INVESTIGATION OF NON-ISOCYANATE URETHANE FUNCTIONAL LATEXES
AND CARBON NANOFILLER/EPOXY COATINGS

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Lei Meng
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INVESTIGATION OF NON-ISOCYANATE URETHANE FUNCTIONAL LATEXES
AND CARBON NANOFILLER/EPOXY COATINGS

Lei Meng
Dissertation

Approved:  Accepted:

Advisor  Department Chair
Dr. Mark D. Soucek  Dr. Sadhan C. Jana

Committee Chair  Dean of the College
Dr. Kevin Cavicchi  Dr. Eric J. Amis

Committee Member  Dean of the Graduate School
Dr. Thein Kyu  Dr. Chand Midha

Committee Member  Date
Dr. Toshikazu Miyoshi

Committee Member
Dr. Chrys Wesdemiotis
ABSTRACT

This dissertation consists of two parts. In the first part, a new class of non-isocyanate urethane methacrylates was synthesized and the effect of the new monomers on the urethane functional latex was investigated. The second part focused on a comparison of carbon nanofillers in inorganic/organic epoxy coating system for anticorrosive applications.

A new class of non-isocyanate urethane methacrylates (UMAs) monomers was synthesized through an environmentally friendly non-isocyanate pathway. The kinetics of seeded semibatch emulsion polymerization of UMAs with methyl methacrylate (MMA) and butyl acrylate (BA) was monitored. The particle size and morphology were investigated by dynamic light scattering (DLS), ultrasound acoustic attenuation spectroscopy (UAAS) and transmission electron microscopy (TEM). The minimum film formation temperature (MFFT), mechanical and viscoelastic properties were studied. It was found that the emulsion polymerization processes all proceeded via Smith-Ewart control, leading to the uniform morphology and particle size. The glass transition temperature ($T_g$) and the mechanical properties of poly(MMA/BA/UMA) decreased with the increasing chain length of urethane methacrylate monomers due to the increasing flexibility of side chains. Without the effect of $T_g$, lower MFFT and improved mechanical properties were observed from urethane functional latexes. The improved mechanical properties were due to the increasing particle interaction by forming hydrogen
bonding. Furthermore, the effect of urethane functionality in terms of the polymer composition, the location and the concentration was investigated by the batch, single-stage and two-stage semibatch polymerization of 2-[(butylcarbamoyl)oxy]ethyl methacrylate (BEM) with MMA and BA. The core-shell and homogeneous structures were evaluated by TEM, differential scanning calorimetry (DSC), and solid state nuclear magnetic resonance (SS-NMR). The compositional drift was observed from the batch polymerization. The mechanical properties were improved with increasing urethane and the best was from the urethane in the shell due to higher concentration of urethane in the continuous phase.

The inorganic/organic alkoxy silane modified epoxy coating system was formulated with carbon nanofillers, i.e. carbon black, mixture of carbon black and nanotubes, unpurified and purified non-fullerene carbon nanotubes and fullerene carbon nanotubes. Mechanical, thermal, electrical and anticorrosive properties of cured films were evaluated by tensile tests, DMTA, DSC, four-point probe method and electrochemical impedance spectroscopy (EIS), respectively. It was found that the most efficient material to enhance the electrical conductivity and anticorrosive properties of nanocomposite coating systems was fullerene CNTs.
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CHAPTER I
INTRODUCTION

The current legislative restrictions about emissions of volatile organic compounds (VOCs) have shown significant influence on the market share of the coatings industry. To lower the emission of VOCs, waterborne coatings have attracted more and more attention in both the academic and industrial field due to the use of water as the dispersing medium. However, the property of waterborne coatings is generally inferior to the solventborne coatings. The solventborne coatings still possess the dominant role in the industrial applications, especially for the heavy duty coatings. This work focus on two types of coating systems, i.e. waterborne latexes and solventborne epoxy coatings.

One part of this research investigates the effect of a new class of monomers on the urethane functional latex. Polyacrylate (PA) and polyurethane (PU) are two of the most popular resins that are widely used in waterborne coating systems. PA and PU both have their own characteristic properties related with their chemical structures\textsuperscript{1,2}, respectively. The main polymer chain of PA consists of carbon-carbon bonds, leading to advantages of excellent water and chemical resistance, weathering properties and hardness. In addition, PA has very low cost. However, the weakness of PA limits its usage in some specific applications, where good elasticity and abrasion resistance are required. On the other hand, PU possesses excellent elasticity, scratch resistance, flexibility and toughness. Therefore, it’s proposed that the beneficial properties of PU and PA can be combined for
specific applications. Physical blending is a practical way. However, the presence of PA and PU in separate particles leads to poor performance. This is due to the incompatibility of PA and PU. To improve the compatibility of the two polymers, the hybrid polyurethane/polyacrylate (PUA) has been synthesized in various ways, including intimately mixing\textsuperscript{3-4}, grafting\textsuperscript{5-12}, interpenetrating polymer networks (IPNs)\textsuperscript{13-18} and core-shell morphology\textsuperscript{19-22}.

However, the idea of incorporating carbamate monomers in latexes is rarely studied. One possible reason may be about the synthesis of the suitable carbamate monomers for emulsion polymerization. The urethane acrylate or methacrylate is generally synthesized through an isocyanate route\textsuperscript{23}. The principal limitation of the isocyanate route is the toxicity issue\textsuperscript{24}. A variety of groups, such as hydroxyl, amine, and carboxylic acid groups can react with the isocyanates. In addition, isocyanates need to be stored, handled and processed following special safety procedures. The use of hazardous isocyanates makes the urethane methacrylates very expensive materials. The replacement of the hazardous phosgene and isocyanates has become a significant concern\textsuperscript{24}.

Alternately, the primary amine can be reacted with cyclic carbonate to form the carbamate group. Therefore, a new class of urethane methacrylate monomers was synthesized through an environmentally friendly non-isocyanate route. The new non-isocyanate urethane methacrylates were characterized and used for preparation of urethane functional latexes by emulsion polymerization in Chapter III. The synthesis and characterization of the new monomers were discussed. The kinetics of emulsion polymerization of the new monomers with methyl methacrylate (MMA) and butyl acrylate (BA) was monitored. As the control, copolymerization of MMA and BA was prepared.
The morphology and particle size of all latexes were observed and compared. The influence of urethane functionality on the minimum film formation temperatures (MFFTs) of all latexes was investigated. The change of mechanical and viscoelastic properties of dry film latexes was discussed. The effect of the new monomers on the urethane functional latex in terms of the polymer composition, the location and the concentration of the functionality were investigated in Chapter IV. The effect of polymer composition was monitored and its effect on the mechanical and viscoelastic properties was investigated. Urethane functional latexes with functionality located in the core, shell or homogeneously in the particle were prepared and discussed in terms of the glass transitions, particle sizes, morphologies as well as molecular dynamics. The change of tensile strength, elongation-at-break and modulus of latexes dry film as a function of concentration and location was studied. The optimum location for improving the mechanical properties of urethane functional latexes was discussed.

Another part of this research is about the carbon nanofiller filled epoxy coating system for anticorrosive applications. Corrosion issues are of great importance in modern societies. The economy of the world has been significantly influenced by the corrosion issues directly and indirectly. The study about the corrosion costs in the United States in 2002 indicates that more than 3% of the gross domestic product (GDP) was from corrosion cost and the direct cost of corrosion is $276 billion\textsuperscript{25}. In addition, corrosion can also result in structural failures, which lead to dramatic consequences for both humans and the surroundings. Therefore, corrosion prevention has attracted many scientific studies. Most commonly, the application of a coating, especially an organic coating, such as epoxy coating\textsuperscript{26}, is used to protect metal against corrosion. The main mechanism is to provide a
physical barrier against corrosive species, such as O\textsubscript{2} and H\textsubscript{2}O. However, the defect of the organic coatings can still result in local corrosion. Therefore, the barrier properties of epoxy coatings have to be improved. Throughout the last decades, coatings science has incorporated very versatile inorganic materials into organic coating. The formed inorganic/organic hybrid products can combine the properties such as durability and stability from inorganic part and processability and toughness from organic polymers. Based on the sol-gel process, Soucek et al.\textsuperscript{27} have prepared alkoxy silane oligomer modified epoxide primers, which bears improved adhesion and anticorrosion properties.

The main drawback of epoxy resin is the inherent brittleness, resulting in reduced damage tolerance. In addition, due to its extremely high dielectric characteristics, epoxy resin has limited application to objects where the formation of electrostatic charges is the primary concern. The key to expand the epoxy coating application is to improve its toughness and electrical properties. Recent and ongoing research on polymer/carbon nanocomposites have shown that typical nanomaterials, i.e. CNTs, have enhanced various characteristics in a given polymer material. Therefore, carbon nanofiller filled epoxy coating system was formulated. In this study, Bisphenol-A (BPA) based liquid epoxide was modified with alkoxy silane oligomers through the sol-gel technique. The nanocomposite coating systems were fabricated by the solution mixing method with ultrasonic dispersion of six types of conductive fillers, i.e. carbon black, unpurified and purified non-fullerene carbon nanotubes and unpurified and purified fullerene carbon nanotubes. As the control, epoxy coatings system without any nanofiller was also prepared. The effect of carbon nanofillers on the epoxy coating systems was investigated in Chapter V. Mechanical, thermal, electrical anticorrosive and other general coating properties of
cured films were evaluated as a function of the type and concentration of nanofillers. Surface morphology of the fracture film was also studied. Finally, Chapter VI summarizes the overall results obtained from Chapter III-V.
2.1 Emulsion polymerization

Emulsion polymerization is a free-radical chain polymerization. During the reaction, a mixture of monomers or a monomer is polymerized in the presence of an aqueous solution of an initiator and a surfactant. The product formed is known as latex. Emulsion polymerization has developed into the most common way for the production of synthetic latexes since the middle 1930s. It has a number of technical advantages over other polymerization processes. First of all, the use of water as the dispersion medium is friendly to the environment and human body. It also allows excellent heat dissipation during the course of the polymerization. Similarly, high weight fractions of polymer can be obtained from the emulsion polymerization due to the very low viscosity of the emulsion. Last but not least, higher polymerization rates and molecular weights are accessible at the same time with the fact that radicals are separated within particles. In the past decades, millions of tons of synthetic latexes are developed by using the emulsion polymerization process for a variety of applications such as adhesives, paper coating, carpet backing and latex paints.
2.1.1 Components of emulsion polymerization

Emulsion polymerization is a complex heterogeneous polymerization process. It involves a dispersed (oil) phase and a continuous (aqueous) phase. The oil phase contains the monomers and other monomer-soluble components while the aqueous phase contains the water-soluble components. In the simplest emulsion polymerization system, the ingredients are comprised of water, monomers, surfactant and water-soluble initiator.

Monomers are of principal interest in emulsion polymerization as they behave as building blocks for making polymers. The requirement for monomer selection is not only based on the performance for the intended application but also other requirements dictated by surface and colloidal properties. In commercial use of latexes, cost is another critical factor in the selection of an appropriate monomer. The common monomers used in emulsion polymerization include styrene, vinyl acetate and acrylic monomers, such as C1-C8 alkyl ester of acrylic and methacrylic. Besides, some functional monomers are often used in very small amounts to provide reactive sites for crosslinking reaction and surface modification. The commonest functional monomers are methacrylic acid (MAA) with carboxyl groups and hydroxyethylmethacrylate (HEMA) with hydroxyl groups. The finite solubility of these monomers plays an important role of polymerization in the latex particles. As a matter of fact, the emulsion polymerization can’t proceed uniformly with extremely hydrophobic monomers. As industrially important hydrophobic monomers, lauryl methacrylate (LMA) and stearyl methacrylate (SMA) with very low solubility (<<0.01g/100g @ 25 °C) are unsuitable for conventional emulsion polymerization. This is attributed to the fact that the solubility of LMA and SMA are too low to swell the latex.
particles, which shift polymerization location from latex particles to monomer droplets, resulting poor conversion and formation of coagulum.

Surfactant, also known as emulsifier is added to the system for several purposes. First of all, it helps the dispersion of monomer droplets in emulsion, which serves as monomer vessel during the reaction. In addition, the formation of monomer swollen micelles will serve as nucleation sites, and stabilize the growing particles. The surfactants, which have been used in preparing emulsions, can be divided into three categories, i.e. anionic surfactants, cationic surfactants and nonionic surfactants.

The initiator is added to the system to nucleate the particles and provide a radical flux needed for polymerization. There are two considerations when selecting the initiator. First of all, the partition of the initiator in the oil phase and aqueous phases is very important when selecting the initiators for different types of emulsion polymerization. In addition, the selection of the initiators is also based on their half-life. Depending on the phase in which the free radicals are generated, initiators are divided into two categories, either water or oil soluble. The oil soluble thermal initiators include peroxides and azo compounds. Typical water soluble initiators are the persulfate thermal initiators and redox initiator systems.

For various purposes, many other components have been added during polymerization or after polymerization is complete. These components can have significant effects on the kinetic and mechanistic processes during the reaction and the properties of the final latex formed as well. For example, buffer solution is commonly used to regulate pH in emulsion polymerization and chain transfer agent is added to adjust the molecular weight and so on³⁰.
2.1.2 Process of emulsion polymerization

A typical batch emulsion polymerization reaction has been described into three intervals, i.e. Intervals I, II and III\textsuperscript{31}.

In the particle formation stage, Interval I, monomer droplets, micelles and monomer-swollen micelles are in the system and the particle nucleation happens in this stage. A small portion of the monomer is dissolved in water and another small portion enters the micelles, but the largest amount is located in monomer droplets stabilized by surfactant molecules adsorbed on the surface of the droplet. Monomer droplets are comparatively larger than micelles; however total surface area of the micelles is much larger than that of the droplets\textsuperscript{32}. The particle nucleation stage (Interval I) ends immediately after the exhaustion of micelles.

In the particle propagation stage, Interval II, only mature latex particles and monomer droplets are in the system. Under this situation, the particle number density remains relatively constant. In the presence of monomer droplets, the particles grow by propagation in the monomer-swollen particles. The monomer droplets serve as reservoirs to supply the growing particles with monomers. In addition, the monomer droplets also provide growing particles with surfactant species desorbing from the droplets surface. The particle growth stage (Interval II) ends immediately when monomer droplets disappear in the system.

In the last stage, Interval III, the latex particles continues to propagate under the monomer-starved situation to the end of polymerization. The polymerization rate continues to decrease with the decrease of the concentration of monomers inside the latex particles. Above a certain conversion of monomers into polymers, a phenomenon termed gel effect\textsuperscript{33}. 
is often observed. This phenomenon is explained with the decrease of termination rate. In the very viscous particles, the termination between two radicals is largely reduced.

2.2 Radical entry event in emulsion polymerization

Despite of various advantages of emulsion polymerization as a relatively simple polymerization process, emulsion polymerization is consisted of many mechanistic events, which are very difficult to understand. In 1988, Adams\textsuperscript{35} firstly refuted a proposed mechanism. After this, the mechanistic events have been determined separately. This is useful for understanding the mechanistic events during the emulsion polymerization. As discussed in the following, the mechanism of radical entry process can be determined by controlling the adjustable parameters.

2.2.1 The entry mechanisms

In emulsion polymerization, the polymerization happens in the particles. Therefore, the primary free radicals generated in the aqueous phase have been recognized\textsuperscript{36} to be transferred from the polar aqueous phase to the organic particle phase. In order to understand the entry mechanism, mainly collisional\textsuperscript{37}, diffusive and colloidal\textsuperscript{38} models have been proposed, but all have been refuted by Adams et al.\textsuperscript{35} in some manner. From the study by Adams et al.\textsuperscript{35}, the change of the particle surface didn’t affect the entry mechanism directly.

The now accepted ‘control by aqueous-phase growth’ (‘Maxwell-Morrison’) entry mechanism was proposed by Maxwell et al.\textsuperscript{39} by focusing the behavior in the aqueous phase before the entry event. It is qualitatively consistent with all the general experimental observations\textsuperscript{35} in comparison with all the previously proposed mechanisms. In order to
enter the particles, the initiator-derived radicals have to become surface-active oligomers (z-mer) by adding enough monomers. It is assumed that this z-mer enters ‘instantaneously’ as the only possible fate of z-mer. The reaction scheme that governs the entry process is shown in Figure 2-1.

Initiator decomposition \[ \text{Initiator decomposition} \quad I_2 \xrightarrow{k_d} 2I^* \]

Initial propagation step \[ \text{Initial propagation step} \quad I^* + M \xrightarrow{k_{p1}} IM^* \]

Subsequent propagation \[ \text{Subsequent propagation} \quad IM_i^* + M \xrightarrow{k_p} IM_{i+1}^* \]

Termination \[ \text{Termination} \quad IM_i^* + T^* \xrightarrow{k_d} \text{inert products, } i < z \]

Entry \[ \text{Entry} \quad IM_z^* + \text{latex particle} \rightarrow \text{entry} \]

Figure 2-1 The reaction scheme in the entry process

Where M is a monomer unit, I$^*$ is the initiator derived radical, IM$^*$ is a monomeric radical, IM$_i^*$ is an radical after adding i monomer units, T$^*$ is any radicals in the aqueous phase and IM$_z^*$ is a surface-active oligomer containing z monomer units. $k_d$, $k_p$, $k_t$ and $\rho$ are the rate coefficients for initiator decomposition, propagation, termination and entry, respectively.

Quantitatively considering the Maxwell-Morrison mechanism, it is the number of monomers that added to make the radicals surface-active. In other words, the radical is large enough to be surface active to enter the particles and less likely to desorb. The hydrophilicity of the initiator has significant influence on the value of z. For the commonly used persulfate-initiated systems, the critical chain length can be obtained from the following formula:

\[ z = \frac{k_d}{k_p} \]
\[ z = 1 + \text{int}\left(\frac{-23k/mol^{-1}}{RT\ln C_{\text{sat}}^w}\right) \]  

(2-1)

where the ‘int’ stands for the integer function, rounding off the value into the lower integer and R, T and \(C_{\text{sat}}^w\) are the gas constant, temperature and the saturated concentration of the monomer in the aqueous solution, respectively.

2.2.2 Experimental investigations of entry event

Maxwell et al. concluded the value of \(z\) of styrene is 2-3. This value was successfully fitted to the experimental data\(^{40-41}\). After that, Kim and Lee\(^{42}\) focused on the major premise of Maxwell-Morrison mechanism that the latex particles can capture the surface-active oligomeric free radicals in the aqueous phase instantaneously and irreversibly. It was shown by a modelling that the entry event is only affected by events within particles only at the very beginning of the the reaction. Thus, the assumptions of Maxwell-Morrison approach are solid and correct and the only essence of this theory is that the free radical must reach a certain size for it to enter the latex particle. Since the ‘control by aqueous-phase growth’ mechanism was supported by related experimental proof, radical entry has been a widely studied event.

Except for styrene, radical entry of other monomers has also been studied. The radical entry of vinyl acetate was studied by Kshirsagar and Poehlein\(^{43}\) in the seeded emulsion polymerization by doping a water-insoluble inhibitor in the seed. It was shown that 5-6 monomer units consisted the formed oligomers, which was in agreement with the Maxwell-Morrison mechanism. The surfactant-free emulsion polymerizations of methyl methacrylate (MMA) were studied by Rudin et al.\(^{44}\). The \(z\) value of the oligomers measured by MALDI-TOF mass spectrometry was estimated to be in the range 5-9, in consistence
with the Maxwell’s predictions. The value of z in MMA systems was obtained from an experimental evidence by Marestin et al.\textsuperscript{45} by putting a radical trap into the seed latex. The trap can capture the oligomers that were surface-active to enter particles. The maximum number of the monomer units of the trapped oligomers, measured by either Fourier transform infrared spectroscopy (FTIR) or gel permeation chromatography (GPC) was found to be 5, in agreement with Maxwell-Morrison mechanism. The kinetics of vinyl neodecanoate was studied by De Bruyn et al.\textsuperscript{46}. Vinyl neodecanoate is an extremely water-insoluble monomer and the critical length z was found to be only 1-2 units, supporting the developed entry mechanism.

Radical entry involving more than one monomer has also been studied. Seeded emulsion copolymerizations of styrene/acrylic acid (AA), styrene/MAA and styrene/MMA\textsuperscript{47-48} were studied by Poehlein and co-workers. The oligomers were characterized by a range of spectroscopic techniques, i.e. FT-IR spectroscopy used to measure the oligomer composition and mass spectroscopy used to measure the molecular weight, respectively. It was found that critical length was significantly influenced by the overall composition of a copolymer radical. With the increasing hydrophilic nature of copolymer, the length increased, which is in agreement with Maxwell-Morrison mechanism. Dong and Sundberg\textsuperscript{49} developed a lattice model to estimate the critical length of entry radicals. The model also predicted that the significant effects of overall composition of a copolymer radical on the critical length, while the sequence of adding monomers had little influence, which is consistent with experimental results.
2.3 Particle formation in emulsion polymerization

Particle formation is one of the important events in emulsion polymerization. Many kinetic studies have been done regarding this process.

2.3.1 The fundamentals of particle formation

It is generally accepted that there are three major models for particle formation in emulsion polymerization, which are categorized as below depending on the location of nucleation:


2. *Homogeneous nucleation*: Growing free radicals in the aqueous phase, exceeding solubility limit, precipitate to form a particle nucleus and polymerization proceeds therein.

3. *Droplet nucleation*: Free radicals growing in the aqueous phase enter monomer droplets and polymerization proceeds in the droplets.

*Particle formation: below the CMC*

Below the CMC, homogeneous nucleation is predominant and is illustrated in Figure 2-2. Priest\(^{36}\) proposed the qualitative theory; monomers with high water solubility proceeds more likely by aqueous phase nucleation. The best-known quantitative model was proposed by Fitch and co-workers\(^{50}\) and improved by Hansen et al.\(^{51}\). According to this model, growing free radicals propagate to a length \(j_{\text{crit}}\) to be insoluble in the aqueous phase. Then they are swollen with monomers to form precursor particles. Stable particles are formed from these precursor particles by propagation or coagulation. Similar to consideration of oligomer needed to be surface active, the value of \(j_{\text{crit}}\) was estimated in
terms of thermodynamic by Maxwell et al.\textsuperscript{39} for the persulfate initiators; for example, $j_{\text{crit}} = 5$ for styrene.

![Figure 2-2 Representation of the homogeneous nucleation mechanism below CMC](image)

*Particle formation: above the CMC*

Micellar nucleation, which predominates above the CMC, is illustrated in Figure 2-3. The well-known Smith-Ewart model\textsuperscript{52} originally is the foundation of the “micelle nucleation” mechanism and has been extended\textsuperscript{28} to account for a variety of phenomena. Based on the accepted ‘control by aqueous-phase growth’ mechanism\textsuperscript{39}, the oligomeric radicals propagate in the particles and the growing particles consume the surfactants in the aqueous phase. At the same time, the radicals to the length $j_{\text{crit}}$ can homogeneously nucleate new particles, which can be benefited from the consumption of free surfactant and the entry and exit events of radicals. Particle formation ceases when stable particles are formed. It is noted homogeneous nucleation can still occur above CMC, but the micellar nucleation dominates.
Figure 2-3 Representation of micellar nucleation mechanism above CMC

*Particle formation in miniemulsion system*

Droplet nucleation predominates in the miniemulsion polymerization as an important source of particle formation. In this special system, the particle size is generally less than 0.5 μm. The submicron monomer droplets are obtained by breaking up emulsions under high shear of a sonicator. With submicron monomer droplets present in the system, surfactant/costabilizer system is used for stabilizing the submicron monomer droplets. In this situation, the submicron monomer droplets can compete successfully with any remaining micelles to capture the free radicals generated in the aqueous phase. In addition, the micelles will be broken up to release free surfactant to support a larger interfacial area due to the growth of the submicron monomer droplets. The droplet nucleation is led to be the dominant particle nucleation in the miniemulsion polymerization.

2.3.2 Experimental investigations of particle formation

Particle formation significantly influences the particle size and its distribution, which is important to control the population of particles in the plant production. Particle formation is generally influenced by particle growth in an emulsion polymerization
reaction. It was found by Nomura that particle formation is enhanced\textsuperscript{54} when the rate of growth was depressed by polymerization in the presence of small quantity of monomer. It was also reported\textsuperscript{55-59} that the number of particles generated in semibatch processes were much larger than the batch processes.

Particle nucleation has been studied by a few groups in the semibatch processes to figure out how reaction conditions (the surfactant concentration \([S]\) and monomer feed rate \(R_a\)) affect the particle size and number \((N_p)\). Different monomers were involved: for MMA and butyl methacrylate (BMA) investigated by Puig’s group\textsuperscript{60-61}, the exponent values of particle size and particle number in terms of \([S]\) and \(R_a\) were found to be around \(-0.20\pm 0.01\), \(0.17\pm 0.03\) and \(0.68\pm 0.02\), \(-0.48\pm 0.01\), respectively; for a series of monomers, eg. Styrene, butyl acrylate (BA), MMA and vinyl acetate (VA) researched by Sajjadi and co-workers\textsuperscript{62-64}, different exponent values of final \(N_p\) with respect to \(R_a\) were reported as \(-0.65\), \(-0.68\), \(-1.98\) and \(-2.36\), respectively. In all these studies cited above, the end of particle nucleation was not clearly notified. Therefore, it’s not surprise to observe the difference of reported values of the dependence of particle size and number on \(R_a\) and \([S]\). The data at the end of nucleation needs to be obtained to exclude the difference of reported values. In Sajjadi’s recent studies\textsuperscript{65}, the end of nucleation, when the change of particle numbers was negligible, was closely monitored in the monomer-starved semicontinuous polymerization of styrene. In this way, the effects of particle growth on nucleation were excluded. It was found the exponent values of final \(N_p\) with respect to \(R_a\) and \([S]\) were close to the theoretical values\textsuperscript{66}. The model for semibatch polymerization of styrene indicated the exponent values of final \(N_p\) with respect to \(R_a\) and \([S]\) were around \(-2/3\) and 1, respectively. In comparison with the batch process, semibatch process showed a higher dependence on the reaction conditions.
That is to say, the number of particles can be controlled more easily in monomer-starved polymerization.

Droplet nucleation predominant in the miniemulsion polymerization has also been studied. Particles from miniemulsion polymerization are expected to be smaller and more uniform than that from macro-emulsion polymerizations. The droplet nucleation was initially studied by Ugelstad et al.\textsuperscript{51}. Since then, many studies have appeared to study more in-depth characteristic of the miniemulsion systems. It was found by Miller et al.\textsuperscript{67} that the nucleation occurred in the early conversions. In their following studies, polymers were incorporated into miniemulsion droplets before the reaction started. It was reported\textsuperscript{68-69} that the rate of polymerization was found to be enhanced. The understanding of the “enhanced droplet nucleation” was suggested by the Lehigh group\textsuperscript{70} to be attributed to the extra stability of the miniemulsion droplets. With the extra stability both prior to and during the polymerization, the polymerization rate was increased in and the particle size was reduced. The more polymer are in the droplets, the more they can contribute into droplet nucleation\textsuperscript{71}. It’s proposed by Sajjadi et al.\textsuperscript{72} that the stability of the droplets have great effect on the droplet nucleation during the batch and semibatch miniemulsion polymerizations. With the presence of polymers, the same number of polymer particles was observed from both batch and semibatch polymerization. However, in the absence of polymers, batch reaction generated a larger number of particles, which was attributed to longer presence of droplets in the batch reaction.

2.4 Particle morphology development and Characterization

Polymer latexes have been widely used in various everyday products. There are two main reasons. On the one hand, it is because of advantages of emulsion polymerization,
i.e. high polymerization rates and high molecular weights at the same time, use of water as environmentally friendly solvent and no heat transfer limitations. On the other hand, polymer latexes can be designed as multiphase to combine properties from each phase. For example, the lower film formation temperatures and good mechanical properties of the formed films, which always contradict with each other, are desirable from the industrial requirement. This motivated people to design the multiphase polymer latexes for coatings, adhesives and other latexes applications. In these applications, the particle morphology is essentially important to obtain high performance latex products. The polymers formed during different stages have to have a tendency to be phase separated and result in the multiphase morphology within the particles.

