulting in maximum contact of the functional groups (acrylate or AAEMA-amide). Two glass transition temperatures were observed in dynamic mechanical analysis indicating the immiscibility of hard and soft domains. This observation was in agreement with a previous study of composite latex with seed (polystyrene) and shell (BA-AAEMA).65 After crosslinking the AAEMA functionality with 1, 6-hexadiamine, the miscibility of the two phases increased, observed as closer transitions and higher area under tan δ plot.

In differential scanning calorimetry (DSC), multiple transitions were observed for the latex films (see Figs. 8.2-3). This was in agreement with the previous report.260
Multiple transitions were observed for the latex films formed from latexes with seed and polymer II phases. The authors ascribed the multiple transitions in DSC thermograms to the formation of multiphase morphology due to the minor difference between solubility parameters of the seed and polymer II. As the photoinitiator concentration increased, the transitions for the hard and soft segments became broader, implying that the miscibility between the hard and soft segments increased.

8.4 Conclusions

Amide- and acrylate-functionalized dual-cure latex dispersions were prepared. The highest tensile and storage modulus was obtained from the film (50acr50tri). Elongation % strength and storage modulus of 50acr50tri increased as photoinitiator concentration increased. As the photoinitiator concentration increased, glass transitions of latex films were broadened due to the formation of multiple domains. All latex formulations showed two glass transition temperatures, likely due to induced immiscibility after the reactions either between acetoacetoxy- and amide-functionalities or acrylic groups.
CHAPTER IX
CONCLUSIONS

In this dissertation, it was observed that both hydrophilic and hydrophobic functional monomers had important effects on the physical properties of latexes, such as modulus, polymerization kinetics, colloidal stability, and latex morphology. Three methods were used to prepare polysiloxane-polyacrylate hybrid latexes with varying morphologies. A very broad particle size distribution was observed in TEM analysis for all the polymerizations as a consequence of excess surfactant used to stabilize the siloxane in the emulsion. Surface energy of hybrid latex was significantly lower than that of polyacrylate. Two distinct glass transitions at -125 and -55 °C were assigned to polyacrylate and polysiloxane phases, respectively. Polysiloxane content of hybrid latex prepared via copolymerization of methacrylate-terminated polysiloxane, EHA, and EA (B-MS) was higher in the F-A interface than in the F-S interface compared to other hybrid latexes (SC-CS and B-RH). This was likely due to higher phase separation as a consequence of the higher molecular weight of polysiloxane.

Two important factors affecting polymerization kinetics in the formation of core-shell latexes are the copolymerization of hydrophilic functional monomers and the type of surfactant. The critical micelle concentration (CMC) of the surfactants played an important role in particle size and particle size distribution. However, the CMC of
surfactant did not profoundly influence the rate of polymerization during the synthesis of core phase. Higher fractions of functional monomers (HEMA and MAA) yielded more homogeneous nucleation, observed by longer nucleation time. As a consequence of homogeneous nucleation, it was proposed that the HEMA and MAA increased the secondary nucleation due to their propensity to form longer oligomers in the aqueous phase. Additionally, a higher amount of HEMA and MAA led to lower instantaneous rate of polymerization ($R_p$). This could be attributed to poor nucleation ability of oligomers in the aqueous medium. The entry rate of oligomers into particles influenced not only the rate of polymerization, but also the particle size and particle size distribution. The slower entry rate led to significant fluctuations in the number of particles ($N_p$) when anionic surfactant (Triton X-200) was used.

The mechanical properties of thermoset latex films depend on several characteristics such as the crosslinkable functional group and the type of crosslinker. These parameters influence the rate of polymer chain interdiffusion and the degree of crosslinking. Even though several crosslinking chemistries have been studied, a quantitative comparison of the mechanical properties of thermoset latexes has not been reported previously. Therefore, core, shell or both core-shell with hydrophilic functional groups was crosslinked with melamine-formaldehyde (MF), zinc, ’N, N-dicyclohexylcarbodiimide, hexamethylene diisocyanate (HDI) isocyanurate and cycloaliphatic diepoxide. The toughest films were obtained when MF resins were used. This could be attributed to a higher extent of polymer chain inter-diffusion since MF crosslinks only the core phase. Films crosslinked with HDI isocyanurate and carbodiimide had poor toughness. However, carbodiimide and HDI isocyanurate showed
very high Young’s modulus. This could be attributed to abundant H-bonding at room temperature. Zinc crosslinked latex films resulted in the highest Young’s modulus, likely due to either inorganic bonds between zinc ion and carboxylic acids or residual zinc salts remaining in the polymer matrix. As opposed to MF crosslinker, zinc crosslinking of shell phase led to lower pencil hardness. Interestingly, surfactant type had a significant effect on mechanical properties of thermoset films. The anionic surfactant (Triton X-200) caused a broader particle size distribution. The films obtained from latex with Triton X-200 showed higher pencil hardness and solvent resistance. This was likely due to enhanced polymer chain interdiffusion.

The rate of through cure of thermoset films can be augmented by adding a second curing mechanism into latex systems with thermal curing. The longer pot life of the latexes was achieved by blending acrylate- and amide-functionalized latexes. The rate of visible light of the unsaturated acrylic groups curing was higher compared to thermal curing between acetoacetoxyl and amide functionalities on the basis of NMR analysis. As the blend ratio of acrylate- and amide-terminated latexes was varied tensile and dynamic mechanical properties changed. This was likely due to variations in polymer chain interdiffusion or adhesion of latex particles. The highest elongation % and storage modulus at room temperature was observed for the blend (50/50 wt/wt%). The tensile strength and storage modulus of films increased as the photoinitiator concentration increased. However, micro-heterogeneity of the films increased when the photoinitiator concentration increased. The sequential crosslinking reactions firstly between unsaturated acrylic and later acetoacetoxyl- and amide-functionalities induced the phase separation,
which was supported by two glass transition temperatures as revealed from dynamic mechanical analysis.
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