2.4.1 Typical process for producing composite particles

There are three ways to get the heterogeneous morphologies. The core-shell structure, as the most popular multiphase latexes, is generally produced by using two distinct and separate emulsion polymerization stages. In the commonly commercial process, a small loading of initial monomers is polymerized in the first stage and the resulted polymer particles are often referred as the seed particles for the second stage. In the second stage, most of the rest of the monomer are semicontinuously fed along with initiators. By controlling conditions properly, the polymers formed in the second stage will grow within the existing first stage particles and achieve certain particle size and composition. The core-shell structure is commonly consisted of incompatible polymers to combine good properties for end use applications. Generally, the hybrids can be consisted of acrylics with polyurethanes, polysiloxanes, epoxy resins and alkyd resins. Moreover, the outermost region of the particle can be surface modified with functional groups to
incorporate reaction sites. The functional groups could be hydroxyl group, carboxylic acids, amines, epoxies or isocyanates. In addition, the gradual change of the chemical composition also helps to form heterogeneous structures. With the monomer feed kept constant, the molecular characteristic changes can be achieved by separately incorporating crosslinkers or chain transfer agents during feeding monomers.

2.4.2 Characterization methods

With a lot of emphasis on the significance of the control of complex particles, it’s also important to characterize these morphologies. A lot of techniques have been used and more than one characterization are generally used to interprete the exact morphology. The recent characterization methods are generally divided into two groups: one is mainly based on the contrasted observation of the morphology of composite particles, such as scanning electron microscope (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM); another is less direct way to indicate the composite morphology, such as differential scanning calorimetry (DSC), $^1$H, $^{13}$C nuclear magnetic resonance (NMR) and dynamic mechanical thermal analysis (DMTA).

Electron microscopy is the direct way to study the morphology by imaging. It is based on the contrast between domains and chemical staining is usually an effective way to increase the contrast between heterogeneous phases. For most acrylic latexes, the simple way is to use styrenic monomers. The styrenic monomers can be easily stained because of the electron density. By incorporating the chemically stained syreneenic polymers, other polymers can be distinguished due to the electronic contrast. In comparison with TEM as a bulk observation method, AFM is primarily a surface method, making interpretation simpler. Phase contrasting can be done in the ‘tapping mode’ by recording mechanical
properties of each phase. Indirectly, the DMTA and DSC are widely used to determine the glass transitions in polymer blends and complex phase polymers for long time. The advantage of DSC results from sample preparation, which doesn’t require processing the polymer latexes into a film for analysis. The multiphase of composite latexes is characterized from the glass transitions. Around T_g, the change of the heat capacity of each polymer phase is representative of the amount of that phase. Therefore, the amount of each polymer phase can be quantified by comparing the heat capacity changes of each component with that of the respective polymer. The remaining will then be mixed in the interface between the two polymer phases. However, only glass transition data could not give a conclusion of the exact morphology of the particles. Therefore, it is widely used to quantify the amount of interfacial polymers in the particles. DMTA is used to characterize the multiphase structure in the same way as DSC. The glass transitions are related to the distinct phases. Yet, DMTA also has been limited to determine the presence of multiphase, instead of concluding the specific morphology. NMR has also been a good candidate for morphology study. Based on the temperature dependence of spin relaxation time of carbons or protons, the phase information can be obtained. Solid-state NMR has successfully been applied to study the molecular dynamics in amorphous, semi-crystalline polymers as well as supper molecular structures. McGrath et al. found that the temperature dependences of the solid-state NMR spectra with the Hartmann-Hahn cross polarization technique. The broadening corresponded to the segmental relaxation properties. Therefore, segmental dynamics can be studied by solid-state NMR spectroscopy. In another way, solid-state NMR methods can be used based on 1H spin-diffusion with the dipolar filter technique. In the spin-diffusion experiment, the dipolar filter is very sensitive to the
dynamics of polymers, i.e. different polymer chain mobility. The dynamic difference of
different polymer chains in the system can be correlated to different \( T_g \)s of different
polymers. Detailed morphology information\(^{80-81}\) can be obtained from the spin-diffusion
experiments.

Other techniques, such as minimum film-forming temperature (MFFT), surfactant
absorption, scattering technique and fluorescence spectroscopy, have also been explored
to be used in analyzing the morphology of composite latexes. The widespread of these new
techniques is limited due to their own limitations. For example, in order to model the
scattering data, it’s necessary to assume a particular morphology when using small angle
neutron scattering (SANS). The availability and cost of the equipment is another significant
draw back.

Since each technique has their own limitation and advantages, some researchers
have successfully correlated the observed morphology of latex particles by combining
several characterization techniques\(^{82-84}\). The combined methods have overcome drawbacks
of the individual characterization way.

Kirsch et al.\(^ {82}\) prepared core-shell particles with poly\((n\)-butyl acrylate)/poly(methyl
methacrylate) (PBA/PMMA) as the core and PMMA as the shell. The particle morphology
was quantitatively determined by TEM and solid state \(^1\)H spin diffusion NMR. It was found
that both the coverage and thickness depended on the shell content and the compatibility
of the phases. Kirsch et al.\(^ {83-84}\) also used the AFM methods to study the same polymer
systems. Particle morphology of freeze-dried and tempered single particle characterized by
AFM was consistant with TEM and NMR results.
The glass transition of polymer blends has been characterized with the differential of heat capacity, \( \frac{dC_p}{dT} \), with temperature signal\(^{85}\). For the miscible polymer blends, a single transition exists while more than one transitions exist for the immiscible polymer blends. Based on the sensitive differential of heat capacity to the polymer components, Song et al.\(^{85}\) developed the combination of modulated differential scanning calorimetry (MDSC) method and TEM. The thickness of core, shell and interphase and the weight fraction of each component were quantitatively determined.

2.5 Film formation from latexes

Latexes are typically dispersed polymer solid in water. The latex film is formed by coalescence of polymer particles. The ability of a given latex to coalesce into a film is characterized by its MFFT. MFFT is defined\(^{2}\) as the lowest temperature for latexes to form a continuous film. In most of the time, the main controlling factor of MFFT is the \( T_g \) of the polymer particles. However, the development of multiphase latexes makes it difficult to correlate MFFT to different \( T_g \) values of different components in the polymer particles. In the experiment determining MFFT, samples are placed on a temperature gradient stage. The critical temperature at which the film is formed is selected as the MFFT of the polymer latexes. Below the measured MFFT, the solidified polymer particles can be easily powdered.

The film formation of latexes is generally divided into three overlapping steps as shown in Figure 2-4:

1. The void-free arrays of polymer particles are formed in the first step. In this step, water and water-soluble solvents evaporate and particles approach each other, leading to the close packed particles.
2. The second step is the deformation of the particles that leads to a weak film. In this stage, a temperature higher than MFFT is required in order to complete deformation of particles. With the close packed latex particles, the polymer particles start to deform. The generated capillary forces from spaces between particles can overcome the steric and electrical repulsions between particles. It has been found that the broader distribution of particles helps form a film rapidly.

3. The last step, also the relatively slow step, is the coalescence. The polymer chains in one particle diffuse into another particles and entangle with other chains to strengthen the film. This step is crucial to the film properties. The temperature must be higher than the glass transition temperature of polymer particles in order to get the complete inter diffusion.
Figure 2-4 Schematic representation of main steps in latex film formation (a) particles in latexes as water evaporates. (b) particles approaching each other after water evaporates. (c) deformation of particles at T>MFFT. (d) inter-diffusion of polymer chains to obtain a continuous film

Therefore, solutions have to be found to figure out the problems that the film formation requires T_g low enough while the properties will then be compromised. Volatile solvents can help coalescence, but the emission of volatile organic compounds (VOC) has been limited by environmental regulations. Other methods involve the design of the latexes. The particles can be designed with a gradient of T_g to have the relatively lower T_g at the outer periphery. Core-shell latexes are involved with the hard core controlling film properties and soft shell controlling the film formation.

2.6 Hybrid polyurethane/acrylic latexes

Polyacrylate and polyurethane, as the most popular resins in latexes coatings, both have very good comprehensive properties. The acrylic polymers were first introduced in the 1950s. Since then, the application of acrylic polymers has been widely explored as coatings, carpet binders, additives, inks and other applications. The good properties of acrylic latexes include hardness, water resistance as well as the weatherability. Also, acrylic polymer are relatively cheap. Since the middle 1970s, commercial application of aqueous polyurethane dispersions (PUDs) has become widespread due to the technical significance and environmental issues. With the morphology of hard/soft domain, PUDs possess excellent properties, such as elasticity, scratch resistance, flexibility and toughness. Physical blending is a practical approach to make use of each polymer’s properties for specific applications. However, the obtained physical blends do not show the properties as expected from the “rule of mixtures”. In many cases, the superior performance
properties are compromised. The possible reason could be that the two polymers are not compatible with each other on the molecular level, leading to the presence of PU and PA in separated particles as shown in Figure 2-5. Therefore, the performance is diminished due to the discontinuous phase morphology.

![Diagram of Polyurethane and Polyacrylate particles](image)

Figure 2-5 Physical blends of PU and PA: PU and PA polymers remain in separated particles

2.7 Development of hybrid polyurethane/acrylic latexes

To overcome the poor compatibility of the two polymers, many studies have been done to deal with the hybrid polyurethane/polyacrylate (PUA).

2.7.1 The crosslinked blends

At the very beginning, one proposal suggested developing one–pack crosslinkable composite polymer emulsion systems, in which different reactive groups were incorporated into each polymer. A novel crosslinking system was used to obtain urethane acrylic composite polymer emulsions to combine the advantages of the two polymers. Keto groups were incorporated into PA and the hydrazine was used to chain extend PU. During the film formation process, covalent bonds were formed as shown in Figure 2-6. Crosslinking reactions were observed after several days of curing at ambient temperature. Good properties were obtained with the formed IPN (Interpenetrating Polymer Network)-like
structure, such as good elasticity, toughness and abrasion resistance. Therefore, a single package of crosslinkable blends was obtained. It was also mentioned that there is another possible resin system\textsuperscript{90}, in which both of the PU and PA had carbonyl groups to be reacted with the dihydrazide crosslinker.

\[
\begin{align*}
R_1 & \quad \text{Polyacrylate} \\
R_2 & \\
R_3 & \quad \text{Polyurethane} \\
C\equiv O & + \text{NH}_2\text{-NHR}_3 \rightarrow C\equiv\text{N-NHR}_3 + \text{H}_2\text{O}
\end{align*}
\]

Figure 2-6 Crosslinking mechanism in the crosslinked blends

2.7.2 The PUD seeded emulsion polymerization

To incorporate both of polymers in the same particles, the most common method is to use a polyurethane dispersion as the seed for the emulsion polymerization\textsuperscript{20, 87-88, 91-94}.

M. Hirose et al.\textsuperscript{91} prepared the core-shell PU/PA latexes by soapfree emulsion polymerization by introducing ketone-hydrazide crosslinking systems as shown in Figure 2-7. The three types, i.e. A/U-type, U/A-type and A/U-A-type latexes were prepared and the ketone-hydrazide crosslinking reaction were introduced into these latexes. The crosslinking reaction was confirmed from thermomechanical analysis model study by FT-IR. However, the formed network was not strong enough, indicated from the sharply drop of the storage modulus.

Figure 2-7 The core-shell type acrylic-polyurethane hybrid aqueous emulsions
Kukanja et al.\textsuperscript{87} prepared PU/PA hybrids by semibatch emulsion polymerization with a polyurethane dispersion seed. The hybrids were compared with the equivalent physical blends in terms of acrylic and polyurethane contents. Improved miscibility was observed from DSC with a single $T_g$ and the improved mechanical properties.

Wu et al.\textsuperscript{92} also used polyurethane dispersions as the seed to prepare the core-shell urethane/ acrylic composite latex. The FT-IR and X-ray photoelectron spectroscopy (XPS) were used to quantitatively analyze the structure and composition of the surfaces of the films obtained from the composite latex. It was found from FT-IR and XPS that the richer PU was observed at surfaces compared with the bulk composition. This indicated that there could be reorientation happening during the processes of the latexes preparation and/or film formation.

Lee and Wang\textsuperscript{93} prepared PU/P(tert-BA) hybrids emulsified with the help of ionic polyurethane dispersions. With the fixed content of ionic PU dispersions, particle sizes and viscosity of the hybrid latexes showed an ascending trend with increasing tert-BA. Moreover, the shifting of two $T_g$s in the composite toward each other and enhanced the thermal and abrasion resistances may imply the improved compatibility of the hybrid dispersions. This was presumably attributed to the increasing hydrogen bonding interactions with the increasing tert-BA contents.

Brown et al.\textsuperscript{88} compared the PU/PA hybrids with the physical blending in terms of the acrylic emulsion design parameters, i.e. the particle size, the molecular weight, the acid content and the choice of $T_g$. No clear trends were observed with changes of the particle size and the acid content. The hybrids showed better mechanical performance than the corresponding blends. The difference in performance was attributed to twofold. On the
one hand, the increased phase mixing in the hybrid was found from modulated DSC results. The qualitative analysis results showed that there were approximately 20–30% of PU and 35–50% of PA in the hybrids. On the other hand, AFM analysis showed the acrylics were dispersed well in the hybrids.

Chai et al.\textsuperscript{54} prepared the nanograde Core-shell polyurethane/polyacrylate composite emulsion by soap-free seeded emulsion polymerization with polyurethane as the shell and with polyacrylate as the core. Two transitions for films from composite latex, and three transitions for the film from blend latex were observed from DSC results. It was also found that the composite latex showed much lower N-H peaks from FT-IR results compared with the blends. Based on the DSC and FT-IR results, the crosslinking reaction was assumed to exist in composite emulsion and was claimed to result in a superior performance than blends. A possible crosslinking mechanism of composite emulsion was proposed. Chai et al.\textsuperscript{20} also studied particle sizes in terms of variables, such as the content of the hydrophilic chain extender, PU and PA and initiators. It was found the amounts of the hydrophilic chain extender showed significant influence while the others showed little influence on the particle sizes.

2.7.3 The intimately mixing IPN-like structure\textsuperscript{3, 13}

New NMP-free, low odor urethane-acrylic hybrid polymers were prepared by Air Products and Chemicals, Inc.\textsuperscript{13}, motivated by the market needs. The acrylic monomers were mixed with the polyurethane prepolymer as a homogenous mixture. The intimately mixing IPN-like structure was formed from the concurrently polymerization of urethane and acrylics. There was a broad glass transition temperature from DMA results for the formed hybrid polymers. The IPN-like morphology apparently brought outstanding properties for the hybrids.
Kim et al. investigated the properties of PU/PA hybrids in terms of the acrylic content. Hybrid latexes with 0-40 wt% acrylic contents based on the PU content were prepared by soap free emulsion polymerization. Below 40 wt%, the hybrid latex samples showed unimodal distributions whereas a bimodal distribution at 40 wt%. With the increasing acrylic monomer content, the single tan delta peak was broadened and extended to higher temperature range. These findings for all hybrids were strong evidences for IPN-like structure, in which different polymer molecules were intertwined, resulting good polymer–polymer mixing. It was found that the best balance of performance was from the hybrid with 30 wt % acrylic monomer content.

2.7.4 Grafting between two polymers

In 1989, Mekras et al. prepared the hybrids by incorporation of unsaturation into the polyurethane with synthesized erythrol. Therefore, the unsaturated side chains can undergo radical polymerization with acrylic acid and there formed the grafting between PU and PA.

Saija et al. prepared the hybrids with grafting between two polymers. Maleic anhydride was used in the process of preparation of unsaturated urethane macroionomers. The solubility tests showed the grafting efficiency was around 40%, which clearly appeared that maleic double bond successfully copolymerized with the acrylic monomers.

Based on the same strategy with the use of maleic anhydride, Athawale et al. prepared polyurethane acrylate hybrid emulsions. The chemical and mechanical properties were improved due to the better compatibility induced by the grafting in hybrids. The optimum coating performance properties were exhibited with equal weight of PU and PA in the hybrids.
Generally, the grafting obtained by the above chemical induction is too low to enhance the properties of the hybrids. In order to increase the grafting ratio, $^{60}\text{Co }\gamma$-ray radiation was used as the initiation source in preparation of the hybrid emulsions based on the solvent-free method$^{12}$. The FTIR analysis proved the enhanced grafting reaction between acrylate with the polyurethane dispersion induced by $60\text{Co }\gamma$-ray radiation.

Zhang et al.$^{14}$ synthesized the Polyurethane/Polyacrylate hybrids via a solvent-free method. Aromatic toluene diisocyanate (TDI) of low price was used to replace high cost and low polar IPDI in the cases of less demand for yellowing resistance. In this method, the hydroxyethyl acrylate was used to endcap the urethane prepolymer. In this way, the compatibility of acrylate and polyurethane was improved by grafting reaction between unsaturated polyurethane and acrylics. The stable emulsion was obtained with the molar ratio of NCO/OH groups being 1.18.

In order to solve the instability of the fluorinated emulsion in the previous research, Zhifang Zhao et al.$^{19}$ copolymerized fluorinated polyurethane with fluorinated polyacrylate by endcapping the polyurethane prepolymer with the hydroxyethyl acrylate (HEA). Both polyurethane and polyacrylate were fluorinated based on the traditional theory of similarity and compatibility. With the increasing HEA content, thermal stability, tensile properties and antifouling ability of the hybrids were improved as well as the $T_g$. In addition, the tensile strength of the films increased 50%.

The end capping agent could also be 2-hydroxpropyl acrylate (HPA)$^{96}$. It was found by H. T. Zhang et al. that addition of HPA improved the strength of latex films.
2.7.5 The IPN structure

The interpenetrating polymer network (IPN) is also used, in which interlocking structure is formed without covalent bond between the polymers\textsuperscript{11, 97-99}.

K. H. Hsieh and L. M. Chou\textsuperscript{97} prepared IPNs of PU and polystyrene ionomers by simultaneous bulk polymerization. The polyurethane and polystyrene ionomers contained tertiary amine and carboxyl groups, respectively. With the ionic interaction between AA and triethylamine (TEA), both the polyurethane (PUN) and poly(styrene–acrylic acid) (PSAA) chains had grown intimately, leading to the IPN in the final polymer systems. The single phase morphology was observed for the polymer systems with charge groups. The compatible polymer system showed increased mechanical strength and crosslinking density.

Eli Ruckenstein and Hancquan Li\textsuperscript{98} synthesized semiinterpenetrating polymer network latexes by using the concentrated emulsion of a partially cross-linked PU, MMA and an initiator. The interpenetration was achieved in the latexes from the DSC and TEM studies. It was found that the elongation at the break point and the toughness increased, but the tensile strength decreased with the increasing ratio of PU/PMMA. The influence of the molar ratio of isocyanate to hydroxyl groups on the elongation at the break point and the toughness was optimized when isocyanate and hydroxyl groups had equal molar for concentrated emulsion polymerization.

Novel PU/PA latex interpenetrating networks (LIPNs) were prepared via the soap free emulsion polymerization by Su Chen and Li Chen\textsuperscript{99}. The effects of different PU/PA ratios and the NCO/OH molar ratio were studied. The mechanical properties were found to be improved due to the increasing interpenetrating among the two polymers. From the
DLS results, larger particle size was obtained when the higher NCO/OH molar ratio or more acrylic content was used.

Yongshang Lu and Richard C. Larock\textsuperscript{11} prepared new hybrid latexes by using emulsion polymerization. In this method, the soybean oil-based polyol (SOL) was used to prepare the PU dispersion. The thermal and mechanical properties of the resulting latexes showed a significant increase. About 15-60 wt\% of the final resulting latexes was SOL, leading to a new way to prepare hybrid latexes with using renewable resource.

2.8 Non-isocyanate carbamate groups

Due to its outstanding properties, such as elasticity, toughness and abrasion resistance, PUs have drawn significant attention from the industrial fields. The wide applications of polyurethane coatings can be found in furniture, automotive and packaging coatings. Generally, polyurethanes are produced by the reactions between isocyanates and polyols, as shown in Figure 2-8. The isocyanate can be either aliphatic or aromatic. Aromatic isocyanates have relatively low cost compared with aliphatic isocyanates, making aromatic isocyanates based polyurethane good for applications that don’t require UV resistance. The polyol reagent can be polyester, polyether, or polycarbonate.

\[
\text{Reactor} 
\begin{align*}
n \text{OCN-R-NCO} + n \text{HO-R'-OH} & \rightarrow \left(\text{O-R'-OC-NHR-NH} \right)_n \cdot 
\end{align*}
\]

Figure 2-8 The reaction between isocyanates and hydroxyl groups

The use of isocyanates as the starting material is very troublesome in terms of their toxicity, high reactivity at room temperature, storage and handling process\textsuperscript{100}. First of all, the use of isocyanate is very toxic. A variety of reactive groups, such as hydroxyl group, amines, and carboxylic acids can easily react with the isocyanates. Therefore, isocyanates
are very toxic to human body, since there are many materials having reactive substituents\textsuperscript{101} in the body. Hazardous monomers (phosgene and isocyanates) are generally used for synthesis of urethane monomers. In addition, in current industrial processes, the use of expensive and hazardous isocyanates often makes polyurethane the most expensive resin in a formulation. This in many cases hinders its use in an optimum amount. The use of isocyanates in a large scale requires secure industrial equipments to store, handle and process by following special safety procedures. This is especially true when volatile isocyanate is used for preparation of moisture curing urethane coatings. Because of the sensitivity and reactivity of isocyanates with water, it’s very essential to isolate isocyanate groups before the application. Otherwise, irreversible reactions between the polyisocyanate component and isocyanates with the moisture would undergo, as shown in Figure 2-9 and result in a hardened product\textsuperscript{102}. In the industrial applications, the moisture curing PU coatings are generally formulated with the use of additional moisture scavenging compounds to partly solve the problem.

\[
\begin{align*}
R-\text{NCO} + H_2O & \rightarrow \left( \begin{array}{c} H \\ R-N-C-OH \end{array} \right) \rightarrow RNH_2 + CO_2 \\
RNH_2 + R-\text{NCO} & \rightarrow \begin{array}{c} H \\ R-N-C-N-R \end{array}
\end{align*}
\]

Figure 2-9 The reaction between isocyanates and water

Alternately, the urethane functionality can be formed by reacting the primary amines with cyclic carbonates\textsuperscript{103-104}, as shown in Figure 2-10. As a pioneering work in the field of PU preparation, Groszos et al.\textsuperscript{105} first proposed the new method of preparing a polyurethane in 1957. In the new method, the carbamate groups were synthesized from the reaction of the cyclocarbonate and polyamine urea. This method also inspired the starting

34
of PU preparation without the use of isocyanate. Since then, the study of non-isocyanate polyurethane has been prevalent in the field of PU preparation. The commercially available difunctional hydroxyalkyl urethanes, which act as blocked isocyanates to produce desired polyurethane\textsuperscript{106}, were patented in 1989 by Blank, W. from King Industries by applying the reaction of alkylene carbonates with aliphatic diamines. A lot of studies\textsuperscript{107-108} have been reported on the substituent effect of the cyclic carbonate on the reactivity and selectivity of the ring opening reactions.

\[
R-O-C\overset{\text{H}}{\text{H}}\overset{\text{CH}_2}{\text{C}}\overset{\text{CH}_2}{\text{O}} - \text{NH}_2-R'-\text{NH}_2 \rightarrow R-O-C\overset{\text{H}_2}{\text{H}}\overset{\text{H}_2}{\text{C}}\overset{\text{O}}{\text{C}} \text{-NH}R'-\text{NH}_2
\]

\(R=\text{aliphatic, aromatic groups}\)
\(R'=\text{aliphatic groups}\)

Figure 2-10 The reaction between cyclo-carbonates and amines

2.8.1 Mechanism for non-isocyanate carbamate groups preparation

Garipov et al. studied the reaction of cyclic carbonate groups with amino groups and proposed the nucleophilic reaction mechanism as shown in Figure 2-11. In the first step, the aliphatic amine attacks the carbon in the carboxyl group. This leads to the formation of a tetrahedral intermediate. Then, the tetrahedral intermediate will be attacked by another amine and deprotonated by the removal of hydrogen ions. In the last step, the carbon-oxygen bond in the carboxyl group is broken, resulting in a new alkyl-oxygen ion. This step is influenced by the substituent groups to form two isomers. The final product will be formed by combining the alkyl-oxygen ion with hydrogen.
The mechanism for reaction between cyclic carbonates and amines can be effectively catalyzed with base-, acid- or metal-type catalyst. Five-membered cyclic carbonates, unlike six- or seven-membered cyclic carbonates, scarcely polymerize due to the stability of five-membered rings. The reaction product of mono-substituted cyclic carbonates with primary amines were two isomers as shown in Figure 2-12. It was shown that the final product contained the isomer bearing secondary hydroxyl group around 70–75%. The substituent effect was thoroughly studied. With the presence of an electron-withdrawing group, the electrophilicity of the carbonyl carbon increased, leading to more urethanes with secondary hydroxyl groups.
The reaction of mono-substituted 1, 3-dioxolan-2-one with primary amines

2.8.2 Reactants for the non-isocyanate carbamate groups preparation

In preparation of the non-NCO urethane, amines are one of the key reactants. So many kinds of amines are available as commercial products that the selection of amines is very flexible. The amines could be aromatic or aliphatic, monoamine, diamine or polyamine, small molecules or oligomers. The lower basicity of aromatic amines retards the reaction. The presence of phenyl group leads to the low reactivity due to the steric hindrance.

Cyclic carboantes are another key reactant. The cyclic carboantes are widely used because of their good properties, such as the high boiling points, biodegradability, very low toxicity and wide reactivities. The cyclic carbonates could be mono-, bi-, tri-, and functional cyclic carbonate\textsuperscript{116-117}. The most commonly used are ethylene carbonate (EC) and propylene carbonate (PC), which have been used a lot in the past four decades.

2.9 Inorganic/Organic Hybrid coatings

Throughout the last decades, versatile inorganic materials have been incorporated into organic coatings to form a variety of inorganic/organic hybrids for various applications\textsuperscript{118-120}. The hybrid products have combined the unique properties such as
durability and stability from inorganic part and processability and toughness from organic polymers.

The hybrids are generally prepared from a sol-gel process of hydrolysis and condensation. The sol-gel process is a chemical reaction process, in which the metal or semi-metal salts undergo hydrolysis and condensation. The alkoxy silane precursors has been proved to improve the adhesion to the metal substrates as well as corrosion prevention of the metals\textsuperscript{121-125}. Tetraethoxysilane is one of the most common sol-gel precursors used. As the thoroughly studied sol-gel precursors, the sol-gel process of tetraethoxysilane is shown in Figure 2-13. The sol-gel process starts with the hydrolysis by reacting with a water molecule to form the silanol. Two silanols or silanols with alkoxy silanes can react to produce siloxanes and condense out a water molecule or an alcohol, respectively. The reverse reactions of the hydrolysis and condensation can occur at the same time. The mechanism of the hydrolysis reaction is believed to be $SN_2$ type, as depicted in Figure 2-14. Under acidic conditions, the alkoxide groups are easily protonated. Therefore, the silicon atom is easily attacked by water due to the lower electron cloud density. The transitional adduct gives a silanol with an alcohol as the byproduct.

\[
\begin{align*}
\text{Hydrolysis of alkoxy silanes} & \quad \equiv\text{Si(OR)} + \text{H}_2\text{O} \rightarrow \equiv\text{Si(OH)} + \text{ROH} \\
\text{Condensation between silanols} & \quad 2\equiv\text{Si(OH)} \rightarrow \equiv\text{SiOSi≡} + \text{H}_2\text{O} \\
\text{Condensation between silanols and alkoxy silanes} & \quad \equiv\text{Si(OH)} + (\text{RO})\text{Si≡} \rightarrow \equiv\text{SiOSi≡} + \text{ROH} \\
\text{Re-esterification} & \quad \equiv\text{SiOSi≡} + \text{H}_2\text{O} \rightarrow 2\equiv\text{Si(OH)} \\
\text{Hydrolysis of siloxanes} & \quad \equiv\text{SiOSi≡} + \text{ROH} \rightarrow \equiv\text{SiOH} + \equiv\text{Si(OR)} \\
\text{Alcoholysis of siloxanes} & \quad \equiv\text{Si(OR\textsuperscript{1})} + \text{R\textsuperscript{2}OH} \rightarrow \equiv\text{Si(OR\textsuperscript{2})} + \text{R\textsuperscript{1}OH}
\end{align*}
\]

Figure 2-13 The sol-gel process of tetraethoxysilane precursor
Polyurea and polyurethane hybrids have been prepared by using a variety of sol-gel precursors\textsuperscript{126-132}. In these systems, the organic polyurea or polyurethane possessed the improved mechanical properties and the inorganic polysiloxane provided good adhesion and corrosion resistance. Similarly, alkoxysilane oligomer modified epoxide primers were prepared\textsuperscript{133}, which also bears improved adhesion and corrosion properties. The mechanism for the improved properties was proposed in Figure 2-15.

\[ \text{Figure 2-14 The mechanism of acid catalyzed hydrolysis of alkoxysilanes} \]

\[ \begin{array}{c}
\text{Si} - \text{OR} & \xrightleftharpoons{\text{H}^+} & \text{Si} - \text{OR} \\
\text{H} & \text{H}_2\text{O} & \xrightarrow{\text{Si} - \text{OR}} \left[ \begin{array}{c}
\text{O} \\
\text{H} \\
\text{Si} \\
\text{O} \\
\text{H}
\end{array} \right] + \text{O} \\
\end{array} \]

\[ \text{Figure 2-15 Proposed mechanism of the interaction between ceramer coatings and aluminum substrate} \]
2.10 CNT/epoxy coatings

The first discovery of carbon nanotube (CNT) was dated back to the early 1990s\textsuperscript{134}. The nanotubes reported were consisted of several tens of graphitic shells. Therefore, the first type of CNT found is called Multi-Walled Carbon Nanotubes (MWCNTs). Later, the observations of Single-Walled Nanotubes (SWNTs) were also reported by Iijima. Since then, CNTs have occupied a significant position in the fields of nanotechnology due to their superior properties. By far, CNTs are found to possess the highest tensile strength $\sim 1$ TPa\textsuperscript{135-136} and modulus 150-180 GPa\textsuperscript{137}, known for any material. In addition, carbon nanotubes have been known for the best conductor with a thermal conductivity $> 200$ Wm$^{-1}$K$^{-1}$\textsuperscript{138-139}, more than twice that of diamond. Besides the thermal conductivity, the electrical conductivity of CNTs can be above $10^4$ Scm$^{-1}$\textsuperscript{140}. Because of the above major and other more interesting properties, CNTs have attracted significant interest after its first production.

The first incorporation of CNT as a filler into a polymer was done in 1994 by Ajayan et al.\textsuperscript{141}. Since then, extensive studies have been done to incorporate CNTs into various polymers. Epoxy resins are an important thermoset system for high performance engineering applications due to the excellent overall mechanical properties as well as good adhesion to substrates\textsuperscript{142-143}. Therefore, epoxy resins are widely used in the protective and marine coatings applications.

Overall, by incorporating CNTs into epoxy resins, it’s expected to improve the already excellent performance of epoxy resins. In addition, additional functionalities from CNTs can be brought into epoxy resins, showing tremendous potential for high performance applications. Therefore, a large variety of research has been done to explore
the combination of properties from epoxy and CNTs. Due to large variations in choice of raw materials, techniques and formulations, the properties from experimental usually have a great disparity and generally are not compared with each other. The presence of CNTs in epoxy coating systems not only can improve the performance of epoxy, but also bring additional excellent properties, such as toughness, electrical conductivity, and thermal conductivity.

2.10.1 Mechanical properties

During the past several decades, a large variety of CNT nanocomposites have been investigated in terms of the mechanical properties. Several factors were found to govern the mechanical properties of CNT reinforced epoxy composites, such as the curing process and temperature, the properties of epoxy resins, the catalysts for the production of CNT as well as the types of CNTs and their modification. In a study, two different curing cycles were followed in the study of the mechanical properties of SWNT/epoxy composites, i.e. one curing cycle with room temperature for 24 h and post cured 60 °C for 4 h, and the other one for 48 h and 24h. It was demonstrated that the curing cycles improved the tensile strength of the epoxy matrix with the increase of the curing time. The increment of tensile strength of the composites was found to be proportional to the increment in the pure epoxy tensile strength. The ductile matrices were obtained by Ci and Bai using small proportion of hardener and shorter curing time. Breton et al. studied the influence of the catalyst systems used in the production of CNTs on the mechanical properties of CNT/Epoxy composites. It was observed that the different catalysts resulted in the difference in specific surface area and mesoporous volume, leading to the difference of ease of dispersion of MWNTs with epoxy resin. It’s well known that the properties of composite are mostly
determined by the dispersion state of CNTs. So the types of CNTs and their modification can have significant influence on the mechanical properties of the nanocomposites. Gojny et al.\textsuperscript{154-155} evaluated the mechanical properties of the nanocomposites containing SWNT or DWNT with or without amino modification. It was found that DWCNT–NH2 reinforced epoxy significantly enhanced the strength and modulus due to the enhanced interfacial adhesion by reaction between amino groups and epoxy. The SWNTs didn’t improve the mechanical properties more than DWCNT as expected. But SWNTs is expected to be very potential candidate if the good interfacial adhesion with good dispersion of CNTs is obtained.

2.10.2 Electrical properties

The high electrical conductivity\textsuperscript{148,149} of CNTs has also drawn a lot of attention. The conductive epoxy/CNT nanocomposites have been widely applied in many applications, such as the anti-static coatings and electromagnetic interference shielding. To achieve the high conductivity of CNTs/epoxy composites, the key is to obtain the conductive CNT network. Two aspects should be balanced to improve the electrical conductivity by forming a conductive CNT network. On the one hand, any approaches that can improve CNT dispersion should be considered, such as modification or functionalization of CNTs. On the other hand, any approaches that can deteriorate the intrinsic conductivity of CNTs should also be paid attention to, such as modification or functionalization of CNTs and any processed to facilitate CNT dispersion. Various strategies have been developed to improve the electrical conductivity by forming a conductive CNT network.
The aspect ratio has great influence on the increase of the electrical conductivity and the decrease of the percolation threshold. Kim et al.\textsuperscript{156} prepared the SWNT/epoxy composites and determined the corresponding percolation threshold. A very small value of percolation threshold was observed.

The CNTs could be modified or functionalized to help improve their dispersion in the epoxy resins by interaction with resins. Kim et al.\textsuperscript{157} functionalized MWCNT with the chemical treatment by using HNO\textsubscript{3} of different concentrations and a mixture of H\textsubscript{2}O\textsubscript{2} and NH\textsubscript{4}OH. The MWNT oxidized under mild conditions with low concentration of nitric acid exhibited very low percolation while the one with high concentration of nitric acid showed an exceptionally high percolation threshold. The difference was explained as that the high concentration of HNO\textsubscript{3} could partially damage the crystalline structure of the MWNT, resulting in the disturbed electronic structure of CNTs.

The CNTs dispersion can also be improved with adjusting some processing parameters, such as the stirring rate, the stirring strength and the duration of stirring. However, the sever process might destruct some parts of the CNT network, resulting in low electrical conductivity\textsuperscript{158}.

Compared with SWNT, MWCNTs have relatively high aspect ratio and low cost, making them the most popular candidates for the nanocomposites in the industry. During the whole process, any treatment that leads to a reduction of the aspect ratio or damaged electrical structure should be avoided to in order to obtain the high electrical conductivity.

2.10.3 Thermal properties

Compared with the conductive effect, the effect of CNTs on the glass transition temperature is more complicated. Active studies regarding the effect of CNTs on T\textsubscript{g} have
been done due to the close relation between $T_g$, cure degree, mechanical properties and other performance. In a review\(^{159}\) of the influence of the unmodified MWNT on the $T_g$ of epoxy, several causes were proposed for the depressed $T_g$, such as the bundling tendency of SWNT and residual solvent. In most studies of the SWNTs filled epoxy, the $T_g$ showed a decreasing trend. One possible reason was believed to be the results of bundling tendency of SWNTs\(^{160}-^{163}\). After debundling of those SWNTs by Moniruzzaman et al.\(^{164}\), it was observed that the $T_g$ was not affected by the incorporation of CNTs. The residual solvent after curing may be another important reason for the decrease in $T_g$. The residual solvent with high boiling point led to the decrease in $T_g$ as well as mechanical properties\(^{165}-^{166}\), even after long time evaporation.

When it comes to the MWNTs, the results were even more complicated. An increase\(^{167}\), decrease\(^{167,168,169}\) or no change\(^{169,170}\) in the $T_g$ of nanocomposites have all been reported with the cross-linked epoxy composites. Among that, the decreased $T_g$ has been frequently observed with the incorporation of CNTs. The decrease in $T_g$, however, may not be attributed to the presence of CNTs; instead, it’s possibly from the change of the curing process of epoxy resins.

The curing kinetics in presence of CNTs can’t be uniformed since CNTs are prepared and modified by different ways and therefore have different grades of purity\(^{159}\). The catalyst particles remaining in CNTs can affect cure reaction and the modified CNTs with functional groups, such as $-\text{NH}_2$, $-\text{OH}$ and $-\text{COOH}$, even makes the situation more complicated than unmodified CNTs. Gojny and Schulte\(^{171}\) studied the thermo-mechanical properties in terms of different loadings of functionalized and non-functionalized CNTs. It was observed that the increasing loadings of CNTs led to an increasing $T_g$. In comparison
with the unmodified CNTs, functionalized CNT had much stronger effect on $T_g$ of the nanocomposite samples. It was postulated that the stronger influence resulted from the improved adhesion between the epoxy and CNTs.

2.10.4 Other properties

Other interesting properties of CNT have also been studied. For the epoxy nanocomposites with the MWCNTs prepared by depositing the iron (II) phthalocyanine in the presence of Ar/H$_2$ atmosphere$^{172}$, their magnetic properties were improved due to the presence of magnetic nanoparticles at the end of the MWCNTs. More and more other potential properties are expected from the high aspect ratio of CNTs. However, the improved dispersion of the CNTs without compromising their intrinsic properties is still the challenge. The improvement of epoxy/CNT nanocomposites strongly relies on the properties of CNT and epoxy resins as well as how well they are prepared. In the academic field, extensive research has been done to solve the challenges and continued research is needed for significant improvement in the practical applications in the industry.
CHAPTER III

A NEW CLASS OF NON-ISOCYANATE URETHANE METHACRYLATES FOR
THE URETHANE FUNCTIONAL LATEX BY EMULSION POLYMERIZATION

3.1 Summary

A series of new urethane methacrylate (UMA) monomers were synthesized with
the reaction of the ethylene carbonate and aliphatic amines, followed by the reaction with
the methacrylic anhydride. Urethane functional latexes were prepared by monomer-starved
semibatch polymerization of the new urethane methacrylate with methyl methacrylate
(MMA) and butyl acrylate (BA). The behavior of the UMA monomers in emulsion
polymerization and the effect of the urethane functional monomers on the thermal stability,
minimum film formation temperature (MFFT) and mechanical properties were studied.
The monomers were characterized by $^1$H, $^{13}$C nuclear magnetic resonance (NMR), mass
spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR). The size of the
urethane functional latexes were evaluated by dynamic light scattering (DLS), ultrasound
acoustic attenuation spectroscopy (UAAS) and transmission electron microscopy (TEM).
In addition, the latexes were investigated using gas chromatography (GC), surface tension,
differential scanning calorimetry (DSC), MFFT, tensile and dynamic mechanical thermal
analysis (DMTA). The aqueous solubility of the new urethane methacrylate monomers was
in the range of 0.5888-0.0095 wt%. The monomer-starved semibatch polymerization was successfully achieved with almost 100% conversion. The uniform morphology and particle size were observed by combination of DLS, TEM and UAAS. The difference between \( T_g \) and MFFT of urethane functional latexes was found to be much smaller than that of the control sample poly(MMA/BA) due to interaction of particles by hydrogen bonding between the urethane groups during the film formation. In comparison with the control sample poly(MMA/BA), the urethane functionality showed significant improvements in mechanical properties of poly(MMA/BA/HEM) bearing similar \( T_g \), i.e. higher tensile modulus, tensile strength and elongation-at-break.

3.2 Introduction

Polyurethanes are generally synthesized from the reaction of polyisocyanates, polyols, and chain extenders\(^{23}\). The principal limitation of the isocyanate route is the toxicity\(^{24}\). Isocyanates are harmful to both the environment and body\(^{173-174}\) in terms of inhalation, skin, or eye contact. Human body contains proteins and other materials having the substituents, such as hydroxyl, amine, and/or carboxylic acid groups that can be reacted with the isocyanates. Therefore, isocyanates need to be stored, handled and processed following special safety procedures. The use of hazardous isocyanates makes the urethane products very expensive materials. Besides the toxicity of isocyanate itself, the production process of isocyanates is also harmful. In the commercial process, the reaction of phosgene with amines is used to produce isocyanates. Severe respiratory effects can be caused by exposure to phosgene, which is a colorless, highly reactive, and highly toxic gas. It has been reported\(^{175}\) that the exposure to phosgene is hazardous and can even cause death. The avoidance of the use of phosgene and isocyanates has become a significant concern\(^{24}\).
With the awareness of the need to lower the cost and ensure the working safety of both people and environment\textsuperscript{173-174}, environment friendly alternative methods and products are highly demanded. In a recent review paper\textsuperscript{176}, three general polymer synthetic methods were concluded to obtain non-isocyanate polyurethanes (NIPUs), i.e. polyaddition, poly(ring-opening), and polycondensation. Among them, the ring-opening polymerization between cyclic carbonates and aliphatic diamines or polyamines\textsuperscript{176} seems to be the most attractive method. This may be mainly attributed to the demand of low cost and biobased starting material from both academic and industrial fields\textsuperscript{177}.

It is known that the synthesis of the carbamate group from cyclic carbonates can be dated back to 1956\textsuperscript{178}. In the same year, a patent was proposed by Groszos et al.\textsuperscript{105} regarding the synthesis method of hydroxycarbamates from cyclic carbonates and a “urea polyamine”. After that, synthesis of the carbamate group from cyclic carbonate has been studied widely. The commercially available difunctional hydroxyalkyl urethanes, which act as blocked isocyanates to produce desired polyurethane\textsuperscript{106}, were patented in 1989 by Blank, W. from King Industries by applying the reaction of alkylene carbonates with aliphatic diamines. A lot of studies\textsuperscript{107-108} have been reported on the ring opening reactions in terms of the substituent effect of cyclic carbonates.

Waterborne coatings with very low volatile organic compounds (VOCs) have attracted lots of attention in the past decades. Polyacrylate\textsuperscript{14} (PA) and polyurethane\textsuperscript{15} (PU) are two of the most popular resins that are widely used in waterborne coating systems. A combination of PU and PA is proposed to combine the beneficial properties, i.e. excellent water and chemical resistance, weathering properties and hardness as well as low cost\textsuperscript{14} from PA and excellent elasticity, scratch resistance, flexibility and toughness\textsuperscript{15} from PU.
Physical blending compromise the superior performance properties with the fact that the acrylic/PU polymers remain phase separated during film formation\textsuperscript{7,87}. A more widely used way is to synthesize the hybrid polyurethane/polyacrylate (PUA), including intimately mixing\textsuperscript{3-4}, grafting\textsuperscript{5-12}, interpenetrating polymer networks (IPNs)\textsuperscript{13-18} and core-shell morphology\textsuperscript{19-22}. However, the idea of preparation of carbamate monomer and its copolymerization in emulsions is rarely studied. One possible reason may be due to the synthesis of the suitable carbamate monomers for emulsion polymerization. The toxicity\textsuperscript{24} of isocyanates used for synthesis of the suitable urethane functional monomers is the principal limitation. These statements above possibly describe why there are little studies, if any, about improving compatibility of PA and PU starting from monomers in the past 20 years.

In our group, the non-isocyanate urethane di-methacrylates had been prepared based on the similar reactive strategy and used as reactive diluents for making UV-curable polyurethane coatings\textsuperscript{179}. The non-isocyanate urethane di-methacrylates had great effects on reduction of the viscosity of the pre-cured coatings, and improvement of the impact resistance and mechanical properties of the final cured coatings. Herein, in this study, new non-isocyanate urethane mono-methacrylates with varying chain length were prepared through an environmentally friendly non-isocyanate way, and used for emulsion polymerization to prepare latexes for the first time. The series of UMA monomers were synthesized by reacting cyclic carbonates with different aliphatic amines, including methyl, ethyl, butyl, hexyl and octyl amines, followed by the reaction of the resultant product with the methacrylic anhydride. Urethane functional latexes were prepared by copolymerization of new UMA monomers with methyl methacrylate (MMA) and butyl acrylate (BA) by
semibatch monomer-starved emulsion polymerization. The kinetics of polymerization process was monitored. The effect of the urethane functional monomers on the minimum film formation temperature (MFFT), thermal, tensile and viscoelastic properties was studied and compared. For comparison, the latex without urethane functionality was also prepared as the control.

3.3 Materials

Ethylene carbonate (EC, 98%), methylamine solution (40 wt% in H₂O), ethylamine solution (66-72 wt% in H₂O), butylamine (BA, 99%), hexylamine (HA, 99%), octylamine (OA, 99%), methacrylic anhydride (MAA, 94%), dichloromethane (99%), hydroquinone (99%), triethylamine (TEA, 99%), dimethyl sulfoxide-d₆ (DMSO-d₆, 100%), anhydrous magnesium sulphate (99%), hydrochloric acid (HCl, 36.5-38 wt%), methyl methacrylate (MMA, 99%), butyl acrylate (BA, 99%), ammonium persulfate (APS), sodium bicarbonate (NaHCO₃), sodium dodecyl sulfate (SDS, 99%), all purchased from Sigma-Aldrich, were used as received. 4-(dimethylamino) pyridine (DMAP, 99%) was obtained from Acros Organics. Acrylic monomers were purified by an inhibitor removal resin (Alfa Aesar) before use. The purified monomers were stored in the refrigerator before synthesis. Deionized water with conductivity below 15µS/cm was used in the preparation of the latexes.

3.4 Instrumentation

The \(^1\text{H}, \text{ }^{13}\text{C}\) nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury 500 MHz spectrometer using DMSO-d₆ as the solvent for liquid samples. The Nicolet 380 Fourier transform infrared spectroscopy (FT-IR) instrument (Thermo Electron
Corp.) was used to obtain the FT-IR spectra by using a KBr crystal plate with very thin layer of a liquid sample. Electro spray ionization (ESI) mass spectra were acquired on a HCT Ultra II quadrupole ion trap mass spectrometer (Bruker Daltonics, Billerica, MA) with sample concentration of 0.03 mg/ml in CH$_2$Cl$_2$:MeOH 50:50 with addition of 1 mg/ml sodium trifluoroacetate (1% volume in sample solution). Gas Chromatography (CP-3800, Varian Inc.) was used to detect the unreacted monomers using the WCOT fused silica capillary column. Surface tension was measured from the Interfacial tensiometer (DuNouy). The particle sizes were obtained on Zetasizer Nano ZS90 (Malvern) and DT1200 ultra acoustic attenuation spectrometer (UAAS) (Dispersion Technology Inc.). Particle morphologies was obtained on JSM-1230 transmission electron microscopy (TEM) (JEOL). Thermal analysis was performed on 1000 DSC (Q1000, TA Instruments). Tensile properties were studied on an Instron 5567 (Instron Corp.). The viscoelastic study were performed on a dynamic mechanical thermal analyzer (DMTA) (Q800, TA Instruments). Minimum film formation temperatures (MFFT) were obtained using MFFT Bar.60 (Rhopoint Surface Instrument).

3.5 Synthesis

The non-isocyanate urethane functional methacrylate monomers and their respective latexes were synthesized.

3.5.1 Synthesis of the non-isocyanate urethane functional methacrylate monomers

Reaction of methyl amine, ethylene carbonate and methacrylic anhydride (MA-EC-MAA)
The synthesis process of the urethane functional methacrylate monomers consists of two steps. Firstly, ethylene carbonate (88.06 g, 1.00 mol) along with the dichloromethane (300 mL) was added into a 1L three-neck flask. Then methyl amine solution, 40 wt% in H₂O, (85.42 g, 1.10 mol) was dropwise added into EC-CH₂Cl₂ solution mixture at 0 °C by using the ice bath under N₂ atmosphere and magnetic stirrer. The reaction was performed at room temperature for 24 h. After the 24 h reaction, rotary evaporation was used to remove the dichloromethane and water. The yellow liquid (yield: 90-95%), MA-EC, the hydroxyalkylcarbamate, was then obtained. In the second step, hydroxyalkylcarbamate (59.6 g, 0.5 mol), 4-(dimethyl-amino) pyridine (DMAP) (610 mg, 5 mmol), and hydroquinone (79.0 mg, 0.72 mmol) along with the dichloromethane (300 mL) was added into the flask at 0 °C under N₂ atmosphere and magnetic stirrer. Then triethylamine (TEA) (70.8 g, 0.7 mol) was dropwise added and followed by dropwise addition of methacrylic anhydride (98.4 g, 0.6 mol). After the addition, the mixture was stirred at 0 °C to continue reaction for 24 h. After 24 h reaction, 200 mL dichloromethane was added. The extraction of final products MA-EC-MAA was done with the following steps: the saturated brine (300 mL) was first put into the mixture to separate into two phases and the product in the bottom layer was collected, washed with 1M hydrochloric acid solution (300 mL × 3) saturated sodium bicarbonate solution (300 ml × 3) and saturated brine (300 mL × 1). The product was then mixed with anhydrous magnesium sulphate to remove water. After the filtration process and the rotary evaporation of dichloromethane, the product was left in the vacuum oven until there is no change of weight. A light yellow liquid product was obtained with overall yield around 60-65%. ¹H NMR (500 MHz, DMSO-d₆) δ (ppm) = 1.87 (s, 3 H, -CH₃), 2.56 (d, J = 4.6 Hz, 3 H, CH₃-NH-), 4.18 (m, 2 H, -OCH₂CH₂O-), 4.24 (m, 2 H, -
OCH₂CH₂O-), 5.68 (m, 1 H, cis C=CH₂), 6.02 (s, 1 H, trans C=CH₂), 7.04(s, 1 H, -NHCOO-). ¹³C NMR (500 MHz, DMSO-d₆) δ (ppm) 18.33 (-CH₃), 27.65 (CH₃NH-), 62.13 (-NHCOOC₂H₅), 63.53 (-CH₂CH₂O-), 126.34 (C=CH₂), 136.16 (C=CH₂), 156.93 (C=O, carbamate), 166.58 (C=O, ester). MS (ESI-MS) calculated for C₈H₁₃NO₄ (m/z), 187.1; found, 186.9 [M-Na⁺] (see Supplementary Data).

Reaction of ethyl amine, ethylene carbonate and methacrylic anhydride (EA-EC-MAA)

EA-EC-MAA was prepared and purified using a similar procedure as for MA-EC-MAA. From ethylene carbonate (88.06 g, 1.00 mol) and the ethyl amine solution, 66-72 wt% in H₂O, (75.0 g, 1.10 mol), the slightly yellow liquid (yield: 90-95%), EA-EC, the hydroxyalkylcarbamate, was obtained. In the second step, from EA-EC, the hydroxyalkylcarbamate (66.6 g, 0.5 mol) and methacrylic anhydride (98.4 g, 0.6 mol) with 4-(dimethyl-amino) pyridine (DMAP) catalyst (610 mg, 5 mmol), triethylamine (TEA) (70.8 g, 0.7 mol) and hydroquinone inhibitor (82.5 mg, 0.75 mmol), a light yellow liquid product was obtained with overall yield around 60-65%. ¹H NMR (500 MHz, DMSO-d₆) δ (ppm) = 0.99 (t, J = 7.3 Hz, 3 H, -CH₃), 1.87 (s, 3 H, -CH₃), 2.99 (m, 2 H, -CH₂CH₃), 4.18 (m, 2 H, -OCH₂CH₂O-), 4.24 (m, 2 H, -OCH₂CH₂O-), 5.68 (m, 1 H, cis C=CH₂), 6.02 (s, 1 H, trans C=CH₂), 7.15 (s, 1 H, -NHCOO-). ¹³C NMR (500 MHz, DMSO-d₆) δ (ppm) = 15.40 (-CH₂CH₃), 18.33 (-CH₃), 35.48 (-CH₂NH), 62.13 (-NHCOOC₂H₅), 63.53 (-CH₂CH₂O-), 126.34 (C=CH₂), 136.16 (C=CH₂), 156.93 (C=O, carbamate), 166.58 (C=O, ester). MS (ESI-MS) calculated for C₉H₁₅NO₄ (m/z), 201.1; found, 200.9 [M-Na⁺] (see Supplementary Data).
Reaction of butyl amine, ethylene carbonate and methacrylic anhydride (BA-EC-MAA)

BA-EC-MAA was prepared and purified using a similar procedure as for MA-EC-MAA. The only difference was that shorter time and lower temperature were needed for rotary evaporation due to the absence of water. From ethylene carbonate (88.06 g, 1.00 mol) and butyl amine (80.5 g, 1.10 mol), the slightly yellow liquid (yield: 95-98%), BA-EC, the hydroxyalkylcarbamate, was obtained. In the second step, from BA-EC, the hydroxyalkylcarbamate (80.6 g, 0.5 mol) and methacrylic anhydride (98.4 g, 0.6 mol) with 4-(dimethyl-amino) pyridine (DMAP) catalyst (610 mg, 5 mmol), triethylamine (TEA) (70.8 g, 0.7 mol) and hydroquinone inhibitor (89.5 mg, 0.82 mmol), a light yellow liquid product was obtained with overall yield around 65-70%. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm) = 0.84 (t, $J = 6.9$ Hz, 3 H, -CH$_3$), 1.26 (m, 2 H, -CH$_2$CH$_3$), 1.36 (m, 2 H, -CH$_2$CH$_2$CH$_3$), 1.87 (s, 3 H, -CH$_3$), 2.97 (m, 2 H, -CH$_2$NH), 4.20 (m, 2 H, -OCH$_2$CH$_2$O-), 4.24 (m, 2 H, -OCH$_2$CH$_2$O-), 5.67 (m, 1 H, cis C=CH$_2$), 6.03 (s, 1 H, trans C=CH$_2$), 7.15 (s, 1 H, -NHCOO-). $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm) 13.53 (-CH$_2$CH$_3$), 17.82 (-CH$_3$), 19.34 (-CH$_2$CH$_3$), 31.45 (CH$_2$), 39.98 (-CH$_2$NH), 61.47 (-NHCOOC=CH$_2$), 63.08 (-CH$_2$CH$_2$O-), 125.77 (C=CH$_2$), 135.70 (C=CH$_2$), 155.92 (C=O, carbamate), and 166.36 (C=O, ester). MS (ESI-MS) calculated for C$_{11}$H$_{19}$NO$_4$ (m/z), 229.1; found, 229.0 [M-Na$^+$] (see Supplementary Data).

Reaction of hexyl amine, ethylene carbonate and methacrylic anhydride (HA-EC-MAA)

HA-EC-MAA was prepared and purified using a similar procedure as for BA-EC-MAA. From ethylene carbonate (88.06 g, 1.00 mol) and hexyl amine (102.2 g, 1.00 mol),
the slightly yellow liquid (yield: 95-98%), HA-EC, the hydroxyalkylcarbamate, was obtained. In the second step, from HA-EC, the hydroxyalkylcarbamate (94.6 g, 0.5 mol) and methacrylic anhydride (98.4 g, 0.6 mol) with 4-(dimethyl-amino) pyridine (DMAP) catalyst (610 mg, 5 mmol), triethylamine (TEA) (70.8 g, 0.7 mol) and hydroquinone inhibitor (96.5 mg, 0.88 mmol), a light yellow liquid product was obtained with overall yield around 65-70%. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm) = 0.85 (m, 3 H, -CH$_3$), 1.23 (m, 6 H, -(CH$_2$)$_3$CH$_3$), 1.37 (m, 2 H, -CH$_2$CH$_2$NH), 1.87 (s, 3 H, -CH$_3$), 2.94 (m, 2 H, -CH$_2$NH), 4.20 (m, 2 H, -OCH$_2$CH$_2$O-), 4.24 (m, 2 H, -OCH$_3$CH$_2$O-), 5.67 (m, 1 H, cis C=CH$_2$), 6.03 (s, 1 H, trans C=CH$_2$), 7.15 (s, 1 H, -NHCOO-). $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm) 14.05 (-CH$_2$CH$_3$), 18.22 (-CH$_3$), 22.17 (-CH$_2$CH$_3$), 26.12 (CH$_2$), 31.5 (-CH$_2$CH$_2$CH$_3$), 39.98 (-CH$_2$NH), 61.07 (-NHCOOCH$_2$-), 63.58 (-CH$_2$CH$_2$O-), 126.00 (C=CH$_2$), 136.20 (C=CH$_2$), 156.39 (C=O, carbamate), and 166.58 (C=O, ester). MS (ESI-MS) calculated for C$_{13}$H$_{23}$NO$_4$ (m/z), 257.1; found, 256.9 [M-Na$^+$] (see Supplementary Data).

Reaction of octyl amine, ethylene carbonate and methacrylic anhydride (OA-EC-MAA)

OA-EC-MAA was prepared and purified using a similar procedure as for BA-EC-MAA. From ethylene carbonate (88.06 g, 1.00 mol) and hexyl amine (130.5 g, 1.00 mol), the slightly yellow liquid (yield: 95-98%), OA-EC, the hydroxyalkylcarbamate, was obtained. In the second step, from OA-EC, the hydroxyalkylcarbamate (108.7 g, 0.5 mol) and methacrylic anhydride (98.4 g, 0.6 mol) with 4-(dimethyl-amino) pyridine (DMAP) catalyst (610 mg, 5 mmol), triethylamine (TEA) (70.8 g, 0.7 mol) and hydroquinone inhibitor (104.0 mg, 0.94 mmol), a light yellow liquid product was obtained with overall
yield around 65-70%. \textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}_6) \( \delta \) (ppm) = 0.85 (t, \( J = 7.1 \) Hz, 3 H, -CH\textsubscript{3}), 1.23 (m, 10 H, -(CH\textsubscript{2})\textsubscript{3}CH\textsubscript{3}), 1.37 (m, 2 H, -CH\textsubscript{2}CH\textsubscript{2}NH), 1.87 (s, 3 H, -CH\textsubscript{3}), 2.94 (m, 2 H, -CH\textsubscript{2}NH), 4.20 (m, 2 H, -OCH\textsubscript{2}CH\textsubscript{2}O-), 4.24 (m, 2 H, -OCH\textsubscript{2}CH\textsubscript{2}O-), 5.67 (m, 1 H, cis C=CH\textsubscript{2}), 6.03 (s, 1 H, trans C=CH\textsubscript{2}), 7.15 (s, 1 H, -NHCOO-). \textsuperscript{13}C NMR (500 MHz, DMSO-\textit{d}_6) \( \delta \) (ppm) 14.10 (-CH\textsubscript{2}CH\textsubscript{3}), 18.32 (-CH\textsubscript{3}), 22.52 (-CH\textsubscript{2}CH\textsubscript{3}), 26.67 (CH\textsubscript{2}), 31.68 (-CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 40.02 (-CH\textsubscript{2}NH), 61.93 (-NHCOOCH\textsubscript{2}-), 63.56 (-CH\textsubscript{2}CH\textsubscript{2}O-), 126.26 (C=CH\textsubscript{2}), 136.16 (C=CH\textsubscript{2}), 156.36 (C=O, carbamate), and 166.82 (C=O, ester). MS (ESI-MS) calculated for C\textsubscript{15}H\textsubscript{27}NO\textsubscript{4} (m/z), 285.2; found, 285.2 [M-Na\textsuperscript{+}] (see Supplementary Data).

3.5.2 Synthesis and design of latexes

As the preliminary study of the non-isocyanate urethane functional latexes, the latexes were designed with the urethane functionality uniformly distributed in the whole particles. The poly(MMA/BA) was also prepared as the control sample. The Latexes were prepared by seeded semibatch emulsion polymerization. The seeds used were prepared by batch emulsion polymerization. For the kinetic study, Optimax (Mettler Toledo) working station was chosen to control the temparature (accuracy ± 0.1 °C).

Seed: A batch reaction was used to prepare the seed latex. BA (24 g), MMA (56 g), NaHCO\textsubscript{3} (1.5 g), SDS (2.4 g) and distilled water (200 g) were added to a 1000 mL reactor equipped with a condenser and mechanical stirrer. Before addition of the initiator, the mixture was under nitrogen atmosphere for 20 mins and heated to 65 °C. Then the ammonium persulfate solution (2 wt%, 40.8 g) was added to the reactor. The temperature was set up at 75 °C and polymerization continued for another 90 min.
The same experimental setup was used for preparation of the following latexes. The seed (25 g) was charged in the reactor along with NaHCO$_3$ (1.32 g) and H$_2$O (300 g) and heated to 75 °C. Then a pre-emulsion of BA, MMA, the respective urethane functional methacrylate monomer (if required), APS (2.2 g), NaHCO$_3$ (0.88 g) and H$_2$O (220 g) was fed continuously for 240 min. Table 3-1 presents the amounts of each component for latex formulations. The mole ratio MMA/BA was kept constant. 15 mol% for each type of the urethane methacrylate monomers based on the total monomer content was used in each reaction. The mixture was heated at 85°C and stirred to continue reaction for another 120 min after completing the pre-emulsion feed.

Table 3-1 Composition of pre-emulsion for urethane-functionalized latexes

<table>
<thead>
<tr>
<th></th>
<th>control</th>
<th>15 mol% MEM</th>
<th>15 mol% EEM</th>
<th>15 mol% BEM</th>
<th>15 mol% HEM</th>
<th>15 mol% OEM</th>
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<td>Reactor Seed latex/g</td>
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<td>Reactor DI Water/g</td>
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<td>Pre-emulsion MMA/g</td>
<td>138.0</td>
<td>106.0</td>
<td>104.1</td>
<td>100.6</td>
<td>97.4</td>
<td>94.3</td>
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<td>Pre-emulsion BA/g</td>
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<td>61.0</td>
<td>60.1</td>
<td>58.1</td>
<td>56.2</td>
<td>54.5</td>
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<tr>
<td>Pre-emulsion Urethane methacrylate/g</td>
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<td>53.5</td>
<td>59.0</td>
<td>64.1</td>
<td>68.9</td>
</tr>
<tr>
<td>Pre-emulsion SDS/g</td>
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<td>1.54</td>
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</tr>
<tr>
<td>Pre-emulsion DI Water/g</td>
<td>220</td>
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<tr>
<td>Pre-emulsion Sodium Bicarbonate/g</td>
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<tr>
<td>Pre-emulsion APS/g</td>
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<tr>
<td>Pre-emulsion Theoretical Solid Content</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
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</tr>
</tbody>
</table>

57
3.6 Measurement of aqueous solubility of the urethane functional methacrylate monomers

The aqueous solubility of monomers was determined by GC analysis. GC analysis was based on the external standard calibration with known concentration. Standard solutions were prepared by mixing a precise amount of volatile compound with water (20 ml). The concentration known solution was homogenized by an ultrasonic treatment for 30 min after preparation and kept for 24 h at room temperature (25 °C). A precise volume of the solution was introduced using a micropipette in a 10-25-50 ml volumetric flasks and the volume made up with water. Saturated solutions were prepared by mixing a large amount of volatile compound (0.02 to 0.2 g) with water (20 ml), for 24 h at room temperature (25 °C). The mixtures were centrifuged at 10000 rpm at 25 °C for 60 min to get the clear saturated solutions. The saturated solutions were then diluted with water by using volumetric flasks.

3.7 Latex characterization

The obtained latexes were characterized in terms of particle size, conversion, morphology and the minimum film formation temperature.

3.7.1 Particle size analysis

For dynamic light scattering measurement, the latex samples were diluted to be less than 0.1 vol %. The measurement were carried out with a fixed angle of 90° at 25 °C.

For UAAS analysis, the latex samples were used without dilution, around 100 mL for each measurement. For each sample, there were three replicas and the average values of $D_w$ and median $\bar{D}_w$ were calculated.
3.7.2 Conversion analysis

Total overall and the instantaneous conversions of each specific monomer were determined from Gas Chromatography with respective standard calibration curves.

3.7.3 Morphological analysis

The latex samples were cleaned by using membrane analysis to remove excess amount of ionic materials, such as surfactants and buffer salts. The typical procedure was as following. A latex sample was placed inside the regenerated cellulose dialysis membrane (MWCO 12000–14000). The membrane was put into a beaker filled with distilled water for several days with water replaced every 12 h. The cleaning of the latexes was done when the conductivity of the external water was around 20 μS/cm.

After the cleaning process, the latexes were diluted to 0.5-1 wt%. Then one to two drops of the diluted sample was put on the thick carbon coated 400-mesh copper grid. Samples were left at room temperature to dry for 24 h prior to imaging.

3.7.4 Minimum film formation temperature analysis

According to ISO-2115, dispersions were applied on rectangular stainless steel plate with temperature gradient 23-50 °C or 15-33 °C. Applicator was used to apply about 20 mm wide wet films with wet thickness 75 μm. After few hours of drying under slight current of dry air, MFFT was determined as "the lowest temperature where a continuous, homogeneous film without cracks is formed". Accuracy was ± 1°C.
3.7.5 Mathematical calculations during synthesis of latexes

The definition of the instantaneous conversion is the weight ratio of the polymer converted from the monomers to the monomers added into the reactor. The instantaneous conversions of each specific monomer were calculated from equation (3-1).

\[ X_{\text{instantaneous,monomer}}(t) = \frac{W_{\text{theoretical monomer}}(t) - W_{\text{free monomer}}(t)}{W_{\text{theoretical monomer}}(t)} \quad (3-1) \]

where \( W_{\text{theoretical monomer}}(t) \) represents weight of the monomer fed in the system at given time and \( W_{\text{free monomer}}(t) \) represents weight of the monomer unreacted in the system at given time, which was determined from gas chromatography.

The overall instantaneous conversion at a given time \( X_{\text{instantaneous}} \) was then calculated from equation (3-2).

\[ X_{\text{instantaneous}} = \frac{W_{\text{theoretical monomers}}(t) - W_{\text{free MMA}}(t) - W_{\text{free BA}}(t) - W_{\text{free UMA}}(t)}{W_{\text{theoretical monomers}}(t)} \quad (3-2) \]

where \( W_{\text{theoretical monomers}}(t) \) represents weight of total monomers fed in the system at given time and \( W_{\text{free MMA}}(t) \), \( W_{\text{free BA}}(t) \) and \( W_{\text{free UMA}}(t) \) represent weight of unreacted MMA, BA and UMA, respectively in the system at given time, which were determined from gas chromatography.

The theoretical particle size was calculated based on the mass balance with the equation (3-3)\(^{180}\).

\[ d_f = \left(1 + \frac{W_m}{W_s}\right)^{1/3} d_s \quad (3-3) \]

where \( W_m \) is the amount (g) of monomer feed; \( W_s \) is the amount (g) of seed particles; \( d_s \) and \( d_f \) is the particle diameter (nm) of the seed and final latexes, respectively.
The number of particles \( N_p, \text{1/dm}^3 \) was computed from equation (3-4):

\[
N_p = \frac{6M_0x}{\pi \rho D^3}
\]

(3-4)

where \( M_0 \) is the monomer injected to the reactor \( \text{g/dm}^3 \), \( x \) is the conversion fraction by time, and \( D \) is the diameter of latex particle \( \text{dm} \) obtained from DLS. The density of polymer, \( \rho \) \( \text{g/dm}^3 \), is the density obtained from gas pycnometry.

The definition of the surface coverage \( \theta \) is the ratio of the surface area covered by the surfactants to the total particle surface area, which can be calculated from equation (3-5):

\[
\theta = \frac{(N_{SDS} - N_{SDS_w}) \times A_{1SDS}}{N_p \times \pi D^2}
\]

(3-5)

where \( N_{SDS} \) presents total number of surfactant molecules, \( N_{SDS_w} \) is number of surfactant molecules in water\(^{181} \), \( A_{1SDS} \) represents the occupation area of one SDS surfactant molecule on the particle surface\(^{182} \) (Based on the ration of MMA and BA, adsorption area of 0.74 nm\(^2 \) per SDS molecule was used for calculations).

3.8 Film preparation and characterization

The latex films were formed by casting onto glass plates and drying the latexes at elevated temperature. The latex films were peeled off from the glass plates and kept at room temperature for one week before testing. The obtained films were very smooth with thickness around 0.10-0.12 mm. The tensile tests were performed with a crosshead speed at 50 mm/min at room. Ten specimens (40 mm length \( \times \) 13-14 mm width \( \times \) 0.10-0.12 mm thickness) were prepared for each sample and the average was taken as the results. The viscoelastic behavior were studied by DMTA in tensile mode from \(-20\) to \(120 \, ^\circ C \) with a heating rate of \(3\, ^\circ C / \text{min} \). The frequency was fixed at 1 Hz. At least three specimens (15
mm length × 10 mm width × 0.10-0.12 mm thickness) were prepared for each sample and the average was taken as the results. The thermal properties was evaluated by DSC experiments. The sample was heated to 150 °C in the first cycle to exclude the thermal history. The glass transition temperature was determined from the second cycle with a heating rate of 20 °C/min.

3.9 Results

The study focused on the effect of the urethane methacrylate monomers on the polymerization process and the final latex film properties by emulsion polymerization. The hydrophobicity of urethane methacrylate monomers was adjusted based on the chain length; the chain length was controlled by selecting amines with aliphatic chain varying from methyl, ethyl, butyl, hexyl to octyl amine. Monomer-starved semibatch emulsion polymerization was chosen to prepare all the urethane functional latexes. The concentration of urethane functionality was 15 mol% based on the total mole amount of monomers. Poly(MMA/BA) latex was also prepared as the control sample in order to study the effect of the urethane methacrylate monomers on the polymerization process and the final latex film properties.

3.9.1 Non-isocyanate urethane methacrylates

The reaction scheme for the synthesis of non-isocyanate urethane methacrylates was shown in Figure 3-1. It is a two-step non-isocyanate method. The first step is the aminolysis of ethylene carbonate\textsuperscript{183}. The substituent effect had shown significant effect on the ring-opening reaction of cyclic carbonates with amines\textsuperscript{107}. Two adducts, urethanes with primary and secondary hydroxyl groups can be formed during the ring-opening process. It
was found the cyclic carbonate with a stronger electron-withdrawing group would increase the formation of the adduct with a secondary hydroxyl group. The ethylene carbonate was chosen because there was no substituent effect. The reaction is a nucleophilic attack at the electrophilic carbon of the ethylene carbonate by the amines. Therefore, only one adduct, urethane with the primary hydroxyl group was obtained from step I. The second step is the DMAP-catalyzed acetylation\textsuperscript{184} of the alcohol adduct. The esterification reaction involved a nucleophilic attack at the electrophilic carbon of the methacrylic anhydride by the formed hydroxyl group.

Figure 3-1 A two-step non-isocyanate route for the synthesis of the non-isocyanate urethane functional methacrylate monomers
Table 3-2 The molecular structures of intermediate and final products with respective amines

<table>
<thead>
<tr>
<th>Amine type</th>
<th>Intermediates</th>
<th>UMAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl amine</td>
<td><img src="image" alt="Methyl amine Intermediate" /></td>
<td><img src="image" alt="Methyl amine UMA" /></td>
</tr>
<tr>
<td>Ethyl amine</td>
<td><img src="image" alt="Ethyl amine Intermediate" /></td>
<td><img src="image" alt="Ethyl amine UMA" /></td>
</tr>
<tr>
<td>Butyl amine</td>
<td><img src="image" alt="Butyl amine Intermediate" /></td>
<td><img src="image" alt="Butyl amine UMA" /></td>
</tr>
<tr>
<td>Hexyl amine</td>
<td><img src="image" alt="Hexyl amine Intermediate" /></td>
<td><img src="image" alt="Hexyl amine UMA" /></td>
</tr>
<tr>
<td>Octyl amine</td>
<td><img src="image" alt="Octyl amine Intermediate" /></td>
<td><img src="image" alt="Octyl amine UMA" /></td>
</tr>
</tbody>
</table>

The molecular structures of intermediates and UMAs were listed in Table 3-2. FT-IR and NMR spectra for methyl amine based monomer, MEM are presented in Figure 3-2 and 3-3, respectively. The spectra for other UMA monomers are listed in the Supplementary Data. In the FT-IR spectrum of MA-EC shown in Figure 3-2a, the disappearance of C=O from ethylene carbonate at 1795 cm\(^{-1}\) and the appearance of new bands at 3350 cm\(^{-1}\) for the urethane (NH) stretching and at 1710 cm\(^{-1}\) for the C=O stretching showed the formation of urethane functionality. In the FT-IR spectrum of MA-EC-MAA shown in Figure 3-2b, the C=O stretching shifted from 1710 cm\(^{-1}\) to higher wavenumber 1720 cm\(^{-1}\), indicating the change of the chemical environment due to the
esterification. In addition, the appearance of band at 1630 cm\(^{-1}\) showed the C=C stretching. With the 1630 cm\(^{-1}\) for the C=C stretching or 3350 cm\(^{-1}\) for the urethane (NH) stretching as the internal standard, the sum of 2997, 2952 and 2873 cm\(^{-1}\) spectra can be used to qualitatively characterize the aliphatic chain length because it was the sum of C-H stretching from -CH\(_3\) or -CH\(_2\)-. For the methyl to octyl series of UMA monomers, the sum of the signal at 2997, 2952 and 2873 cm\(^{-1}\) became stronger (see Supplementary Data), indicating longer aliphatic chains.

(a) MA-EC

Appearance of 3350 cm\(^{-1}\), N-H stretching in -NH-CO-O-

Disappearance of 1795 cm\(^{-1}\), C=O stretching in -O-CO-O-

Appearance of 1710 cm\(^{-1}\), C=O stretching in -NH-CO-O-
Figure 3-2 FT-IR spectra of MA-EC (a) and MA-EC-MAA (b). The spectrum of MEM shows bands 3350 cm$^{-1}$ for the urethane (NH) stretching and at 1720 cm$^{-1}$ for the C=O, which was overlapped with the acrylate carboxyl group. The C=C double bonds appearing at 1630 cm$^{-1}$ is for the C=C stretching. The bands at 2997 cm$^{-1}$, 2952 cm$^{-1}$ and 2873 cm$^{-1}$ are attributed to the C–H bond stretching vibrations of the –CH$_3$ and –CH$_2$- groups, respectively and the band at 1444 cm$^{-1}$ is attributed to the bending vibration of the C–H bonds of the –CH$_3$ group.

The expected $^1$H NMR resonances of MA-EC and MA-EC-MAA are noted and assigned in Figure 3-3. Integration of the $^1$H NMR resonance areas was obtained to be close to the expected values. In the $^1$H NMR spectrum of MA-EC shown in Figure 3-3a, the appearance of resonance at $\delta$ (ppm) = 4.68 was for the proton from the hydroxyl groups, indicating the first step reaction between ethylene carbonate with the methyl amine. In the $^1$H NMR spectrum of MA-EC-MAA shown in Figure 3-3b, the resonance of methylene protons shifted to higher chemical shift, indicating the esterification of the hydroxyl group.
with methacrylic anhydride. From the analysis of NMR and FTIR spectra, UMA monomers were successfully prepared by using a non-isocyanate route.

Figure 3-3 $^1$H NMR spectra of MA-EC (a) and MA-EC-MAA (b) monomers
The aqueous solubility results of urethane methacrylates monomers measured by GC were listed in Table 3-3. The results were within the 5% error. The solubility of urethane methacrylates decreased with the increasing aliphatic chain length as expected, with 0.5888 wt% for methyl amine based urethane methacrylates (MEM) to 0.0095 wt% octyl amine based urethane methacrylates (OEM). For comparison, the solubility of typical monomers used in latexes, such as styrene (St), butadiene, BA, MMA and lauryl methacrylate (LMA) were also listed in Table 3-3. There is no transportation limitation for emulsion polymerization of styrene, 1,3-butadiene, BA or MMA. The LMA was observed with low conversion in conventional emulsion polymerization due to the very low aqueous solubility.

Table 3-3 The aqueous solubility of urethane methacrylates and common monomers to latex production

<table>
<thead>
<tr>
<th></th>
<th>MEM</th>
<th>EEM</th>
<th>BEM</th>
<th>HEM</th>
<th>OEM</th>
<th>MMA</th>
<th>BA</th>
<th>St</th>
<th>butadiene</th>
<th>LMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Solubility at 25 °C</td>
<td>0.5888</td>
<td>0.4737</td>
<td>0.1222</td>
<td>0.0273</td>
<td>0.0095</td>
<td>1.56</td>
<td>0.2</td>
<td>0.032</td>
<td>0.735</td>
<td>0.00077</td>
</tr>
<tr>
<td>% g/ml</td>
<td>0.0257</td>
<td>0.0157</td>
<td>0.0052</td>
<td>0.0012</td>
<td>0.0003</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.9.2 Kinetic study of emulsion polymerization

The poly(MMA/BA/UMA) latexes with the same monomer mole ratio were synthesized by using the seeded semibatch emulsion polymerization illustrated in Figure 3-4.
The conversion in the emulsion polymerization is generally determined by using gravimetrical analysis, which is easy and convenient for the volatile monomers, such as MMA and BA. However, the gravimetrical analysis is not suitable for monomers that are not so volatile. Many other techniques have been relied on to detect unreacted monomers and monitor reaction processes, such as NMR, GC, HPLC and real time FT-IR. In this study, gas chromatography analysis was applied to detect the remaining free monomers in the latexes during and after the polymerization. Time evolution of overall conversion ($X_{\text{overall}}$), instantaneous overall conversion ($X_{\text{instantaneous}}$) and the rate of polymerization ($R_p$) were depicted in Figure 3-5. The instantaneous overall conversion of all poly(MMA/BA/UMA) latexes was above 85% after initial several minutes, indicating that the monomer-starved condition had been reached. Therefore, the rate of polymerization was stable under the monomer-starved condition, as shown in Figure 3-5. In addition, it can be seen that the instantaneous overall conversions were comparable

Figure 3-4 The synthesis of poly(MMA/BA/UMA) latexes
among the poly(MMA/BA), poly(MMA/BA/MEM), poly(MMA/BA/EEM) and poly(MMA/BA/BEM) latexes while the instantaneous overall conversions slightly decreased for poly(MMA/BA/HEM) and poly(MMA/BA/OEM) latexes. The overall conversion, which was calculated based on the instantaneous overall conversion, showed the similar trend. For all these latexes, the final overall conversion was very close to 100% after 300 mins reaction.

(a) Poly(MMA/BA/MEM)

(b) Poly(MMA/BA/EEM)
(c) Poly(MMA/BA/BEM)

(d) Poly(MMA/BA/HEM)
The instantaneous conversion of each monomer was calculated based on the residue monomers detected by GC. The instantaneous conversion ($X_{\text{inst.}}$) of each monomer during

Figure 3-5 Evolution of overall conversion, instantaneous overall conversion and the rate of polymerization in the semibatch polymerization of poly(MMA/BA/UMA) latexes
semibatch emulsion polymerization and batch emulsion polymerization was shown in Figure 3-6. For MMA, its instantaneous conversions were comparable in the preparation of poly(MMA/BA/UMA) latexes. After initial several minutes of unstable stage, the instantaneous conversions of MMA, BA and UMA were above 85%, which indicated that the monomer-starved condition had been reached. In comparison, there was little difference of the instantaneous conversions of UMA among poly(MMA/BA/UMA) latexes.

(a)

(b)
Figure 3-6 Evolution of instantaneous conversion of each monomer in the semibatch polymerization: (a) MMA, (b) BA, (c) UMA

Table 3-4 compared final monomer conversion, solid content, surface tension, surface coverage, wet and dry densities and conductivity of poly(MMA/BA/UMA) latexes.
No significant differences were found in final monomer conversion, solid content, surface tension, surface coverage. According to an experimental calibration curve of surface tension versus SDS concentration\textsuperscript{181}, the surface tensions of poly(MMA/BA/UMA) latexes were in the range of 41-46 mN/m, which corresponded to 0.26–0.40 g of SDS per liter\textsuperscript{181}. The amount of SDS surfactant was well below CMC, which was estimated to be 0.6-0.7 g/L\textsuperscript{193}. The surface coverage calculation indicated that 55-62\% of particle surface was covered. The wet density of latexes showed a descending trend with the increasing size of the third comonomers, i.e. the aliphatic chain length of urethane methacrylates. Similar trend was observed for the solid densities of dry poly(MMA/BA/UMA) latexes. The solid densities results can then be used in the calculation of the particle number of the final latexes in the following section.

Table 3-4 Comparison of characteristics of final urethane functional latexes

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (wt%)</td>
<td>29.6</td>
<td>30.5</td>
<td>30.6</td>
<td>29.4</td>
<td>30.3</td>
<td>29.4</td>
</tr>
<tr>
<td>Monomer conversion (wt%)</td>
<td>98.3</td>
<td>99.1</td>
<td>99.5</td>
<td>98.7</td>
<td>99.1</td>
<td>98.6</td>
</tr>
<tr>
<td>Surface tension (mN/m)</td>
<td>46</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>43</td>
<td>42</td>
</tr>
<tr>
<td>Surface coverage</td>
<td>62%</td>
<td>57%</td>
<td>56%</td>
<td>55%</td>
<td>55%</td>
<td>56%</td>
</tr>
<tr>
<td>Wet density (g/mL)</td>
<td>1.043</td>
<td>1.051</td>
<td>1.048</td>
<td>1.045</td>
<td>1.043</td>
<td>1.039</td>
</tr>
<tr>
<td>Solid density (g/mL)</td>
<td>1.171</td>
<td>1.199</td>
<td>1.185</td>
<td>1.182</td>
<td>1.167</td>
<td>1.156</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>4.73</td>
<td>3.93</td>
<td>4.25</td>
<td>4.86</td>
<td>4.03</td>
<td>4.11</td>
</tr>
</tbody>
</table>
3.9.3 Particle size and morphology

The particle size was measured by DLS and TEM and compared with the theoretical result to evaluate the stability of particles during the polymerization processes. The overall results of particle size were listed in Table 3-5.

The theoretical particle size was around 190 nm, which was calculated based on the mass balance with the equation below\(^{180}\). DLS, UAAS and TEM were combined to use in this study to check the particle size and its distribution. As the most widely used method, DLS directly gives the z-average (d\(_z\)) particle size. The particle size results were listed in the Table 3-5. The particle size d\(_z\) from DLS showed little difference compared with the theoretical values. In addition, the particle sizes for all latexes were comparable within the error. The particle size was further checked with TEM. The number-average (d\(_n\)) particle size can be calculated from TEM. Figure 3-7 showed the typical morphologies of poly(MMA/BA/UMA) latexes. The latexes in TEM images showed a uniform spherical morphology. Around 400 particles were statistically analyzed to calculate the particle sizes. The particle size from TEM was much smaller than DLS and theoretical results. The smaller particle size was due to the shrinkage of particles during drying, which was consistent with other studies of TEM particle sizes\(^{194}\). The ratio of particle size from TEM to that from DLS was constricted to the range of 0.68-0.76.

Table 3-5 Particle size results from DLS and theoretical calculation

<table>
<thead>
<tr>
<th></th>
<th>UAAS</th>
<th>DLS</th>
<th>TEM</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dw</td>
<td>Dz</td>
<td>PDI</td>
<td>Dn</td>
</tr>
<tr>
<td>Poly(MMA/BA)</td>
<td>226</td>
<td>286</td>
<td>203</td>
<td>0.03</td>
</tr>
<tr>
<td>Poly(MMA/BA/MEM)</td>
<td>226</td>
<td>260</td>
<td>203</td>
<td>0.04</td>
</tr>
<tr>
<td>Poly(MMA/BA/EEM)</td>
<td>226</td>
<td>263</td>
<td>201</td>
<td>0.01</td>
</tr>
<tr>
<td>Poly(MMA/BA/BEM)</td>
<td>233</td>
<td>263</td>
<td>202</td>
<td>0.03</td>
</tr>
<tr>
<td>Poly(MMA/BA/HEM)</td>
<td>212</td>
<td>261</td>
<td>205</td>
<td>0.02</td>
</tr>
<tr>
<td>Poly(MMA/BA/OEM)</td>
<td>210</td>
<td>265</td>
<td>200</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 3-7 TEM of morphology study for poly(MMA/BA/UMA) latexes

The UAAS was used to further check for the secondary nucleation. It has been reported that accurate particle sizes in concentrated dispersions can be acquired by using UAAS. The attenuation spectra and respective fitting curves of undiluted latex samples were shown in Figure 3-8. Unimodal distribution model was observed for all poly(MMA/BA/UMA) latexes. The median average size of poly(MMA/BA/UMA) latexes obtained from UAAS was listed in Table 4. Again, the particle sizes for all poly(MMA/BA/UMA) latexes were comparable within the error.

<table>
<thead>
<tr>
<th>Uncertainty</th>
<th>±5</th>
<th>±5</th>
<th>±5</th>
<th>±0.005</th>
<th>±5</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(MMA-BA-MEM)</td>
<td>Poly(MMA-BA-EEM)</td>
<td>Poly(MMA-BA-BEM)</td>
<td>Poly(MMA-BA-HEM)</td>
<td>Poly(MMA-BA-OEM)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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77
Figure 3-8 Particle size distributions and cumulative undersize curves for poly(MMA/BA/UMA) latexes, obtained using UAAS. The particle number was compared among the initial seed latex with the control poly(MMA/BA) and the urethane functional latexes poly(MMA/BA/UMA). As shown in Figure 3-9, no significant difference of particle numbers was observed from the seed latex and the final latexes.
3.9.4 Thermal properties and film formation

The thermal property of the latexes include not only the glass transition temperature but also the minimum film formation temperature (MFFT). The glass transition temperatures of the latexes measured by DSC were compared in Figure 3-10 and the overall thermal results were listed in Table 3-6. There was only one glass transition showed from the heat flow curves for all of the poly(MMA/BA/UMA) latexes. The glass transition temperature decreased with the increasing side chain length. Similarly, the MFFT also showed a descending trend with the increase side chain length. The difference of $T_g$ and MFFT was around 11 °C for the poly(MMA/BA) latex. In comparison, much larger difference of $T_g$ and MFFT, which was around 16-19 °C, were observed for all poly(MMA/BA/UMA) latexes.
Figure 3-10 DSC thermograms of poly(MMA-BA-UMA) latexes

Table 3-6 Overall result of glass transition temperatures and MFFTs

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (DSC)</td>
<td>42.4±0.6</td>
<td>53.9±0.9</td>
<td>48.2±0.4</td>
<td>46.2±0.5</td>
<td>42.3±0.7</td>
<td>36.5±0.9</td>
</tr>
<tr>
<td>MFFT</td>
<td>31.0±1.0</td>
<td>36.0±1.0</td>
<td>32.0±1.0</td>
<td>27.0±1.0</td>
<td>25.0±1.0</td>
<td>21.0±1.0</td>
</tr>
<tr>
<td>$T_g$-MFFT</td>
<td>11.4</td>
<td>17.9</td>
<td>15.8</td>
<td>19.2</td>
<td>17.3</td>
<td>15.5</td>
</tr>
</tbody>
</table>

3.9.5 Mechanical properties

The mechanical properties of poly(MMA/BA/UMA) latex films were evaluated by tensile tests. The tensile properties of latexes prepared from seeded semibatch polymerization were compared in Figure 3-11. The modulus decreased with the increasing side chain length. In comparison with the control sample, the modulus of
poly(MMA/BA/UMA) latexes based on methyl, ethyl, butyl and hexyl amine were much higher. Then the modulus of poly(MMA/BA/UMA) latexes based on octyl amine decreased to a much lower value than that of the control sample. The maximum modulus was around 2650 MPa from the poly(MMA/BA/MEM) latex film. The tensile strength had a similar trend as the modulus with the maximum strength 26.5 MPa from the poly(MMA/BA/MEM) latex film. The elongation-at-break increased with the increasing side chain length. For the methyl and ethyl amine based the poly(MMA/BA/UMA) latex films, there were very small elongation before failure of films. In comparison, much larger elongation-at-break values were observed for longer side chain based poly(MMA/BA/UMA) latex films.

Figure 3-11 Tensile properties of poly(MMA/BA/UMA) latex films
3.9.6 Viscoelastic properties

Figure 3-12 $E'$ and $\tan \delta$ as a function of temperature for Poly(MMA-BA-UMA) latexes
The dynamic properties were studied by DMA. The viscoelastic properties of poly(MMA/BA/UMA) latexes prepared from semibatch polymerization were compared in Figure 3-12. The storage modulus decreased with the increasing side chain length. In comparison with the control sample, the modulus of poly(MMA/BA/UMA) latexes based on methyl, ethyl, butyl and hexyl amine were much higher. Then the modulus of poly(MMA/BA/UMA) latexes based on octyl amine decreased to a lower value than that of the control sample. The maximum modulus was around 2400 MPa from the poly(MMA/BA/MEM) latex film. The glass transition had a similar trend as the storage modulus. From the storage modulus curves, the poly(MMA/BA/UMA) latexes based on amines with longer aliphatic chains started the glass transition at lower temperatures in comparison with the other latexes with shorter aliphatic chains. After the glass transition stage, there were obvious plateaus shown at high temperatures. The similar trend of the storage modulus was observed in the rubbery stage. In the tan δ curves, the glass transition temperatures were obtained from the position where the maximum tan δ located. The T_g decreased with the increasing chain length of amines. The glassy storage modulus, E’, glass transition temperatures, T_g and maximum tan δ transition as a function of the chain length of the urethane functional monomers are summarized in Table 3-7.

Table 3-7 Viscoelastic properties of poly(MMA/BA/UMA) latex films as a function of the chain length of the urethane functional monomers

<table>
<thead>
<tr>
<th></th>
<th>Max. E’ (MPa)</th>
<th>T_g (°C)</th>
<th>Max. Tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(MMA/BA)</td>
<td>1282</td>
<td>66.3</td>
<td>2.21</td>
</tr>
<tr>
<td>Poly(MMA/BA/MEM)</td>
<td>2386</td>
<td>77.8</td>
<td>1.75</td>
</tr>
<tr>
<td>Poly(MMA/BA/EEM)</td>
<td>1687</td>
<td>72.9</td>
<td>1.85</td>
</tr>
<tr>
<td>Poly(MMA/BA/BEM)</td>
<td>1434</td>
<td>67.4</td>
<td>1.90</td>
</tr>
<tr>
<td>Poly(MMA/BA/HEM)</td>
<td>1330</td>
<td>65.4</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Poly(MMA/BA/OEM)</td>
<td>1200</td>
<td>61.4</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Uncertainty</td>
<td>±60</td>
<td>±1.0</td>
<td>±0.02</td>
</tr>
</tbody>
</table>

3.10 Discussion

While hybrid PUA latexes have been widely studied\(^3\)\(^{-22}\), PUA latexes starting from non-isocyanate urethane functional monomers haven’t been previously reported. For these studies\(^3\)\(^{-22}\), isocyanates were used for the preparation of hybrid PUAs. Since isocyanates are toxic to the environments and body\(^173\)\(^{-174}\), it is of great importance to prepare such urethane functional latexes without using isocyanates. Consequently, a series of new non-isocyanate urethane functional monomers were put into latexes for the first time.

The Smith-Ewart theory has been widely used to explain the behavior of water-insoluble monomers in emulsion polymerization, such as styrene and butadiene\(^196\). The aqueous solubility of UMAs falls in between styrene and butadiene (See Table 3-2). The emulsion polymerization processes for all non-isocyanate urethane functional latexes proceeded under the control of Smith-Ewart theory\(^52\), providing uniform particle sizes and stable particle numbers. First of all, the high instantaneous conversion (>85%) and the constant rate of polymerization (See Figure 3-5) indicated that the monomer-starved conditions had been reached. The instantaneous conversions of all UMAs were very close to 100% (See Figure 3-6), indicating the absence of mass transfer limitation. Secondly, the main locus for particle nucleation is the micelle particles. Uniform particle size was observed from DLS (See Table 3-5). Due to the limitation of DLS for secondary nucleation\(^195\), the uniform particles morphology was further observed from the TEM and UAAS results (See Figure 3-7 and 3-8). No secondary or coagulative nucleation was evidenced since the uniform particle sizes from DLS, UAAS and TEM, were pretty close.
to that from the theoretical calculation and the number of particles remained constant (See Figure 3-9). Therefore, the polymerization of UMA monomers with the finite solubility doesn’t fall outside the Smith-Ewart control.

The urethane functionality had a direct impact on the MFFTs of urethane functional latexes such that it influenced the film formation processes. For thermoplastic latexes, lower MFFT is desired for better film formation while higher T<sub>g</sub> is desired for better film properties. To exclude the influence of T<sub>g</sub> on the MFFT, the difference of the T<sub>g</sub> and the MFFT of the latexes, ΔT was used to evaluate the ability of film formation for poly(MMA/BA/UMA) latexes<sup>197</sup>. The ΔT observed for all poly(MMA/BA/UMA) latexes was 30-50% larger than that observed for the control poly(MMA/BA) latex (See Table 3-6). The ability of urethane functional latexes to lower MFFT was attributed to the hydrogen bonding formed from urethane groups in the poly(MMA/BA/UMA) latexes. It has been observed that the presence of hydrogen bonds can lower MFFT in latexes<sup>198-200</sup>. Due to the formation of hydrogen bonds between water and the polymer, the water can be absorbed into the polymeric matrix. The absorbed water can be considered as effective plasticizer during film formation of latexes and therefore exert plasticizing effect to lower the MFFT of latexes.

The urethane functionality also showed effects on the tensile properties. With the increasing chain length of the third comonomer, UMA, the tensile modulus, tensile strength, storage modulus and elongation of poly(MMA/BA/UMA) latexes showed a descending trend due to the addition of flexible side chains of polymers resulted from the increasing aliphatic chains of the UMA.
When $T_g$ is not the factor, the effect of the urethane functionality on the tensile properties, were only compared between the control poly(MMA/BA) and the poly(MMA/BA/HEM) latexes. Higher tensile modulus, tensile strength, storage modulus and elongation were observed from the poly(MMA/BA/HEM) latex than the control poly(MMA/BA) latex (See Figure 3-11, 3-12 and Table 3-7). Such behavior was attributed to the increasing particle interaction by forming hydrogen bonding among urethane groups. A possible mechanism is proposed to explain the improvement of tensile properties of the urethane functional latexes, depicted in Figure 3-13. With the single transition observed from $E'$ and tan $\delta$ curves, there formed homogeneous structure for the urethane functional latexes, i.e. homogeneous urethane functionality in the whole particles. During the coalescence stage of film formation, the polymer chains of one particle diffuse into another one and then the hydrogen bonding can be formed from ester-urethane and urethane-urethane interaction between polymer chains present in different particles. The presence of the urethane functionality in the continuous phase increased the interaction between particles and therefore contributed to the improvement of the tensile properties of latex film.
The use of the non-isocyanate urethane methacrylates in latexes, providing a technical platform of urethane functional latexes with low MFFT and improved mechanical properties, is very attractive in commercial use of special latexes\textsuperscript{201}. First of all, all non-isocyanate urethane methacrylates were successfully incorporated into latexes by emulsion polymerization regardless of hydrophobicity (up to octyl substitution). Secondly, the simple emulsion polymerization process is more desirable than the other currently complicated methods\textsuperscript{3-22} for preparation of hybrid PUAs. In addition, there is absence of poor compatibility problems as usual in the hybrid PUAs\textsuperscript{3-22, 87}. Finally, as possible regulatory issues about isocyanates continues, the demand for developing non-isocyanate urethane functional latexes is on the rise to obtain a cost/performance balance.
3.11 Conclusion

A series of urethane functional acrylate monomers were synthesized through an environmentally friendly nonisocyanate route. All non-isocyanate urethane methacrylates were successfully incorporated into latexes by emulsion polymerization regardless of hydrophobicity (up to octyl substitution). The aqueous solubility of the new urethane methacrylate monomers is in the range conclusive to the Smith-Ewart behavior. The glass transition temperature and the film properties of poly(MMA/BA/UMA) decreased with the increasing chain length of urethane methacrylate monomers due to the increasing flexibility of side chains. The ability of film formation, represented by the difference between $T_g$ and MFFT, was improved by the presence of urethane functionality. The incorporation of urethane functionality improved the mechanical properties, i.e. higher tensile modulus, tensile strength and elongation-at-break. This improvement in mechanical properties is the result of hydrogen bonds formation in the urethane groups.
CHAPTER IV

INVESTIGATION OF THE NON-ISOCYANATE URETHANE FUNCTIONAL MONOMER IN LATEX BY EMULSION POLYMERIZATION

4.1 Summary

A urethane methacrylate monomer, 2-[(butylcarbamoyl)oxy]ethyl methacrylate (BEM) was synthesized using a cyclic carbonate route. Urethane functional latexes were prepared by copolymerization of BEM with methyl methacrylate (MMA) and butyl acrylate (BA). The effects of polymer composition, concentration and the locus of urethane functionality in the polymer particles were studied. Urethane functional latexes were evaluated by Fourier transform infrared spectroscopy (FT-IR), solid state nuclear magnetic resonance (SS-NMR), dynamic light scattering (DLS), differential scanning calorimetry (DSC), tensile tests and dynamic mechanical thermal analysis (DMTA). It was found that there was compositional drift occurred during batch polymerization which resulted in blocks rich in MMA and BEM. This resulted in the higher modulus and tensile strength in latexes derived from batch polymerization. The tensile properties were enhanced with the increasing BEM. It was found that the urethane functionality in the shell gave the best overall properties.
4.2 Introduction

Polyacrylate\(^2\) (PA) and polyurethane\(^1\) (PU) are two of the most popular resins that are widely used in waterborne coating systems. Combining PU and PA is beneficial for specific applications. To some extent, physical blending is a practical way. Some good properties have been combined by physical blending. However, the acrylic/PU polymers have a tendency to stay in separate particles during the film formation process, which can compromise the film properties. Therefore, the physical blends of the two polymers result in properties of low quality\(^7, 87\).

A more successful method to deal with combination of polyurethane with polyacrylate is to synthesize the hybrid polyurethane/polyacrylate (PUA) together. Various methods of preparing hybrid PUA have been explored\(^202\), including intimately mixing\(^3-4\), grafting\(^5-12\), interpenetrating polymer networks (IPNs)\(^13-18\) and core-shell morphology\(^19-22\). A polyurethane dispersion is generally used as the seed for the polymerization of acrylic monomers to obtain hybrid emulsions\(^10, 87, 203\). A series of PUA hybrid latexes with different acrylic contents were prepared by in situ polymerization\(^3\). It was found that around 50 wt % was the upper limit value of acrylic content to be incorporated without external surfactants. Acrylates were intimately mixed into PUD by using semibatch emulsion polymerization\(^4\). The optimum performance came from the hybrid with 50:50 weight ratio of PU and PA components\(^4\).

Another approach is the grafting between polyurethane and acrylic emulsion\(^7-12\). The presence of grafted copolymer helps improve the compatibility of acrylic-polyurethane hybrid emulsions\(^7-11\). Zhang et al. had successfully prepared a series of PU/PA hybrid emulsions by solvent free method using \(\gamma\)-ray initiation\(^12\). The grafting reaction probability
was enhanced as well as the hardness of the films. Larock et al. prepared new hybrids by using a soybean oil-based PU and methyl methacrylate (MMA) / butyl acrylate (BA) copolymers\textsuperscript{11}. The grafting extent between PU and PA was enhanced and led to the improved thermal and mechanical properties.

Other approaches are where IPN-like crosslinked or core-shell structures consisting of acrylic-polyurethane hybrid materials are formed\textsuperscript{91, 204-206}. PUA IPNs have been prepared by mutually polymerizing the urethane prepolymers and acrylic monomers, respectively\textsuperscript{18}. The broad glass transition ranges indicated an interpenetrating network of PA and PU chains. Chai \textit{et al.} prepared core–shell PUA composite\textsuperscript{20} with PU shell and with PA core. The particle sizes were found not significant influenced by PU/PA weight ratios. Reorientation was proved with rich PU at air-facing and substrate-facing surfaces for urethane/acrylic latexes synthesized with PU as the seed\textsuperscript{21}. Kulkarni et al. found performance properties of PUA core-shell hybrid were better than that of the latex IPN hybrids\textsuperscript{22}.

However, the idea of preparation of carbamate monomer and its copolymerization in emulsions is rarely studied. The urethane acrylate or methacrylate is generally synthesized through an isocyanate route\textsuperscript{23}. Isocyanates need to be stored, handled and processed following special safety procedures. The replacement of the hazardous phosgene (used for synthesis of isocyanates) and isocyanates has become a significant concern\textsuperscript{24}. These statements above possibly cause that there are little studies, if any, about improving compatibility of PA and PU starting from monomers in the past 20 years.

Non-isocyanate urethane di-methacrylates had been previously prepared and used as reactive diluents in UV-curable polyurethane coatings\textsuperscript{179}. The non-isocyanate urethane
di-methacrylates reduced the viscosity of the coating formulation, and improved the impact resistance and tensile properties of the final cured coatings\textsuperscript{179}. Herein, a non-isocyanate urethane mono-methacrylate, 2-[(butylcarbamoyl)oxy]ethyl methacrylate (BEM) was prepared for use in latexes. Urethane functional latexes were prepared by semibatch monomer-starved emulsion polymerization of BEM with MMA and BA. The effect of polymer composition, concentration, and the locus of urethane functionality in the polymer particles on urethane functional latexes were studied and evaluated by Fourier transform infrared spectroscopy (FT-IR), solid state nuclear magnetic resonance (SS-NMR), dynamic light scattering (DLS), differential scanning calorimetry (DSC), tensile tests and dynamic mechanical thermal analysis (DMTA).

4.3 Materials

Ethylene carbonate (EC, 98%), methylene chloride (DMC, 99%), butyl amine (BA, 99%), hydroquinone (99%), triethyleneamine (TEA, 99%), dimethyl sulfoxide-\textit{d}_6 (DMSO-\textit{d}_6, 100%), anhydrous magnesium sulphate (99%), hydrochloric acid solution (HCl, 36.5-38 wt%), ammonium persulfate (APS), sodium bicarbonate (NaHCO\textsubscript{3}), methacrylic anhydride (MAA, 94%), and the ionic surfactant Triton X-200 and the nonionic surfactant Triton X-100, were all purchased from Sigma-Aldrich and used as received. 4-(dimethylamino) pyridine (DMAP, 99%) was obtained from Acros Organics and was used as such. Water used was deionized to have conductivity below 15\textmu S/cm. Acrylic monomers, methyl methacrylate (MMA, 99%), butyl acrylate (BA, 99%) were purified by mixing with the inhibitor removal resin (Alfa Aesar). After the purification, monomers were carefully sealed and stored in the refrigerator.
4.4 Instrumentation

The $^1$H, $^{13}$C nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury 500 MHz spectrometer using DMSO-$d_6$ as the solvent for liquid samples. Solid-State NMR $^{13}$C CP MAS experiments were performed on Bruker Avance III 300 NMR spectrometer with a 4 mm double resonance VT CPMAS probe. The frequencies for proton and carbon were 300.1 and 75.5 MHz, respectively. The MAS frequency used was 12000 ± 5 Hz. The $^1$H 90° pulse length was set to 3.75 μs. High-power two pulse phase modulation decoupling with a field strength of 65 kHz was applied to proton channel during acquisition. 1.5 ms and 2 s were chosen for the cross-polarization (CP) contact and recycle delay time. A Nicolet 380 Fourier transform infrared spectroscopy (FT-IR) (Thermo Electron Corp.) was used to obtain the FT-IR spectra by using a KBr crystal plate with very thin layer of a liquid sample. Electrospray ionization (ESI) mass spectra were acquired on a HCT Ultra II quadrupole ion trap mass spectrometer (Bruker Daltonics, Billerica, MA) with sample concentration of 0.03 mg/ml in CH$_2$Cl$_2$:MeOH 50:50 with addition of 1mg/ml sodium trifluoroacetate (1% volume in sample solution). Gel permeation chromatography (GPC) was used to determine the molecular weight by using high-resolution Waters columns with THF at 1 mL/min with polystyrene as the calibration standard. Thermal analysis was performed using 1000 DSC (Q1000, TA Instruments). Two cycles of heating and cooling were performed at rates of 20 °C/min. The glass transition temperature was obtained from the second cycle. Gas Chromatography (CP-3800, Varian Inc.) was used to detect the unreacted monomers using the WCOT fused silica capillary column. The particle sizes were obtained on Zetasizer Nano ZS90 (Malvern) and DT1200 ultra acoustic attenuation spectrometer (UAAS) (Dispersion Technology Inc.). Particle morphologies was obtained.
on JSM-1230 transmission electron microscopy (TEM) (JEOL). Thermal analysis was performed on 1000 DSC (Q1000, TA Instruments). Tensile properties were studied on an Instron 5567 (Instron Corp.). The viscoelastic study were performed on a dynamic mechanical thermal analyzer (DMTA) (Q800, TA Instruments). Linear viscoelastic properties were acquired from the linear oscillatory shear, melt-rheology measurements on an Advanced Rheometric Expansion System (ARES) (G2, TA Instruments).

4.5 Synthesis

The non-isocyanate urethane functional methacrylate monomer and latexes based on this monomer were synthesized.

4.5.1 Synthesis of the non-isocyanate urethane functional methacrylate monomer (BEM)

The synthesis process of the urethane functional methacrylate monomer consists of two steps. Firstly, ethylene carbonate (88.06 g, 1.00 mol) along with the dichloromethane (300 mL) was added into a 1L three-neck flask. Then butylamine (BA, 80.46g, 1.10 mol) was dropwise added into EC-CH$_2$Cl$_2$ solution mixture at 0 °C by using the ice bath under N$_2$ atmosphere and magnetic stirrer. The reaction was performed at room temperature for 24 h. After the 24 h reaction, rotary evaporation was used to remove the dichloromethane. The yellow liquid (yield: 90-95%), BA-EC, the hydroxyalkylcarbamate, was then obtained.

In the second step, hydroxyalkylcarbamate (80.6g g, 0.5 mol), 4-(dimethyl-amino) pyridine (DMAP) (610 mg, 5 mmol), and hydroquinone (98.4 mg, 0.8 mmol) along with the dichloromethane (300 mL) was added into the flask at 0 °C under N$_2$ atmosphere and magnetic stirrer. Then triethylamine (TEA) (70.8 g, 0.7 mol) was dropwise added and followed by dropwise addition of methacrylic anhydride (98.4 g, 0.6 mol). After the
addition, the mixture was stirred at 0 °C to continue reaction for 24 h. After 24 h reaction, 200 mL dichloromethane was added. The extraction of final products BA-EC-MAA was done with the following steps: the saturated brine (300 mL) was first put into the mixture to separate into two phases and the product in the bottom layer was collected, washed with 1 M hydrochloric acid solution (300 mL × 3) saturated sodium bicarbonate solution (300 ml × 3) and saturated brine (300 mL × 1). The product was then mixed with anhydrous magnesium sulphate to remove water. After the filtration process and the rotary evaporation of dichloromethane, the product was left in the vacuum oven until there is no change of weight. A light yellow liquid product was obtained with overall yield around 65-70%. $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ (ppm) = 0.84 (t, $J$ = 6.9 Hz, 3 H, -CH$_3$), 1.26 (m, 2 H, -CH$_2$CH$_3$), 1.36 (m, 2 H, -CH$_2$CH$_2$CH$_3$), 1.87 (s, 3 H, -CH$_3$), 2.97 (m, 2 H, -CH$_2$NH), 4.20 (m, 2 H, -OCH$_2$CH$_2$O-), 4.24 (m, 2 H, -OCH$_2$CH$_2$O-), 5.67 (m, 1 H, cis C=CH$_2$), 6.03 (s, 1 H, trans C=CH$_2$), 7.15 (s, 1 H, -NHCOO-). $^{13}$C NMR (500 MHz, DMSO-d$_6$) $\delta$ (ppm) 13.53 (-CH$_2$CH$_3$), 17.82 (-CH$_3$), 19.34 (-CH$_2$CH$_3$), 31.45 (CH$_2$), 39.98 (-CH$_2$NH), 61.47 (-NHCOOCH$_2$-), 63.08 (-CH$_2$CH$_2$O-), 125.77 (C=CH$_2$), 135.70 (C=CH$_2$), 155.92 (C=O, carbamate), and 166.36 (C=O, ester). MS (ESI-MS) calculated for C$_{11}$H$_{19}$NO$_4$ (m/z), 229.1; found, 229.0 [M-Na$^+$] (see Supplementary Data).

4.5.2 Synthesis of homopolymers poly (BEM)s

In order to determine $T_g$ of poly (BEM) based on the relationship of Mn vs $T_g$, poly (BEM)s with variable molecular weights (low, medium and high Mw) were synthesized by free radical polymerization using 2-mercaptoethanol as the chain transfer agent, AIBN as the initiator and THF as the solvent. Half of the THF (26.67 g, 30 mL) was firstly charged into the reactor. Monomer (5 g), AIBN (3 mol% based on the monomer) and chain
transfer agent (0.5-1 mol% based on the monomer) were dissolved in the remaining half of the THF (26.67 g, 30 mL) to form a solution mixture. After arriving desired temperature 65 °C under purging of N₂, the solution was then charged into the reactor by using the pump at a slow rate (0.3mL/min) and the reaction continued for another 24 h at 65 °C. After the reaction, the polymer product was extracted from THF by precipitation in the cold cyclohexane.

4.5.3 Latex preparation

The Latexes designed with different polymer compositions, different locations of functionality and different concentration of functionality were prepared by seeded batch and semibatch emulsion polymerization processes.

Seed: The seed latex was prepared from a batch reaction. NaHCO₃ (1.5 g), Triton X-200 (0.5 g) and distilled water (150 g) were added to a 500 mL four-neck flask reactor equipped with a condenser and mechanical stirrer. A pre-emulsion of monomers containing BA (41.68 g, 0.33 mol), MMA (38.32 g, 0.38 mol), NaHCO₃ (0.1 g), Triton X-200 (3.6 g) and distilled water (80 g) was added. Before addition of the initiator, the mixture was under nitrogen atmosphere for 20 mins and heated to 75 °C. Then the ammonium persulfate solution (2 wt%, 102 g) was added to the reactor. The temperature was kept at 75 °C and polymerization continued for another 90 min. The same experimental setup was used for the following latexes. The composition of the respective pre-emulsion was listed in Table 4-1.

For batch mode latex with 10 wt % urethane functionality (BFL10%), a batch-wise polymerization process was used. The seed (32 g) was charged in the reactor and heated to 75 °C. After the target temperature was reached, a pre-emulsion of BA, MMA and BEM
(BFL10% in Table 1) and an ammonium persulfate solution (102 g, 2 wt%) were added once into the reactor. The mixture was heated at 75°C and reaction was run for another 240 min at 75°C.

For semibatch mode latex with 10 wt % urethane functionality (BFL10%), semibatch polymerization process was used. The seed (32 g) was poured into the reactor and temperature was set to 75 °C. After the target temperature was reached, a pre-emulsion of BA, MMA and BEM (SBFL10% in Table 1) along with an initiator solution (2 wt% APS solution, 102 g) were fed continuously for 240 min. The mixture was heated at 75°C and reaction was run for additional 240 min after the pre-emulsion feed was complete.

For core-shell latexes (FLC-S, C-FLS and FLH series), single and two-stage semibatch emulsion polymerization processes were used. The composition of the respective pre-emulsion was listed in Table 4-1.

Single stage semibatch emulsion polymerization process was used to prepare the FLH series latexes. The seed (32 g) was charged in the reactor and heated to 75 °C. After the target temperature was reached, a pre-emulsion of BA, MMA and BEM (if needed) along with an initiator solution (2 wt% APS solution, 102 g) were fed continuously for 240 min. The mixture was heated at 75°C and reaction was run for additional 240 min after the pre-emulsion feed was complete.

Two-stage semibatch emulsion polymerization processes were used to prepare the FLC-S and C-FLS series latexes.

Core: The seed (32 g) was charged in the reactor and heated to 75 °C. After the target temperature was reached, a pre-emulsion of BA, MMA and BEM (if needed) along with an initiator solution (2 wt% APS solution, 102 g) were fed continuously for 240 min.
The mixture was heated at 75°C and reaction continued for additional 240 min after the pre-emulsion feed was complete.

Shell: A pre-emulsion of BA, MMA and BEM (if needed) for shell phase and the initiator solution (2 wt% APS solution, 102 g) were fed during shell synthesis for 240 min. After feeding was over, reaction continued for additional 240 min at 75°C to complete conversion. The coagulum for the batches was less than 0.5 wt% based on amount of monomers.

Table 4-1 Composition of pre-emulsion for urethane-functionalized latexes

<table>
<thead>
<tr>
<th>Pre-emulsion</th>
<th>[BEM] wt</th>
<th>DI water /g</th>
<th>NaHCO₃ /g</th>
<th>Triton X200, X100</th>
<th>Monomer amount MMA:BA:BEM(g)</th>
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</thead>
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<tr>
<td>BFL10%</td>
<td>10%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>32 : 40 : 8</td>
</tr>
<tr>
<td>SBFL10%</td>
<td>10%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>32 : 40 : 8</td>
</tr>
<tr>
<td>FLH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>73.6 : 86.4 : 0</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>70 : 82 : 8</td>
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<tr>
<td></td>
<td>10%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>64 : 80 : 16</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>54.5 : 73.5 : 32</td>
</tr>
<tr>
<td>FLC-S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>48 : 32 : 0</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>43.6 : 28.4 : 8</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>37.6 : 26.4 : 16</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>28.1 : 19.9 : 32</td>
</tr>
<tr>
<td>C-FLS</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>48 : 32</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>48 : 32</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>80</td>
<td>0.1</td>
<td>3.6, 0.4</td>
<td>48 : 32</td>
</tr>
</tbody>
</table>
4.6 Latex characterization

The obtained latexes were characterized in terms of particle size, conversion, composition, morphology and molecular dynamics.

4.6.1 Conversion analysis

The overall and instantaneous monomer conversions were measured by gravimetical analysis. During the reaction intervals, around 1 g of latex samples were taken out of the reactor and were quenched by adding one drop of 1% hydroquinone solution. The quenched samples was weighed into aluminum dishes and dry in oven for 2 h at 110 °C. The instantaneous conversions of each specific monomer were determined from Gas Chromatography with respective standard calibration curves as the external standards (see Supplementary Data).

4.6.2 Fourier Transform Infrared (FT-IR) spectroscopy

A thin latex film for FT-IR was directly coated onto the ZnSe plates and dried in the vacuum oven until no weight loss and measured in the range of 500 to 4000 cm\(^{-1}\) wavelength.

4.6.3 Particle size analysis

The particle sizes and particle size distributions were measured by dynamic light scattering. For dynamic light scattering measurement, the latex samples were diluted to be less than 0.1 vol %. The measurement were carried out with a fixed angle of 90° at 25 °C.
4.6.4 Morphological analysis

The latex samples were cleaned by using membrane analysis to remove excess amount of ionic materials, such as surfactants and buffer salts. The typical procedure was as following. A latex sample was placed inside the regenerated cellulose dialysis membrane (MWCO 12000–14000). The membrane was put into a beaker filled with distilled water for several days with water replaced every 12 h. The cleaning of the latexes was done when the conductivity of the external water was around 20 μS/cm.

After the cleaning process, the latexes were diluted to 0.5-1 wt%. Then one to two drops of the diluted sample was put on the thick carbon coated 400-mesh copper grid. Samples were left at room temperature to dry for 24 h prior to imaging. For the core-shell latexes, around 10 g of MMA was replaced with styrene in the core stage to increase the contrast. The core-shell samples were exposed to RuO$_4$ vapors for 15-30 min and left at room temperature to dry for 24 h prior to imaging.

4.7.5 Molecular dynamics analysis

Molecular dynamics was studied by solid-state NMR with $^{13}$C CP MAS experiments. The adamantine was used as an external reference with the CH signal at 29.46 ppm. The temperature was calibrated with the $^{207}$Pb chemical shift of Pb(NO$_3$)$_2$. Each spectrum was performed for 2048 scans at various temperatures. The spectral fitting was performed based on Lorentz peaks.

4.8 Film preparation and characterization

Latexes were cast onto a leveled polytetrafluoroethylene plate and cured at room temperature for two to three days. Films were removed from the plate and kept for
additional 7 days at room temperature before testing. The dry films with constant thickness (around 0.35-0.40 mm) and smooth surface were obtained.

4.8.1 Tensile properties analysis

Tensile properties were tested with 10 specimens (length 40 mm, width 13-15 mm and thickness 0.35–0.40 mm) for each sample at room temperature with a crosshead speed of 50 mm/min applied. An average value of at least ten replicates of each sample was taken.

4.8.2 Dynamic mechanical thermal analysis

The viscoelastic behavior were studied by DMTA in tensile mode from −20 to 120 °C with a heating rate of 3 °C/min. The frequency was fixed at 1 Hz. At least three specimens (15 mm length × 10 mm width × 0.35-0.4 mm thickness) were prepared for each sample and the average was taken as the results.

4.8.3 Rheological analysis

Linear oscillatory shear rheology was performed with a d=8 mm parallel-plate fixture from 30 to 220 °C. The strain amplitude \( \gamma \) and frequency \( \omega \) were fixed at 1% and 1 Hz, respectively. The tensile moduli between 80 and 220 °C were converted from the shear moduli measured by simple shear by assuming \( E' = 3G' \).

The nomenclature developed to represent the urethane functional latexes in this study, is focused on the reaction processes and the location and concentration of urethane functionality in the latex polymer particles. The designation consists of one term and a number. The first term, “SBFL” or “BFL”, defines the latexes prepared from semibatch and batch polymerization processes, respectively. The first term, “FLC-S” “C-FLS” or
“FLH”, defines the urethane functional latexes with the urethane functionality located in the core, in the shell or homogeneously in the whole particles, respectively. The second term (0, 5, 10 or 20 %) designates the percentage of the urethane methacrylate monomer present in the latexes. The number quantifies the weight fraction of urethane methacrylate monomer relative to the total amount of monomers.

4.9 Results

As a continuation of a previous report, this study focused on polymerization process and extension of BEM type monomer in core-shell latex architecture. All latexes were designed with the same overall T_g. Batch and semibatch emulsion polymerization were chosen to compare the influence of the composition of polymer chains. The concentration of urethane functionality was designed from 0 to 20 wt% based on the overall monomer weight. The core-shell structure was investigated by common techniques, such as DSC, DMTA and TEM, as well as SS-NMR. SS-NMR has successfully been applied to study the molecular dynamics in amorphous, semi-crystalline polymers as well as supermolecular structures. Segmental dynamics in glassy polymers in 3-50 kHz scale, which corresponds well with the glass transitions, would broaden the high resolution CP MAS spectra. The resultant urethane functional latex films were evaluated by tensile tests and DMTA.

4.9.1 Characterization of homopolymers of BEM

A series of homopolymer of BEM (PBEM) with low to high molecular weights were synthesized with solution polymerization with AIBN as the initiator and 2-mercaptoethanol as the chain transfer agent. The glass transition temperature of PBEMs
was determined by DSC. The glass transition temperature\textsuperscript{207}, which is independent of molecular weight above a specific molecular weight, is defined as the glass transition temperature of a homopolymer. The number average molecular weights and related glass transition temperatures of PBEMs were plotted in Figure 4-1. The glass transition temperature was dependent of number average molecular weight before the number average molecular weight reached 100,000 g/mol. Then there was a glass transition temperature plateau after 100,000 g/mol. The glass transition temperature at the plateau as defined, which was around 26 \textdegree C, was the glass transition temperature of BEM’s homopolymer, PBEM.

Figure 4-1 The plot of the number average molecular weights and related glass transition temperatures of PBEMs
4.9.2 Comparison of batch and semi-batch emulsion polymerizations

Batch and semi-batch emulsion polymerization processes are widely used in the industry.

4.9.2.1 Kinetic analysis during polymerization

Two latexes poly(MMA/BA/BEM) with the same monomer composition (MMA/BA/BEM: 32/40/8) were prepared with different techniques. The first one was obtained by using the simple batch emulsion polymerization while the second one was prepared through semibatch emulsion polymerization. Time evolution of overall conversion ($X_{overall}$), instantaneous overall conversion (inst.$X_{overall}$) and the rate of polymerization ($R_p$) were depicted in Figure 4-2a and 4-2b for BFL10% and SBFL10%, respectively. For batch polymerization, the monomers were added once and therefore the rate of polymerization increased very quickly at the initial stage and then decreased slowly to zero. For semi-batch polymerization, the instantaneous overall conversion was above 85% after initial several minutes, which indicated that the monomer-starved condition had been reached. The rate of polymerization under monomer-starved condition was relatively stable. The z-average diameter of particles ($d_p$) and the number of total particles ($N_p$) as a function of time during the polymerization were shown in Figure 4-3. Overall particle size increased gradually over time during synthesis for both BFL 10% and SBFL10% latexes. In the initial stage of batch polymerization, there was an instantaneous increase of the particle number due to the presence of high concentration of monomer and initiator. The number of particles ($N_p$) from batch polymerization was higher than the results obtained
from the semi-batch polymerization. The particle size from the batch polymerization was also smaller than the results from semi-batch polymerization.
Figure 4-2 Evolution of overall conversion, instantaneous overall conversion and the rate of polymerization in the SBFL10% (a) and BFL10% (b)

Figure 4-3 Evolution of the number of total particles and volume-average particle diameter in the semibatch (SBFL10%) and batch polymerization (BFL10%)

The instantaneous conversion ($X_{\text{inst.}}$) of each monomer was calculated based on the residue monomers detected by GC. The instantaneous conversion ($X_{\text{inst.}}$) of each monomer during semibatch emulsion polymerization and batch emulsion polymerization was shown in Figure 4-4. In the semibatch emulsion polymerization, comparable instantaneous conversions were shown for all the monomers, i.e. MMA, BA and BEM. At the very beginning, the initial instantaneous conversions of MMA, BA and BEM were above 85%, which indicated that the monomer-starved condition had been reached. The polymer chains, therefore, were homogeneously composed of MMA, BA and BEM with the same
composition of monomer feeding. In the batch emulsion polymerization, it was shown that there was significant difference between the instantaneous conversions of MMA, BA and BEM. The initial instantaneous conversions of MMA and BEM were ~ 80%. The monomer, BA showed much lower instantaneous conversions than that of MMA and BEM. In comparison, it took only several minutes for instantaneous conversions of MMA and BEM to reach 80% while almost 20 minutes for instantaneous conversion of BA to reach 80%. Therefore, BA showed a slower reactivity in its copolymerization with MMA and BEM in the batch polymerization. The difference in the instantaneous conversions of MMA, BA and BEM indicated the possible existence of two rich blocks in the BFL10%: one is the block rich in MMA and BEM and the other one is rich in BA. The existence of rich phases presumably would influence the properties of the latexes, as shown in the following sections.
Zoom in BFL10%

SBFL10%

Dosing Done
Figure 4-4 Evolution of instantaneous conversion of each monomer in BFL10% and SBFL10%

4.9.2.2 Thermal properties

The thermal property of the latexes was studied by DSC. The glass transition temperatures of the batch and semibatch polymerization were compared and the overall results were listed in Table 4-2. The Tgs of latexes were designed based on the Fox equation208 (See Supplementary Data). The theoretical glass transition temperature was designed around 0 °C. There was a little deviation for the experimental glass transition temperatures of both latexes from the theoretical values, i.e. 4.3 °C for BFL10 wt% and 4.6 °C for SBFL10 wt%. However, the experimental glass transition temperatures of BFL10 wt% and SBFL10 wt% were very close due to the same overall composition of monomers. There was only one glass transition showed from the heat flow curves for both the batch and semibatch latexes. However, from the heat flow curves (See Supplementary Data) with the same heating rate, it was observed that the glass transition of the latex from batch
polymerization was broader than the result of the latex from semibatch polymerization. In comparison, the sharp glass transition can represent a relatively homogeneous SBFL10 wt% while the broad one for the BFL10 wt%.

Table 4-2 Overall result of glass transition temperatures of BFL10% and SBFL10%

<table>
<thead>
<tr>
<th></th>
<th>Theoretical $T_g$</th>
<th>Experimental $T_g$ from DSC</th>
<th>Experimental $T_g$ from DMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFL10%</td>
<td>0 °C</td>
<td>4.3 ± 0.7 °C</td>
<td>40 ± 1.0 °C</td>
</tr>
<tr>
<td>SBFL10%</td>
<td>0 °C</td>
<td>4.6 ± 1.0 °C</td>
<td>34 ± 0.9 °C</td>
</tr>
</tbody>
</table>

4.9.2.3 Mechanical properties

Tensile tests were performed to evaluate the mechanical properties of two latexes. The tensile properties of latexes prepared from semibatch and batch polymerization were compared in Figure 4-5. The latex film prepared from BFL10% showed higher Young’s modulus and tensile strength while lower elongation-at-break than that from SBFL10%. From the stress-strain curves, the terpolymer from batch polymerization showed high stresses at small elongations. Then the terpolymer film elongated further to the end of the breakage of the film. On the other hand, the terpolymer from semibatch polymerization exhibited a gradual increase of both stress and strain to the end of the breakage of the film. The modulus and tensile strength for the latex from batch polymerization were 3.7 and 4.2 MPa, respectively, which were 30% and 130% higher than that from the semibatch polymerization with 3.0 and 1.8 MPa, respectively. However, the 570% elongation-at-break observed from batch polymerization was lower than 720% from semibatch polymerization.
Figure 4-5 Stress-strain curves of BFL10% and SBFL10% latex films

4.9.2.4 Viscoelastic properties

The dynamic properties of two latexes were studied by DMTA. The viscoelastic properties of latexes prepared from semibatch and batch polymerization were compared in Figure 4-6. The terpolymer from batch polymerization showed a higher storage modulus than that from semibatch polymerization. The storage modulus of the latex film prepared from batch polymerization in the glassy state was ~2100 MPa while that from semibatch polymerization was ~2000 MPa. In addition, it was observed from the $E'$ that the glass transition was broader for the latex from semibatch polymerization than that from batch polymerization. The glass transition temperatures were obtained from the maximum of the $\alpha$-transition. The glass transition temperatures were 40°C and 34°C for latexes from batch and semibatch polymerization, respectively. In addition, the comparison of the full-width-
at-half-maximum tan δ values indicated significant difference between batch and semibatch polymerization. The full-width-at-half-maximum tan δ was 40°C for batch polymerization, while only 26°C for semibatch polymerization. The broader tan δ transition of BFL10% represented a more heterogeneous composition than that of SBFL10%.

Figure 4-6 Modulus (E’) and tan δ as a function of temperature for BFL and SBFL10% latex films

4.9.3 The urethane functional core-shell latexes

The effect of urethane functionality was further investigated in terms of their concentration and location.

4.9.3.1 Composition of urethane functionality

The composition of urethane latexes were studied by qualitatively analysis of FTIR spectra. The spectra of FLH series, FLC-S series and C-FLS series were depicted in Figure 4-7. The vibrations at 1720 cm\(^{-1}\) was overall sum of the stretching of carbonyl groups (C=O) from each monomer. The vibrations at 1530 cm\(^{-1}\) and at 3350 cm\(^{-1}\) were characteristics of the stretching and bending of urethane groups (NH) only from the urethane methacrylate monomer. In the qualitatively analysis, the stretching of carbonyl groups C=O at 1720 cm\(^{-1}\) were referenced as the internal standard while the stretching of urethane (NH) at 3350 cm\(^{-1}\)
cm\(^{-1}\) and the bending of urethane (NH) at 1530 cm\(^{-1}\) were as the characteristic of urethane functionality from urethane methacrylates. The theoretical ratios of N-H to C=O are 0, 2.62, 5.24 and 10.53 mol\%, respectively. The spectra shown in Figure 4-7 clearly showed the qualitative increase of the urethane functionality of latexes from low concentration to high concentration in the FLH series, FLC-S series and C-FLS series.

Figure 4-7 FT-IR spectra for samples of FLH, C-FLS and FLC-S 5 to 20% prepared on ZnSe crystal
4.9.3.2 Particle size and morphology

The particle size was measured by DLS and TEM and compared with the theoretical result to evaluate the stability of the dispersion. The overall results of particle size were listed in Table 4-3. The theoretical particle size was around 380nm, which was calculated from the equation (4-1) based on the mass equation\textsuperscript{180}.

\[
d_f = \left(1 + \frac{W_m}{W_s}\right)^{1/3} d_s
\]

where \(W_m\) is the amount (g) of monomer feed; \(W_s\) is the amount (g) of seed particles; \(d_s\) and \(d_f\) is the particle diameter (nm) of the seed and final latexes, respectively.

DLS and TEM were combined to evaluate the particle sizes and their distribution. As the most widely used method, DLS directly gives the z-average (\(d_z\)) particle sizes. To compare with theoretical results, \(d_z\) was listed in the Table 4-3. The particle size \(d_v\) from DLS showed a little difference compared with the theoretical values. Moreover, particle sizes of all latexes were comparable within the error. The particle size was further checked with TEM. The contrast of dark and white in TEM images showed the morphology of the core-shell structures while uniform grey showed the morphology of the homogeneous structure. The particle size from TEM was much larger than DLS and theoretical results. This was not consistent with other studies of TEM particle sizes\textsuperscript{58,181}. The inconsistency probably resulted from the flattening due to the low Tg.

Table 4-3 Particle size results from DLS and theoretical calculation

<table>
<thead>
<tr>
<th></th>
<th>DLS</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d_z) / nm</td>
<td>PDI</td>
</tr>
<tr>
<td>FLH0%</td>
<td>377</td>
<td>0.01</td>
</tr>
<tr>
<td>C-S 0%</td>
<td>380</td>
<td>0.01</td>
</tr>
<tr>
<td>FLH5%</td>
<td>394</td>
<td>0.01</td>
</tr>
<tr>
<td>FLH10%</td>
<td>391</td>
<td>0.02</td>
</tr>
<tr>
<td>FLH20%</td>
<td>390</td>
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<tr>
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<tr>
<td>FLC-S5%</td>
<td>384</td>
<td>0.02</td>
</tr>
<tr>
<td>FLC-S10%</td>
<td>383</td>
<td>0.03</td>
</tr>
<tr>
<td>FLC-S20%</td>
<td>374</td>
<td>0.03</td>
</tr>
<tr>
<td>C-FLS5%</td>
<td>385</td>
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</tr>
<tr>
<td>C-FLS10%</td>
<td>380</td>
<td>0.01</td>
</tr>
<tr>
<td>C-FLS20%</td>
<td>390</td>
<td>0.01</td>
</tr>
<tr>
<td>Uncertainty</td>
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<td>±0.01</td>
</tr>
</tbody>
</table>

Figure 4-8 TEM of core-shell morphology study for samples of FLC-S20%, C-FLS20% and FLH20% latexes

4.9.3.3 Thermal properties

The overall results of the glass transition temperatures of a series of latexes prepared from semibatch polymerization were listed in Table 4-4. The T$_g$s of latexes were designed based on the Fox equation$^{208}$ (See Supplementary Data). The morphology of core-shell and homogeneous structure were indirectly proved from the glass transitions. From the heat flow curves, it was observed that there was only one glass transition for the latexes with homogeneous structures while two clear glass transitions were observed for the latexes with core-shell structures. There was a little deviation for the experimental glass transition temperatures from the theoretical values, which shifted to high temperatures.
Table 4-4 Overall result of glass transition temperatures of core-shell and homogeneous latexes

<table>
<thead>
<tr>
<th></th>
<th>T$_g$ from DSC</th>
<th>T$_g$ from DMA</th>
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<tr>
<td>Theoretical</td>
<td>T$_g$=0 °C</td>
<td>T$_g$=0 °C</td>
</tr>
<tr>
<td>FLH5%</td>
<td>-1 ± 0.9</td>
<td>31 ± 0.6</td>
</tr>
<tr>
<td>FLH10%</td>
<td>2 ± 1.0</td>
<td>32 ± 0.7</td>
</tr>
<tr>
<td>FLH20%</td>
<td>4 ± 0.7</td>
<td>38 ± 0.5</td>
</tr>
<tr>
<td>FLC-S5%</td>
<td>21 ± 0.7</td>
<td>45 ± 0.9</td>
</tr>
<tr>
<td>FLC-S10%</td>
<td>21 ± 0.5</td>
<td>51 ± 1.0</td>
</tr>
<tr>
<td>FLC-S20%</td>
<td>26 ± 1.0</td>
<td>52 ± 0.5</td>
</tr>
<tr>
<td>C-FLS5%</td>
<td>24 ± 0.5</td>
<td>50 ± 0.7</td>
</tr>
<tr>
<td>C-FLS10%</td>
<td>24 ± 0.4</td>
<td>51 ± 0.4</td>
</tr>
<tr>
<td>C-FLS20%</td>
<td>30 ± 1.0</td>
<td>54 ± 1.0</td>
</tr>
</tbody>
</table>

4.9.3.4 Mechanical properties

The mechanical properties were evaluated by tensile tests. The tensile properties, modulus, tensile strength and elongation-at-break were compared in Figure 4-9 among three series of latexes prepared from semibatch polymerization, i.e. FLH, FLC-S and C-FLS.

For FLH and C-FLS latexes, the tensile strength increased with the addition of urethane functionality in the range of 5-20 wt%. For FLC-S latexes, the tensile strength showed no change within 0-5 wt% urethane functionality content and gradually increased within 10-20 wt% urethane functionality content. The tensile strength of all three systems reached the maximum at 20 wt% reactive diluents content. In comparison, the tensile strength of FLH system was a little higher than that of the FLC-S system at the same percent loading in the range of 5-20 wt% while the tensile strength of C-FLS system was always 1.1-1.3 times higher than that of the FLH or FLC-S system at the same percent loading in the range of 5-20 wt%.
The elongation-at-break continuously increased with the increasing urethane functionality in the percent loading range of 5-20 wt% and reached the maximum at 20 wt% for all three systems. The maximum elongation-at-break of FLH system was 2.6 times higher than that of FLH0%; and the maximum value of C-FLS and FLC-S systems were 3.0 times and 4.5 times higher than that of C-S0%, respectively. In comparison of the elongation-at-break in the range of 5-20 wt%, the elongation-at-break of C-FLS system was around 1.2-1.4 times and 1.5-1.7 times higher than that of the FLH and FLC-S systems.

The tensile modulus showed a continuous increase with the addition of urethane functionality in the percent loading range of 5-20 wt% and reached the minimum at 20 wt% urethane functionality content for all three systems. The maximum tensile modulus of FLH system was 2.9 times higher than FLH0%; and the maximum elongation-at-break of C-FLS and FLC-S systems were 2.0 times and 3.6 times higher than C-S0%, respectively. In comparison, the trend of tensile modulus was consistent with the elongation-at-break. At 5-10 wt%, the tensile modulus of C-FLS system was around 1.2-1.3 times higher than that of the FLH system while at 20 wt%, 1.6 times. At 5 wt%, the tensile modulus of C-FLS system was around 1.3 times higher than that of the FLC-S system while at 10-20 wt%, 1.7 times.
Figure 4-9 Modulus, tensile strength and elongation-at-break for core-shell and homogeneous latexes

4.9.3.5 Viscoelastic properties

The viscoelastic properties of all latexes were investigated and the storage modulus $E'$ and the tan$\delta$ transition of C-FLS, FLC-S and FLH latexes were shown in Figure 4-10 and Figure 4-11. For the C-FLS latexes with functionality located in the shell, the storage modulus $E'$ of the latex films increased with addition of the urethane content in the load range of 5-20 wt%. There were two glass transitions as shown in Figure 4-10, which gave another support for the core-shell structures. The same phenomena were observed from obvious $\alpha$-transitions, as shown in Figure 4-11. The same trend was observed for the FLC-S latexes with functionality located in the core. For the FLH latexes with functionality located homogeneously in the whole particle, the storage modulus also increased with the increasing urethane functionality in the range of 5-20 wt%. Single glass transition was observed, supporting the homogeneous structure. The storage moduli were compared among different locations in Figure 4-12. In comparison, the storage modulus of FLC-S, FLH and C-FLS systems showed ascending trend in the range of 5-20 wt%.
Figure 4-10 Storage modulus (E’) as a function of temperature for core-shell and homogeneous latexes (The curves at low temperature range were measured from tensile data with frequency $\omega = 1$ Hz and the curves at high temperature range were calculated from shear data measured at a frequency $\omega = 1$ Hz and converted to tensile values by assuming $E = 3G$.)
Figure 4-11 Tan δ as a function of temperature for core-shell and homogeneous latexes

In addition, $T_g$ can be evaluated from the temperature position of the maximum of $\alpha$-transition. One $T_g$ was determined for FLH series of latexes while two $T_g$s for FLC-S and C-FLS series of latexes. The results were listed in Table 4-4. The $T_g$ increased with the increasing of urethane functionality content while the maximum of $\alpha$-transition decreased with increasing of urethane functionality content.
Comparison of storage modulus of core-shell and homogeneous latexes at the (a) glass state and (b) rubbery plateau

4.9.3.6 Molecular dynamics from SS-NMR

Figure 4-13 $^{13}$C CP MAS spectra of sample FLH from -40 to 80 oC. The * indicates the spinning side band

Molecular dynamics was studied by SS-NMR with $^{13}$C CP MAS experiments. $^{13}$C SS-NMR spectral lineshape was sensitive to the mobility change around $T_g$ for amorphous polymers$^{73-75}$. The motional broaden and the sharpen process of resonances, assigned to
different chemical components in polymer blends, were sensitive to the glass transition. The temperature dependence $^{13}\text{C}$ CP MAS spectra for FLH system from -40 to 80 °C were shown in Figure 4-13. The half width of carbon resonance from urethane groups at $\delta=156$ ppm was broadening at 20 °C which was the sign for glass transition. Resonance fitting was performed and summarized in Table 4-5 to quantitatively illustrate this issue. As was indicated in Table 4-5, from 0 to 20 °C, the half width of resonance at $\delta=156$ ppm increase from 1.63 to 3.79, which corresponded well with the glass transition temperature measured by DSC. Different chemical component resonances showed similarly broadening features reflecting the homogenous phase structures and single $T_g$ in the system.

Table 4-5 Typical resonance fitting half widths for sample FLH at variety of temperatures

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>$\delta=176$ /ppm</th>
<th>$\delta=156$ /ppm</th>
<th>$\delta=64$ /ppm</th>
<th>$\delta=31$ /ppm</th>
<th>$\delta=14$ /ppm</th>
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<tbody>
<tr>
<td>-40</td>
<td>3.18</td>
<td>1.59</td>
<td>2.82</td>
<td>1.98</td>
<td>1.41</td>
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<td>0</td>
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<td>40</td>
<td>5.75</td>
<td>2.09</td>
<td>3.78</td>
<td>2.38</td>
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</table>

![Figure 4-14 $^{13}\text{C}$ CP MAS spectra of sample C-FLS 20% from -40 to 60 °C](image-url)

Figure 4-14 $^{13}\text{C}$ CP MAS spectra of sample C-FLS 20% from -40 to 60 °C
In Figure 4-14, the temperature dependence of $^{13}$C high resolution SS-NMR spectra was shown for C-FLS system from -40 to 60 °C. Different chemical groups showed different line broadening and sharpening processes. The carbon resonance from the ester groups at $\delta=174$ ppm showed the broadening process until 40 °C while the urethane group at $\delta=156$ ppm showed the broadening process at 0 °C. The broadening process was attributed to largely mobility change due to the glass transitions. This clearly showed the complex phase structures which are different from the FLH system. According to the synthesis route, the urethane functional monomer was only consisted in the shell structure. The broadening process from 0 °C clearly shows the shell structure has a lower $T_g$. Also, at higher temperature, the relative resonance intensity at $\delta=156$ ppm dramatically decreased showing the cross polarization efficiency largely drop, which also reflected the high mobility of the shell above room temperature. The resonance at $\delta=174$ ppm showed a different dynamics feature from the shell. The broadening process starting from the 40 °C showed the core had a much slower dynamics comparing to the shell. SS-NMR clearly showed the different molecular dynamics process of different chemical components in a complex phase structures. Different resonance half widths were summarized in Table 4-6.

Table 4-6 Typical resonance fitting half widths for sample C-FLS 20 % at variety of temperatures

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>$\delta=176$ /ppm</th>
<th>$\delta=156$ /ppm</th>
<th>$\delta=64$ /ppm</th>
<th>$\delta=31$ /ppm</th>
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<tr>
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<td>2.79</td>
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<tr>
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</tr>
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</table>
Figure 4-15 $^{13}$C CP MAS spectra of sample FLC-S 20% from -40 to 60 °C.

Similar phenomena were observed from the variety temperature $^{13}$C CP MAS experiments of sample FLC-S 20% from -40 to 60 °C with the spectra shown in Figure 4-15 and the resonance fitting results shown in Table 4-7. Similarly, the variable temperature $^{13}$C CP MAS experiments of samples with 10% urethane functionality from -40 to 60 °C were carried out (see Supplementary Data). The experiments of 5% urethane functionality can’t be carried out due to the extremely low signal of urethane functionality that can’t be distinguished from the noise signal at relatively high temperatures.

Table 4-7 Typical resonance fitting half widths for sample FLC-S 20% at variety of temperatures

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>δ=176 /ppm</th>
<th>δ=156 /ppm</th>
<th>δ=64 /ppm</th>
<th>δ=31 /ppm</th>
<th>δ=14 /ppm</th>
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</thead>
<tbody>
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<td>1.56</td>
<td>2.80</td>
<td>2.00</td>
<td>1.51</td>
</tr>
<tr>
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<tr>
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<td>2.67</td>
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<td>0.75</td>
</tr>
<tr>
<td>20</td>
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<td>3.50</td>
<td>2.37</td>
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<tr>
<td>40</td>
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<td>2.59</td>
<td>5.89</td>
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</tr>
<tr>
<td>60</td>
<td>4.28</td>
<td>1.35</td>
<td>2.36</td>
<td>1.59</td>
<td>0.43</td>
</tr>
</tbody>
</table>
In Figure 4-16, the cross polarization spectrum showed additional resonances at \( \delta=69 \) ppm and \( \delta=170 \) ppm comparing to the direct polarization spectrum. The selective enhancement of these resonances was due to the difference in the cross polarization co-efficiencies. The largely different mobility between the core and shell might lead to the largely different cross polarization co-efficiencies.

4.10 Discussion

Generally, isocyanates which are hazardous\(^{24}\) are used to prepare the hybrid PUA latexes by intimately mixing\(^{3-4}\), grafting\(^{4-12}\), IPNs\(^{13-18}\) and core-shell morphology\(^{19-22}\). In this paper, a urethane methacrylate monomer was synthesized through an environmentally friendly non-isocyanate method and polymerized via the seeded emulsion process to form urethane functional latexes. The use of one master batch seed avoided the problematic nucleation stage, and allowed the comparison of polymerization without error from the starting conditions and the preparation of heterogeneous core-shell structure latexes\(^{30}\). This
is the first time the non-isocyanate urethane methacrylate was incorporated into the synthetic core-shell latexes thus far in the reported literature. The polymer composition, the concentration and location of urethane functionality showed significant effects on the final latex film properties of urethane functional latexes prepared by semibatch monomer-starved emulsion polymerization.

The batch and semibatch emulsion polymerization showed effect on the polymer composition and the resultant film properties. There was compositional drift in the batch polymerization, illustrated with much lower instantaneous conversion of BA than MMA and BEM (see Figure 4-4). The broader glass transition in BFL latex also consolidated the less homogeneous composition of polymer chains from batch polymerization. Due to the compositional drift, a rich block consists predominantly of MMA and BEM might exist in the polymer chains, as shown in Figure 4-17. This resulted in higher tensile modulus, tensile strength and lower elongation-at-break in BFL latex. Due to the presence of methyl substitution from MMA and BEM, the free rotation of polymer chains was hindered, which made the polymer chain more rigid. Due to the presence of the rich block of MMA and BEM in BFL, higher $T_g$ was expected in the rigid block and higher extent of entanglement existed, which restricted the movement of polymer chains when the films were stretched. This phenomena has also been observed in copolymerization of MMA and BA$^{209}$ as well as the crosslinking latex$^{210}$. 
The location of urethane functionality in the polymer particles was successfully established. First of all, no secondary nucleation was evidenced since the uniform particle sizes were observed from DLS (see Table 4-3), comparable to the theoretical values within the experimental error for all three systems. Secondly, core-shell and uniform structures were observed from the contrast of darkness and brightness (see Figure 4-8). The single glass transition and two glass transitions observed from DSC thermograms and viscoelastic properties (see Table 4-4, Figure 4-10 and 4-11) further collaborated the presence of two phases. Finally, SS-NMR was used to determine the location of the urethane functionality by correlating the molecular dynamics with the chemical composition. Similar broadening features of different chemical component resonances in the SS-NMR spectra reflected the homogenous phase structures and single \( T_g \) in the FLH series (see Figure 4-13 and Table 4-5). Different molecular dynamics process of different chemical components in a complex phase structures were clearly shown in SS-NMR for the FLC-S and C-FLS series (see Figure 4-14 and Table 4-6, Figure 4-15 and Table 4-7). The overall results gave support to
the conclusion of obtained morphologies with urethane in the core, in the shell or in the whole particle.

The concentration and location of urethane functionality also showed significant effect on the improvement of the final latex film properties of urethane functional latexes. A mechanism was proposed to explain the improvement of the tensile and viscoelastic properties of the urethane functional latexes, depicted in Figure 4-18. The mechanical properties were enhanced with the addition of the urethane functionality content for all these three systems (see Figure 4-9). The trend in the storage modulus was similar to the trend in tensile modulus (see Figure 4-10). This behavior was attributed to the increased entanglement interaction between polymer chains. With the increase of the urethane functionality content, the density of hydrogen bonding increased. The cyclic hydrogen bonding formed among urethane was unknown. However, it was reasonable to assume the presence of cyclic hydrogen bonding. The formation of hydrogen bonding, which can be considered as effective physical crosslinks, hindered the movement of the polymer segmental chains. This phenomena has been observed in a variety of polymer systems. Therefore, the film formed with the increased hydrogen bonding was more intact due to the increased entanglement of polymer chains intra/inter particles.
Figure 4-18 A possible mechanism during film formation process for (1) FLH series, (2) C-FLS series (3) FLC-S series latexes

In comparison, the mechanical properties of the C-FLS system was higher than that of the FLH system; the mechanical properties of the FLH system was higher than that of the FLC-S system in the range of 10-20 wt % of urethane functionality (see Figure 4-19). This was attributed to the higher concentration of hydrogen bonding formed from urethane functionality in the continuous phase. This led to the more intact films and better properties of C-FLS latexes than that of FLC-S and FLH latexes. With the 5 wt % of urethane functionality, there was no significant difference of tensile strength among these systems. This result was attributed to the low interaction sites for the film formation with 5 wt % of urethane functionality. The presence of urethane functionality at the surface of particles in the C-FLS and FLH systems was too low to generate enough hydrogen bonding of inter particles. Therefore, the effective physical crosslinks couldn’t form based on insufficient hydrogen bonding. The further evidence came from the comparison of the storage modulus of FLH, FLC-S and C-FLS (see Figure 4-12).
The incorporation of the non-isocyanate urethane methacrylate into the synthetic core-shell latexes has potential for commercial latexes\textsuperscript{7, 87}. The urethane functional latexes prepared with the BEM monomer showed safer and perhaps more environmental friendly compared with conventional hybrid PUA based on isocyanates. In addition, a simple emulsion polymerization process is more desirable than the other currently complicated methods\textsuperscript{3-22, 87, 91, 202-206} for preparation of hybrid PUAs. Finally, there is absence of compatibility problems as is usual for most hybrid PUAs\textsuperscript{3-22, 87, 91, 202-206}.

4.11 Conclusions

Urethane functional latexes were prepared by copolymerization of BEM with methyl methacrylate (MMA) and butyl acrylate (BA). There was a compositional drift during batch polymerization and a block rich in MMA and BEM might exist in the polymer chains. This resulted in the higher tensile modulus, tensile strength and storage modulus of the polymer prepared from batch reaction than that from semibatch reaction. The homogeneous and core-shell structures were prepared. The incorporation of urethane functionality improved mechanical properties, i.e. higher tensile modulus, tensile strength and elongation-at-break, with increasing concentration, regardless of location. The urethane in the shell gave the best overall properties due to the higher concentration of urethane present in the continuous phase.
CHAPTER V
INVESTIGATION OF THE CARBON FILLED TEOS OLIGOMER MODIFIED EPOXY-AMINE COATING SYSTEMS

5.1 Summary

The epoxy coating systems containing carbon fillers were prepared with carbon black, mixture of carbon black and non-fullerene carbon nanotubes, unpurified and purified non-fullerene carbon nanotubes, and unpurified and purified fullerene carbon nanotubes. The effect of carbon filler type and content on the viscosity of coatings as well as mechanical, thermal and electrical properties of the cured films were evaluated. General coating properties including pencil hardness, impact resistance, cross-hatch, and pull-off adhesion were also investigated. Scanning electron microscope (SEM) was used to observe the surface morphology of a fracture film surface. The storage modulus and crosslink density increased and the maximum tan δ decreased with the increase of filler content. Aggregation of carbon fillers at 1.0 wt% resulted in a decrease in film properties. It was found that the most efficient material to enhance the electrical conductivity and anticorrosive properties of nanocomposite coating systems was fullerene CNTs.
5.2 Introduction

Corrosion issues are of great importance in modern societies. The economy of the whole world were directly and indirectly influenced by the corrosion of metals. The study about the corrosion costs in the United States in 2002 indicates that more than 3% of the gross domestic product (GDP) was from corrosion cost and the direct cost of corrosion is $276 billion. In addition, corrosion results in structural failures, which lead to dramatic consequences for both humans and environment. Therefore, corrosion prevention has recently attracted many scientific studies. The general application of an organic coating, such as epoxy coating, is the protection of various metals against corrosion. Although the anticorrosion mechanism is based on providing a physical barrier against corrosive species, the defect of the organic coatings can result in local corrosion. Consequently, it seems that the barrier properties of epoxy coatings have to be improved.

In the last two decades, many studies have been conducted toward application of carbon nanotubes (CNTs) because of their useful properties including excellent mechanical strength, superior modulus, thermal and electrical conductivity, and large aspect ratio. Hence, CNTs are considered as ideal candidates for high performance engineering applications such as reinforcements in various polymeric materials. In addition, the combination of CNTs with a wide range of organic coatings has led to the development of nanocomposite coatings which can be utilized in various potential applications.

Epoxy resins, which have been commonly used in organic coatings, are inherently brittle and thus reduce damage tolerance. Besides, due to their extremely high dielectric characteristics, they have limited applications to objects where the formation of electrostatic charges is the primary concern. Recent and ongoing research on
polymer/carbon nanocomposites have shown that nanomaterials have enhanced various characteristics in a given polymer material. The incorporation of CNTs into epoxy coatings can not only improve the properties of epoxy\textsuperscript{144,145}, but also bring additional excellent properties, such as toughness\textsuperscript{146,147,148,149}, electrical conductivity\textsuperscript{148,149} and thermal conductivity\textsuperscript{150}. For example, it was found that by the introduction of 5 wt\% of pristine multi-wall carbon nanotubes (MWCNTs), the Young’s modulus increased by about 20\%.\textsuperscript{144} Ayatollahi et al. also reported a growth of 10.5\% in the elastic modulus and 13\% improvement in the hardness using 1 wt\% MWNT\textsuperscript{145}. The enhancement of fracture toughness has also been reported when the CNTs were incorporated into epoxy coatings\textsuperscript{146,215}. In another study, the high electrical conductivity as a result of the formed CNT networks, enabled the CNT/epoxy coatings to be used for anti-static coatings application\textsuperscript{148}. In addition, the electrical behavior can be used to evaluate the dispersion of CNTs. Hsu et al.\textsuperscript{149} claimed that the film capacitance is more accurate to evaluate dispersion than film resistance, according to their results.

The effects of CNTs on the glass transition temperature ($T_g$) is more complicated than those on the conductive properties. Many investigations have been performed on $T_g$ because of the presence of relationship between this parameter and cure degree, mechanical properties, and other characteristics. An increase\textsuperscript{167}, decrease\textsuperscript{167,168,169} or no change\textsuperscript{169,170} in the $T_g$ of nanocomposites have been previously reported with the cross-linked epoxy composites. In a review\textsuperscript{159} about the influence of unmodified CNTs on the $T_g$ of nanocomposites, several factors such as the bundling tendency of single-wall nanotubes (SWNT) and residual solvent were proposed for the decreased values of $T_g$. In fact, the presence of CNTs could catalyze or retard the curing reaction of epoxy coatings. The curing
kinetics in presence of CNTs can not be uniformed since CNTs are prepared and modified by different ways and have different grades of purity\textsuperscript{159}. The catalyst particles remaining in CNTs can affect cure reaction. Moreover, the presence of functional groups such as -NH\textsubscript{2}, -OH, and -COOH on the surface of CNT, makes the situation more complicated than unmodified CNTs.

It is well known that the incorporation of CNTs is an efficient way to improve the corrosion resistance of organic coatings. As one of the most commonly used barrier coatings, epoxy is a good candidate for anticorrosive applications, such as in the marine environment\textsuperscript{216}. However, epoxy generally attracts water from the environment\textsuperscript{217-218} because of the hydrophilic chemical groups such as hydroxyl and amino groups in the cured epoxy structure. An effective method for improving the corrosion resistance of organic coatings is the incorporation of nanoparticles\textsuperscript{219-222} as barriers. For example, Shon et al\textsuperscript{219} reported MWCNTs-containing epoxy coatings which showed improved corrosion resistance for the prepared epoxy-coated steel. The improvement of corrosion resistance was also found in other types of organic coatings, such as polyurethane\textsuperscript{221} and silane coatings\textsuperscript{222}. The principal mechanism of the anti-corrosion behavior of CNTs is through providing a physical barrier against the corrosive species\textsuperscript{219-222}. CNTs with long chain structures can fill pores and flaws in the coating and increase the transporting pathways of the corrosive species.

Throughout the last decades, a variety of inorganic/organic hybrids have been prepared for various applications\textsuperscript{118-120}. The hybrid products have combined the unique properties such as durability and stability from inorganic part and processability and toughness from organic polymers. Based on the sol-gel process, Soucek and coworkers\textsuperscript{27}
have already prepared alkoxysilane oligomer modified epoxide primers which showed improved adhesive and antcorrosive properties.

In the present study, bisphenol-A (BPA) based liquid epoxide was modified with alkoxysilane oligomers through the sol-gel technique. The nanocomposite coating systems were prepared by the solution mixing method with six types of conductive fillers, including carbon black, non-fullerene carbon nanotubes and fullerene carbon nanotubes. The prepared nanocomposites were evaluated by tensile tests, dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), four-point probe method, scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS).

5.3 Materials

DER 317, the Bisphenol-A (BPA)-based epoxide was purchased from Dow Chemicals. Tetraethoxysilane (TEOS), hydrochloric acid (37 wt% in water), 2,4,6-Tris(dimethylaminomethyl)phenol (95%), ethanol (ACS reagent ≥99.5%), and acetone (ACS reagent ≥99.5%) were all obtained from Sigma-Aldrich. The modified polyamidoamine resin (trade name: EPIKURE™ Curing Agent 3192) was obtained from Momentive Corporation. A-36, the 3×6 in aluminum paneles, with bare surface and smooth mill finish, were purchased from Q-Lab Corporation. Six grades of conductive carbon fillers (XS2310 carbon black, XD35496A mixture of carbon black and non-fullerene carbon nanotubes, XW22789 unpurified non-fullerene carbon nanotubes, XW22099 purified non-fullerene carbon nanotubes, XBC9649 unpurified fullerene carbon nanotubes and XBC2364 purified fullerene carbon nanotubes in ascending order of conductivity) were obtained from Continental Carbon Nanotechnologies, Inc. (CCNI). All of the materials were used as received.
5.4 Instrumentation

The nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury 300 MHz spectrometer. The static viscosity was obtained on the Brookfield viscometer (DVII+ PRO Digital) with a spindle SC4-25. An Instron 5567 (Instron Corp.) was used to investigate the tensile properties. A dynamic mechanical thermal analyzer (DMTA, Q800, TA Instruments) was used to study the viscoelastic properties. Differential scanning calorimeter (DSC, Q200, TA Instruments) was used to study the thermal properties. The surface electrical conductivity properties were measured using the four-point probe method, performing on a Lucas Signatone QuadPro Resistivity System (Pro4-440N). Morphology was performed on the scanning electron microscopy (SEM, JEOL JSM5310). The EIS measurements were preformed on a Gamry Reference 600 System with a three electrode cell, including a saturated Calomel as the reference electrode, a niobium platinized mesh as the counter electrode and the tested coating as the working electrode. The frequency varied from from 50 kHz to 10 mHz and the amplitude of 10mV (rms) was fixed at open circuit potential. The electrolyte used was 3.5% NaCl solution with pH = 6.8 and 4.2 cm² was used as the area that was exposed to the electrolyte.

5.5 Preparation of TEOS oligomers and TEOS oligomer modified epoxides

Tetraethylorthosilicate (TEOS, 100 g, 0.48 mol), ethanol (88.32 g, 1.92 mol) and distilled water (8.64 g, 0.48 mol) were added into a round-bottom flask (250 mL) and mixed well for 30 mins under N₂ atmosphere. Then hydrochloric acid (0.175 g, 0.0048 mol) was added dropwise into the mixture. After adding the hydrochloric acid, the reaction continued for additional 96 h at ambient temperature. The TEOS oligomers were then obtained after
the removal of solvent. The TEOS oligomer modified epoxide was prepared by mixing 5 wt% based on total solution to the respective epoxide at 40 °C for 72 h. The modified epoxide was characterized according to ASTM D1652-97 and the end group analysis method to obtain the epoxide equivalent weight. The epoxy equivalent weight (EEW) determined by NMR is based on the ratio of H in CH₂ of oxirane to H on the benzene ring.

5.6 Film preparation and characterizations

Carbon fillers and unmodified or modified epoxy resin were carefully added into acetone. The mixture was then placed in the bath sonicator for 1h before placing into a probe ultrasonicator for 30 min on a pulse mode: 40s on and 20s off. This mixture was submerged continuously in a cooling bath to prevent premature polymerization. Once the cycle was completed, Epikure 3192 curing agent was added to the mixture and mixed using high-speed magnetic stirrer for 30 min. The ratio of epoxy resin to curing agent was based on stoichiometric proportion of oxirane groups in epoxide and -NH groups in the curing agent. For each type of filler, the respective composite were made with loadings of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 wt%, based on the weight of resin and curing agent. The wet films were prepared by using a 6 mil draw-down bar and were kept at room temperature for 24 h before thermal cure. Then the films were cured at 120 °C for 2 h and films of 50–70 μm thickness was obtained.

All films were kept at room temperature for one week before testing. The tensile tests were performed with a crosshead speed at 10 mm/min at room. Ten specimens (40 mm length × 13-14 mm width × 0.05-0.07 mm thickness) were prepared for each sample and the average was taken as the results. The viscoelastic behavior were studied by DMTA in tensile mode from −50 to 200 °C with a heating rate of 3 °C/min. The frequency was
fixed at 1 Hz. At least three specimens (15 mm length × 10 mm width × 0.05-0.08 mm thickness) were prepared for each sample and the average was taken as the results. The thermal properties were characterized with a heating rate of 20 °C/min. The coating tests, i.e. pencil hardness, cross-hatch adhesion, pull-off adhesion and impact resistance were performed according to the ASTM D3363, D3359, D4541 and D2794, respectively.

The nomenclature developed to represent the epoxy coating systems in this study, is focused on the modification of epoxide and the type and concentration of carbon filler in the composition. The designation consists of two terms and a number. The first term, “E” or “TEOS-E”, defines unmodified and TEOS modified epoxides, respectively. The second term, CB, CB-NT, NCNT or PNCNT, FCNT or PFCNT are abbreviated for carbon black (XS2310), mixture of carbon black and non-fullerene carbon nanotubes (XD35496A), unpurified (XW22789) or purified (XW22099) non-fullerene carbon nanotubes, and unpurified (XBC9649) or purified (XBC2364) fullerene carbon nanotubes. The third term (0, 0.2, 0.4, 0.6, 0.8 or 1.0) designates the percentage of carbon filler present in the coating system. The number quantifies the weight fraction of carbon filler relative to the solid content.

5.7 Results

The main goal of this study was improving the inherent brittleness of epoxy coatings and investigating the possibility of application of epoxy coatings to objects where the formation of electrostatic charges is the primary concern. Six types of conductive carbon fillers were incorporated into the alkoxyisilane oligomers modified epoxide coatings from 0 to 1.0 wt% based on the solid content. The resultant coating films were evaluated
in terms of mechanical properties, viscoelastic properties, coating properties, electrical conductivity, and anticorrosive properties.

5.7.1 Preparation and depiction of carbon/modified epoxy nanocomposite coatings

Six carbon fillers were incorporated into the TEOS oligomer modified epoxy nanocomposite coatings. The morphologies of six carbon fillers are shown in Figure 5-1. Six carbon fillers were chosen based on the aspect ratio and purity grade. CB had only the particulate carbon blacks as shown in Figure 5-1a while CB-NT was a mixture of carbon black particulate and relatively flexible carbon nanotubes as shown in Figure 5-1b. Figure 5-1c and 5-1d indicated the relatively flexible nonfullerene carbon nanotubes with unpurified and purified grades, respectively. Figure 5-1e and 5-1f showed the very flexible fullerene carbon nanotubes with unpurified and purified grades, respectively. It showed that the aspect ratio increased dramatically from carbon black, non-fullerene to fullerene carbon fillers.

The TEOS oligomer modified epoxy was cured with a polyamide amine. The epoxy equivalent weight (EEW) of epoxy resin determined by titration and end group analysis of NMR was depicted in Table 5-1. The ratio of epoxy resin to curing agent was based on the stoichiometric proportion of oxirane groups in the epoxide and -NH groups in the curing agent. The chemical reactions during film formation were shown in Figure 5-2. A siloxane layer was expected to form near the metal substrate\textsuperscript{27} as shown in Figure 5-3.
Figure 5-1 Morphologies of carbon fillers: (a) CB (carbon black); (b) CB-NT (mixture of carbon black and non-fullerene carbon nanotubes); (c) NCNT (unpurified) and (d) PNCNT (purified non-fullerene carbon nanotubes); (e) FCNT (unpurified); (f) PFCNT (purified non-fullerene carbon nanotubes).

Table 5-1 The n and EEW results of epoxy DER 317 and TEOS-Epoxy

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Methods</th>
<th>n</th>
<th>EEW (g/equiv.)</th>
</tr>
</thead>
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<td>193</td>
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<td></td>
<td>H(b,c) : H(d)</td>
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<td>194</td>
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<tr>
<td>TEOS-Epoxy</td>
<td>ASTM D1652-97</td>
<td>-</td>
<td>201</td>
</tr>
<tr>
<td></td>
<td>H(b,c) : H(d)</td>
<td>0.155</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5-2 Chemical reactions during film formation

Figure 5-3 Siloxane layer formed near the substrate during film formation

27
5.7.2 Rheological properties of the nanocomposite coatings

The rheological properties of the nanocomposite before film formation were studied by the viscosity measurement. The overall resistance of the nanocomposites to flow was shown by the static viscosities at specific shear rates. Figure 5-4 showed the flow curve obtained for the TEOS-E containing different contents of carbon fillers at different shear rates. From the flow curve of the TEOS-E without any nanofiller, it was observed that the viscosities of TEOS-E did not vary with the change of shear rates which was the characteristics of the Newtonian fluids. With the addition of carbon nanofillers, the flow curves showed that viscosities decreased with increasing of the loading level of carbon nanofillers for all nanocomposite coatings. This trend indicated the shear thinning behavior. At a specific shear rate, the viscosity of the nanocomposites increased with increasing of the amount of carbon nanofillers no matter which carbon nanofiller was used. For example, with the addition of 0.4, 0.6, 0.8, and 1.0 wt% CB-CN, the viscosity increased to 54, 85, 104, and 500 mPas, respectively. The similar behavior was observed for all the other nanocomposite coatings. The aspect ratio of nanofillers also had significant effect on the formation of the microstructure. The longer of the nanofillers, the higher probability of connecting and forming networks. The viscosities of nanocomposite coatings containing fullerene and nonfullerene carbon nanotubes were much higher than that containing CB and CB-CN at any specific shear rate and loading level.
Figure 5-4 The steady state viscosity of carbon/TEOS-E nanocomposites as a function of carbon filler content

5.7.3 Mechanical properties of the nanocomposite coatings

The average tensile properties were plotted in Figure 5-5. According to ASTMD 2370-98 and the linear part of the stress–strain curves, the tensile modulus of carbon/epoxy
nanocomposite systems were calculated and plotted as a function of filler’s loading level as shown in Figure 5-5 (a). The tensile strength at failure was also shown in Figure 5-5 (b). The results of strain-at-break were shown in Figure 5-5 (c). The modulus of TEOS-E was around 1220 MPa. The modulus of nanocomposites with CB increased to 1270, 1310, 1340, and 1390 MPa with 0.4, 0.6, 0.8 and 1.0 wt% loading levels, respectively. For nanocomposites with FCNT, the modulus showed significant increase at low loading levels. The modulus increased to 1530, 1560 to 1610 MPa for nanocomposites with 0.4, 0.6, and 0.8 wt% loading levels of FCNT. The modulus of nanocomposites with the other fillers did not indicate significant enhancement even at low loadings compared with those of coatings without addition of nanofillers. At relatively high loading levels, the modulus showed decreasing trend for all nanocomposite coatings. The tensile strength at break showed the same trend as tensile modulus. The strength of TEOS-E was around 34.5 MPa. The strength of nanocomposites with CB increased to 35.8, 36.3, 37.5, and 38.7 MPa with 0.4, 0.6, 0.8, and 1.0 wt% loading levels, respectively. For nanocomposites with FCNT, the modulus showed significant increase at low loading levels. The modulus increased to 39, 42.5, and 43.7 MPa for nanocomposites with 0.4, 0.6, and 0.8 wt% loading levels of FCNT. All nanocomposites with the other nanofillers did not show significant increase at low loadings and showed decreasing strength at high loading levels. The results of strain-at-break shown in Figure 5-5 (c) were very interesting for the brittle epoxy coating applied on the metal. The addition of carbon black showed no change, if no significant increase of strain-at-break. The strain-at-break of the other nanocomposites increased continuously with the increasing carbon content. The strain-at-break of the nanocomposite with 1.0 wt% FCNT, PFCNT,
CB-NT, NCNT, and PNCNT increased up to 160, 240, 330, 650, and 990\% in comparison with that of the TEOS-epoxy coating.

Figure 5-5 Tensile modulus, tensile strength, and strain-at-break of TEOS-Epoxy nanocomposite as a function of the carbon types and loading levels.
5.7.4 Viscoelastic properties of the nanocomposite coatings

The viscoelastic properties of the nanocomposites were investigated by using DMTA. The average results from these tests were listed in Table 5-2, including the minimum storage modulus, crosslink density, maximum tan δ, glass transition temperature, and breadth of tan δ transition of the nanocomposite films. The storage modulus of nanocomposites which reflects the recoverable energy in the deformed samples was determined from the rubbery plateau of the E’ curves. It was observed that the storage modulus increased continuously with the increasing loading level of CB and FCNT. The storage modulus of the nanocomposites with CB-NT, NCNT, and PNCNT showed increasing modulus in the range of 0.4 to 0.8 wt% while decreasing modulus above 0.8 wt%. It was shown that the storage modulus of nanocomposites with PFCNT decreased continuously with the increasing amount of nanofillers. The similar trends were observed from the comparison of crosslink density. The crosslink density was determined from the theory of rubber elasticity with the E’ at a specific T (T > T_g + 50)\(^{223}\). The T_g values which reflects the thermal stability of the films, was determined from the position of maximum tan δ. There was no typical trend indicated by the results of the glass transition temperature. The difference between the T_g of nanocomposites with different loading levels of one nanofiller type was not large with consideration of the error. The nanocomposite coatings with CB and CB-NT had comparable T_g values with that of TEOS-E. However, compared with the T_g of TEOS-E, the T_g of all the other nanocomposite coatings were relatively lower. The attributes to the scattered glass transition temperature results are complex, as mentioned in the introduction part.
Table 5-2 Viscoelastic properties of the epoxy hybrid coatings

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$E_{\text{min}}$ (MPa)</th>
<th>Crosslink density (mol/m$^3$)</th>
<th>$T_g$(°C)</th>
<th>Max tan δ</th>
<th>Tan δ breadth(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>1.20</td>
<td>121</td>
<td>80</td>
<td>0.96</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E</td>
<td>1.53</td>
<td>156</td>
<td>84</td>
<td>0.94</td>
<td>29</td>
</tr>
<tr>
<td>TEOS-E0.4CB</td>
<td>1.37</td>
<td>139</td>
<td>81</td>
<td>0.89</td>
<td>29</td>
</tr>
<tr>
<td>TEOS-E0.6CB</td>
<td>1.94</td>
<td>197</td>
<td>79</td>
<td>0.94</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E0.8CB</td>
<td>2.09</td>
<td>212</td>
<td>74</td>
<td>0.90</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E1.0CB</td>
<td>2.15</td>
<td>216</td>
<td>79</td>
<td>0.91</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E0.4CB-NT</td>
<td>2.89</td>
<td>294</td>
<td>78</td>
<td>0.98</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E0.6CB-NT</td>
<td>3.33</td>
<td>339</td>
<td>80</td>
<td>1.00</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E0.8CB-NT</td>
<td>4.46</td>
<td>454</td>
<td>82</td>
<td>0.97</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E1.0CB-NT</td>
<td>2.85</td>
<td>290</td>
<td>78</td>
<td>0.98</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E0.4NCNT</td>
<td>2.75</td>
<td>280</td>
<td>74</td>
<td>0.96</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E0.6NCNT</td>
<td>3.28</td>
<td>334</td>
<td>74</td>
<td>0.95</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E0.8NCNT</td>
<td>2.28</td>
<td>232</td>
<td>72</td>
<td>0.93</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E1.0NCNT</td>
<td>2.20</td>
<td>224</td>
<td>69</td>
<td>0.91</td>
<td>29</td>
</tr>
<tr>
<td>TEOS-E0.4PNCNT</td>
<td>2.66</td>
<td>271</td>
<td>71</td>
<td>0.94</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E0.6PNCNT</td>
<td>2.94</td>
<td>299</td>
<td>68</td>
<td>0.94</td>
<td>27</td>
</tr>
<tr>
<td>TEOS-E0.8PNCNT</td>
<td>1.81</td>
<td>184</td>
<td>72</td>
<td>0.90</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E1.0PNCNT</td>
<td>1.37</td>
<td>139</td>
<td>68</td>
<td>0.86</td>
<td>29</td>
</tr>
<tr>
<td>TEOS-E0.4FCNT</td>
<td>1.98</td>
<td>201</td>
<td>76</td>
<td>1.04</td>
<td>22</td>
</tr>
<tr>
<td>TEOS-E0.6FCNT</td>
<td>2.64</td>
<td>269</td>
<td>77</td>
<td>0.95</td>
<td>26</td>
</tr>
<tr>
<td>TEOS-E0.8FCNT</td>
<td>3.71</td>
<td>378</td>
<td>81</td>
<td>0.88</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E1.0FCNT</td>
<td>4.29</td>
<td>436</td>
<td>75</td>
<td>0.87</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E0.4PFCNT</td>
<td>2.72</td>
<td>277</td>
<td>74</td>
<td>0.92</td>
<td>28</td>
</tr>
<tr>
<td>TEOS-E0.6PFCNT</td>
<td>2.46</td>
<td>250</td>
<td>70</td>
<td>0.90</td>
<td>29</td>
</tr>
<tr>
<td>TEOS-E0.8PFCNT</td>
<td>2.12</td>
<td>216</td>
<td>71</td>
<td>0.91</td>
<td>31</td>
</tr>
<tr>
<td>TEOS-E1.0PFCNT</td>
<td>1.57</td>
<td>159</td>
<td>70</td>
<td>0.85</td>
<td>34</td>
</tr>
<tr>
<td>Uncertainty</td>
<td>± 0.06</td>
<td>± 10</td>
<td>± 2</td>
<td>± 0.02</td>
<td>± 1</td>
</tr>
</tbody>
</table>

The results of the maximum tan δ and the breadth of tan δ were listed in Table 5-2. With consideration of the error, the difference between the maximum tan δ of nanocomposites with different loading levels of CB and CB-NT was not large. The
nanocomposite coatings with CB and CB-NT had comparable maximum tan δ with that of TEOS-E. However, the maximum tan δ of all the other nanocomposite coatings showed a decreasing trend with increasing amount of nanofillers. The breadth of tan δ of TEOS-E was around 29 °C. There was no significant difference among variable amounts of nanofillers for the nanocomposites with CB and CB-NT. It was observed that the breadth of tan δ increased with the increasing amount of nanofillers for nanocomposites with NCNT, PNCNT, FCNT, and PFCNT.

5.7.5 Evaluation of the coating properties of the nanocomposite coatings

General coating properties were estimated based on general coating tests (ASTM standards), including impact resistance test, pencil hardness test, crosshatch adhesion test, and pull-off adhesion test. For comparison, the coatings without fillers were also prepared. The results of these general coating properties were listed in Table 5-3. It was observed that there was no effect on the crosshatch adhesion with the increasing amount of the fillers for all nanocomposite coatings. The cross-hatch adhesion results were 5B and no removal of coatings was observed for all nanocomposite coatings. The pencil hardness decreased from 5H to 3H and 2H for FCNT and PNCNT systems with loading level from 0.4 to 1.0 wt%, respectively. There was no change of pencil hardness for all other nanocomposite coatings. The impact resistance of CB-NT and PNCNT systems increased compared with the control sample, but decreased with the addition of fillers in the load range of 0.4-1.0 wt%. The impact resistance of the CB, FCNT, and PFCNT systems remained decent values with addition of 0.4-1.0 wt% carbon fillers compared with the control sample.

Among these general coating tests, pull-off adhesion property was mostly influenced by the inclusion of fillers. The pull-off adhesion properties of FCNT filled
coatings with the increasing loading level remained comparable with the control sample. The pull-off adhesion result of TEOS-E was around 203 lb/in\(^2\). The pull-off results of nanocomposites with 0.4, 0.6, 0.8, and 1.0 wt% loading levels of FCNT were 223, 225, 218, and 237 lb/in\(^2\), respectively. For the nanocomposites with 0.4, 0.6, 0.8, and 1.0 wt% loading levels of PFCNT, the pull-off adhesion properties were 215, 204, 211, and 209 lb/in\(^2\), respectively. For all the other coatings, the pull-off adhesion properties decreased dramatically with the addition of fillers in the loading range of 0.4-1.0 wt%. The pull-off property of the nanocomposite with 1.0 wt% CB decreased to 91 lb/in\(^2\). The pull-off property of the nanocomposite with 1.0 wt% CB-NT decreased to 116 lb/in\(^2\). The pull-off property of the nanocomposite with 1.0 wt% NCNT decreased to 87 lb/in\(^2\). The pull-off property of the nanocomposite with 1.0 wt% PNCNT decreased to 112 lb/in\(^2\). Among the coatings with decreasing adhesion properties, the adhesion properties of nanocomposite coatings with the CB nanofillers decreased the most.

Table 5-3 General coating properties of TEOS-epoxy nanocomposite coating systems

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Impact resistance (lb/in)</th>
<th>Pencil hardness</th>
<th>Crosshatch adhesion</th>
<th>Pull-off adhesion(lb/in(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct</td>
<td>Reverse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEOS-E</td>
<td>22</td>
<td>17</td>
<td>6H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.4CB</td>
<td>32</td>
<td>30</td>
<td>6H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.6CB</td>
<td>31</td>
<td>25</td>
<td>6H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.8CB</td>
<td>32</td>
<td>23</td>
<td>6H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 1.0CB</td>
<td>31</td>
<td>22</td>
<td>6H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.4CB-NT</td>
<td>37</td>
<td>&lt;10</td>
<td>5H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.6CB-NT</td>
<td>24</td>
<td>&lt;10</td>
<td>5H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.8CB-NT</td>
<td>25</td>
<td>&lt;10</td>
<td>5H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 1.0CB-NT</td>
<td>23</td>
<td>&lt;10</td>
<td>5H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.4FCNT</td>
<td>25</td>
<td>&lt;10</td>
<td>6H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.6FCNT</td>
<td>23</td>
<td>&lt;10</td>
<td>5H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.8FCNT</td>
<td>24</td>
<td>&lt;10</td>
<td>3H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 1.0FCNT</td>
<td>22</td>
<td>&lt;10</td>
<td>3H</td>
<td>5B</td>
</tr>
<tr>
<td>TEOS-E 0.4PFCNT</td>
<td>20</td>
<td>12</td>
<td>6H</td>
<td>5B</td>
</tr>
</tbody>
</table>
5.7.6 Electrical conductivity of the nanocomposite coatings

The surface resistivity results of nanocomposites were shown in Figure 5-6. In general, the electrical conductivity of the nanocomposites increased with the increase of the fillers content. However, the improvement is highly based on the dispersing state of fillers and the network that can be formed by the fillers\textsuperscript{224-226}. The decreased sequence of conductive properties were in the order of fullerene CNT > nonfullerene CNT > carbon black systems. The fullerene CNTs showed very promising conductive applications. By addition of only 0.4 wt% loading, the power of conductivity increased by the magnitude of two and three for PFCNT and FCNT, respectively. At the highest loading, i. e. 1.0 wt%, the electrical conductivities of coatings with PFCNT and FCNT were around 0.07 and 0.33 S/m, respectively. The electrical properties of the nonfullerene CNT systems showed slightly increase within the loading range 0.4-1.0 wt%. There was the least increase for carbon black systems, even with the 1.0 wt% loading.
Figure 5-6 Electrical conductivity of TEOS-E with different carbon fillers

5.7.7 Morphology analysis of the nanocomposite coatings

The morphology was studied with SEM of fracture surface after pull-off adhesion. The fracture surface of epoxy and nanocomposite after pull-off were comparatively examined by SEM as shown in Figure 5-7. The fracture surface of TEOS-epoxy was very smooth while all the nanocomposite systems showed roughness with the cleavage edges. With the increasing addition of nanofillers, the surface roughness increased and the distance between cleavage edges decreased gradually.

TEOS-E
TEOS-E0.4CB  TEOS-E0.6CB  TEOS-E0.8CB  TEOS-E1.0CB

TEOS-E0.4CB-NT  TEOS-E0.6CB-NT  TEOS-E0.8CB-NT  TEOS-E1.0CB-NT

TEOS-E0.4FCNT  TEOS-E0.6FCNT  TEOS-E0.8FCNT  TEOS-E1.0FCNT

TEOS-E0.4PFCNT  TEOS-E0.6PFCNT  TEOS-E0.8PFCNT  TEOS-E1.0PFCNT
Figure 5-7 The morphology study of fracture surface of films after pull-off adhesion test

5.7.8 Electrochemical Impedance Spectroscopy

The corrosion resistance of the carbon nanofiller filled epoxy coatings was evaluated using EIS by immersing the coatings in a solution with pH=6.8 for different immersion times. The impedance of the carbon nanofiller filled epoxy coatings was measured. A high impedance magnitude indicates excellent corrosion protection properties and an organic coating system showing this impedance values works as a barrier that avoids the formation of a corrosion cell\textsuperscript{227}.

Figure 5-8 showed the change of impedance with the variation of immersion time for systems with different loading levels of fillers. Figure 1a showed the changes of impedance in the systems with unpurified fullerene CNTs. TEOS-0.4FCNT had the highest impedance value after 120 days of immersion (8.55x10\textsuperscript{6} ohm-cm\textsuperscript{2}) and TEOS-1.0FCNT had the lowest impedance value (2.74x10\textsuperscript{5} ohm-cm\textsuperscript{2}). The changes for TEOS-0.6FCNT and TEOS-0.8FCNT were similar to each other and the impedance magnitudes were between TEOS-0.4FCNT and TEOS-1.0FCNT. The impedance magnitude of TEOS-0.4FCNT, TEOS-0.6FCNT, and TEOS-0.8FCNT did not change a lot over immersion time. This indicated that the interface of the coating was stable to prevent corrosion. However,
the impedance magnitude of TEOS-1.0FCNT decreased gradually over immersion time. The same trends were observed for the systems with purified fullerene CNTs, as shown in Figure 1b. The impedance magnitude changed a lot for TEOS-1.0PFCNT. This indicated that the coatings might start a corrosion process at the metal/coating interface. Figure 1c and 1d showed the changes of impedance in the systems with carbon black and mixture of carbon black and non-fullerene CNTs, respectively. There was no significant difference of impedance values and their evolution between the two systems. The addition of carbon black or the mixture of non-fullerene CNT with carbon black increased the system impedance in comparison with the systems with fullerene CNTs. The impedance of TEOS-1.0CB and TEOS-1.0CB-NT on day 120 is $10^{6-7}$ ohm-cm$^2$, which was two order of magnitude larger than that of TEOS-1.0FCNT and more than two with respect to the TEOS-1.0PFCNT. Figure 1e and 1f showed the changes of impedance in the systems with non-fullerene CNTs. After 120 days, the impedance value in different concentrations became close to each other. There was no apparent effect of the purified non-fullerene carbon nanotubes on the impedance properties of these systems. The impedance magnitude in the systems with non-fullerene CNTs was slightly lower than that with carbon black or the mixture with carbon black and non-fullerene CNTs, while much higher than that with fullerene CNTs.
Figure 5-8 The impedance magnitude at 0.01 Hz of TEOS-E with (a) FCNTs, (b) PFCNTs, (c) CB, (d) CB-NTs, (e) NFCNTs, (f) PNFCNTs and (g) TEOS-E

Figure 5-9 showed Bode plots for all nanocomposites. The capacitive and resistive behavior were shown at high and low frequency, respectively. For the coating system filled with the unpurified fullerene CNTs, it presented very attractive anticorrosion properties because the impedance results did not show any corrosion processes at the metal/coating interface. Similar phenomena were observed for the coating system filled with the purified fullerene CNTs except for at 1% loading level. With 1% purified fullerene CNTs, there was an impedance platform in the Bode plot at low frequencies. In addition, the impedance showed abrupt drop at day 19. This indicated that the coatings started to show a corrosion process at the metal/coating interface.

For the two systems with carbon black and the mixture of carbon black and non-fullerene CNTs, there was no significant difference in Bode plots over immersion time, showing they have similar interface mechanisms. The platform observed at low frequencies, was possibly attributed to the coating interface and related to carbon black filler. For the systems with non-fullerene CNTs, similar interface mechanisms were observed from the Bode plots.
The water uptake content after 120 days was determined with the expression of Brasher and Kingbury\textsuperscript{228}, shown in Equation 5-1.

\[ X_v = \frac{\log(C_c)}{\log(80)} \]  \hspace{1cm} (5-1)

where \( X_v \) is the water uptake content in the coating expressed in volume fraction, \( C_c \) is the coating capacitance after immersion for a specific time, and \( C_{\text{initial}} \) is the capacitance after initial immersion. The change of the coatings capacitance \( (C_c) \) with time was evaluated at a frequency of 10 kHz and was estimated by Equation 5-2\textsuperscript{229}.

\[ C_c = \left( -\frac{1}{\omega Z_{\text{imag}}} \right) \]  \hspace{1cm} (5-2)

where \( Z_{\text{imag}} \) is the imaginary part of the impedance in ohm-cm\textsuperscript{2}, and \( \omega \) is the angular frequency in radians \((1 \text{ rad} = 2\pi f, f = \text{frequency in hertz})\).

The results of coating capacitance and water uptake after 120 days of immersion were listed in Table 5-4. For the coating system filled with the unpurified fullerene CNTs, the TEOS-E0.4FCNT seemed to work as a barrier with the water content nearly 0%. For systems with unpurified fullerene CNTs in the range of 0.6-1.0%, the water uptake was
estimated around 19-30% after 120 days. The effect of the purified fullerene CNTs on the water uptake was also evident; they formed a barrier effect with lower content of purified fullerene CNT. The highest water uptake 77% of TEOS-E1.0PFCNT showed the resistance to the water and other corrosion species was low. For the coating system filled with carbon black, there was no water uptake by TEOS-E0.8CB and TEOS-E1.0CB, while TEOS-E0.4CB and TEOS-E0.6CB showed water uptake 12% and 7%, respectively. For systems with the mixture of carbon black and non-fullerene CNTs, the water uptake was estimated around 5-12% after 120 days. This indicated the water uptake increased with the presence of the non-fullerene CNTs. This observation might be explained by the presence of some voids due to the dispersion of CNTs. The water uptake was similar for systems with unpurified and purified non-fullerene CNTs. There was no apparent effect of the purified non-fullerene carbon nanotubes in the water uptake properties of the system. The water uptake was estimated around 23-30% and 20-32% after 120 days for systems with unpurified and purified non-fullerene CNTs, respectively.

Table 5-4 Impedance and water content of the coatings after 120 days of immersion

<table>
<thead>
<tr>
<th>Coating systems</th>
<th>Cc, F/cm² (0.01 Hz)</th>
<th>Water content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS-E</td>
<td>1.5×10⁻¹⁰</td>
<td>54</td>
</tr>
<tr>
<td>TEOS-E0.4CB</td>
<td>3.9×10⁻¹⁰</td>
<td>12</td>
</tr>
<tr>
<td>TEOS-E0.6CB</td>
<td>4.4×10⁻¹⁰</td>
<td>7</td>
</tr>
<tr>
<td>TEOS-E0.8CB</td>
<td>6.7×10⁻¹⁰</td>
<td>~0</td>
</tr>
<tr>
<td>TEOS-E1.0CB</td>
<td>7.9×10⁻¹⁰</td>
<td>~0</td>
</tr>
<tr>
<td>TEOS-E0.4CB-NT</td>
<td>2.2×10⁻¹⁰</td>
<td>11</td>
</tr>
<tr>
<td>TEOS-E0.6CB-NT</td>
<td>3.9×10⁻¹⁰</td>
<td>12</td>
</tr>
<tr>
<td>TEOS-E0.8CB-NT</td>
<td>3.6×10⁻¹⁰</td>
<td>12</td>
</tr>
<tr>
<td>TEOS-E1.0CB-NT</td>
<td>8.7×10⁻¹⁰</td>
<td>5</td>
</tr>
<tr>
<td>TEOS-E0.4NCNT</td>
<td>1.1×10⁻⁹</td>
<td>30</td>
</tr>
<tr>
<td>TEOS-E0.6NCNT</td>
<td>1.2×10⁻⁹</td>
<td>29</td>
</tr>
<tr>
<td>TEOS-E0.8NCNT</td>
<td>2.4×10⁻⁹</td>
<td>24</td>
</tr>
<tr>
<td>TEOS-E1.0NCNT</td>
<td>3.8×10⁻⁹</td>
<td>23</td>
</tr>
</tbody>
</table>
In general, nanocomposite coatings are formulated by incorporating nanomaterials into various coating systems. In this study, six types of carbon materials with distinctive aspect ratios were selected as fillers and were incorporated into the TEOS oligomer modified epoxy-amine systems. These nanocomposite coatings were expected to be more flexible and conductive compared with the control sample before adding fillers. The anticorrosive properties of nanocomposite coatings may be improved with the addition of nanofillers to increase the transporting path of corrosive species. In addition, these fillers can interact with siloxane layer formed near the substrate and therefore can affect the adhesion to the substrates.

The viscosity of nanocomposite coatings increased with the addition of the nanofillers. This was attributed to the resistance of nanafillers incorporated into the coating systems to the molecular chain mobility; under the condition of the good dispersing, the more the addition of the nanfiller, the more resistance to the molecular chain mobility and the higher the viscosity. The viscosity of nanocomposite coatings with specific addition of nanofiller, decreased with the increase of shear rates. This shear thinning behavior was observed for all nanocomposite coatings. These coatings that were shear thinning were
thixotropic. The shear thinning behavior resulted from the reason that it always took the coatings a finite time to bring back the rearrangements of the microstructural elements after applying external stress. By comparing the viscosities of different nanocomposite coatings, the viscosity increased in the sequence of carbon black, nonfullerene nanotubes, and fullerene nanotubes. This was consistent with other studies\textsuperscript{230-231} of the viscosity of multiwall carbon nanotube suspensions. The formation of a strong interacting MWCNT network was supported by good dispersion, high aspect ratio, and high concentrations. The resistance to the molecular chain mobility also increased from particulate, stick to rope morphology.

The storage modulus gradually increased with the carbon filler contents at lower loading level although it decreased at 1.0 wt % loading probably because of the aggregation. For some carbon fillers, the young’s modulus from static tests did not show a clear trend of increasing of modulus with the increasing of the carbon filler addition. In comparison, two significant differences between the two tests were observed. The first one was the strain rate used during the tests, which was usually one or two order of magnification higher for DMA than for static test\textsuperscript{232}. The other one is the strain range, which was within the linear viscoelastic limitation for DMA. Because of these differences, the phenomenon of discrepancy between two tests were expected and observed for polymer nanocomposites\textsuperscript{232}. Based on the more sensitive DMA test, the clear enhancement of modulus was presented when appropriate dispersion of carbon filler was achieved, i.e. at lower loading levels. With the higher loading levels, the presence of carbon aggregation resulted in the decrease of the modulus. This was more significant for the nanocomposite coating with PFCNT than others, which was also reflected on the results of electrical conductivity. The gap between the
surface conductivities of the nanocomposite coating with FCNT and PFCNT became smaller with the increase of loading level. The poor dispersion of PFCNT resulted in the aggregation, which impeded the formation of the perfect nanotube networks and limited the improvement of the electrical conductivity.

The flexibility of the nanocomposite coating films was investigated by measuring the elongation-at-break. For all nanocomposite systems, the elongation-at-break increased with the addition of the carbon filler content in the sequence of non-fullerene CNT > mixture of CB/non-fullerene CNT > fullerene CNT > CB. The significant increase of area under the stress-strain curve, which was as a result of the increased elongation-at-break, confirmed the improvement of the toughness. It had been mostly reported\textsuperscript{233,147} that the increased elongation-at-break improved the ductility although the films failed immediately after reaching the maximum tensile stress. The ductile failure behavior was also observed from morphological study of the fracture surface\textsuperscript{147,234}. Without any filler, epoxy resin exhibited a smoother surface compared with the nanocomposite coatings. With the presence of carbon filler, the crack propagation was more difficult because of the distorted propagation path resulted from the decreased cleavage plane and increased surface\textsuperscript{147, 234}. By comparing the fracture surface for all nanocomposite coatings containing different types of filler at different loading levels, the development of the surface morphology was consistent with the tendency of the elongation-at-break. The size of the cleavage plane decreased with the increase of the CNT contents, accounting for the high fracture toughness of these filled epoxy nanocomposite coatings.

General coating properties were investigated, including impact resistance, pencil hardness, crosshatch and pull-off adhesive properties. Impact resistance of these
nanocomposite coating systems was the ability of coatings to absorb energy before failure. The decrease or increase of the direct impact resistance of the nanocomposite coating systems with the increase of the filler addition could be attributed to the increase or decrease of the crosslinking density. Crosshatch and pull-off adhesion were used to determine how well those coating systems were bonded to the substrates. The pull-off adhesion property of the fullerene CNTs filled nanocomposite systems showed only slightly decrease while it decreased dramatically with the increased addition of carbon fillers for all other nanocomposite coatings. This phenomenon could be explained with the interaction between the filler and siloxane layer formed near the substrates. In the previous study\textsuperscript{27}, TEOS oligomer modified epoxies was proved to have better adhesion on aluminum and steel substrate due to the formed Si–O–M linkages. This was because of the condensation reaction between the silanol groups (Si–OH) from epoxy and the metal hydroxyls (M–OH). The denser distribution of silicon near the metal substrate for TEOS-E systems indicated more interaction between film and metal substrate, which guaranteed the pull-off adhesion properties. Therefore, it could be postulated that the presence of carbon black and non-fullerene CNTs disturbed the interaction between the film and metal substrate, resulting in poor pull-off adhesion.

The ultimate objective of this study was to apply the conductive nanofiller filled coatings in protecting metals from static electricity and corrosion, namely oil tank coatings and aircraft coatings. Hence, the electrical and the anti-corrosive properties were of significant importance. The electrical properties and anticorrosive properties of the carbon nanofiller filled epoxy coatings were investigated by measuring the electrical conductivity and the impedance, respectively. As widely known, the electrical conductivity of
nanocomposite coating systems not only relies on the aspect ratio of carbon fillers, but also on the dispersing state as well as interaction between fillers. Among the different types of carbon fillers, fullerene carbon nanotubes were the most efficient materials to enhance the electrical conductivity of nanocomposite coating systems. Any process or treatment which reduce the aspect ratio, can decrease the electrical conductivity\textsuperscript{235,236}. This could also be explained from the morphology of the six fillers. Fullerene carbon nanotubes bear the higher aspect ratio compared with carbon black and nonfullerene carbon nanotubes. Besides, the obtained increasing electrical conductivity proved to some extent that there was no significant defect induced under the probe sonication process and the CNTs were well dispersed without big aggregation; otherwise, there would be a reduction of the electrical conductivity. With respect to the anticorrosive properties, the impedance magnitude of coating systems with fullerene CNTs did not change a lot over immersion time. This indicated that the interface of the coating was stable to prevent corrosion. In the Bode plots of the coating system filled with the fullerene CNTs, it showed very attractive anticorrosion properties because the impedance result did not show any corrosion processes at the metal/coating interface. The barrier effect of fullerene CNTs on the water uptake was also evident; they formed a barrier effect with lower content of fullerene CNTs. The impedance magnitude changed a lot over the immersion time for TEOS-1.0PFCNT. In addition, there was an impedance platform in the Bode plot at low frequencies and the impedance showed abrupt drop at day 19. TEOS-E1.0PFCNT also showed resistance to the water and other corrosion species was low with the highest water uptake 77\% of. All these phenomena indicated that the coatings started to show a corrosion process at the
metal/coating interface. Overall, a possible mechanism of film formation was proposed according to the results above, as shown in Figure 5-10.

![Figure 5-10 Proposed mechanism of the interaction between carbon/modified epoxy hybrid coatings and metal substrate](image)

5.9 Conclusion

In conclusions, the nanocomposite coating systems were fabricated by the solution mixing method with ultrasonic dispersion of six types of conductive fillers into the alkoxy silane modified epoxy coatings. The shear thinning behavior was observed for all nanocomposite coating systems. The viscosity of different coating systems increased in the sequence of carbon black (particulate), nonfullerene nanotubes (stick) and fullerene nanotubes (rope). Below 0.8 wt % loading, the storage modulus and the crosslink density increased and the tan delta decreased with the increase of filler content. The decreased mechanical properties at higher loading were presumably due to the presence of
aggregation. The increased elongation-at-break was as a result of the distorted crack propagation path resulted from the decreasing of the cleavage planes and the increasing of the surface roughness. The pull-off adhesion property of nanocomposites depended on the interaction between the filler and siloxane layer formed near the substrates. The interaction was proved from poorer pull-off adhesion properties of CB, CB-NT, NFCNT, and PNFCNT filled coatings than FCNT and PFCNT filled coatings. It was found that the most efficient material to enhance the electrical conductivity and anticorrosive properties of the nanocomposite coating systems was fullerene CNTs.
CHAPTER VI
CONCLUSIONS

In this dissertation, a new class of non-isocyanate urethane methacrylates was synthesized and incorporated into latexes by emulsion polymerization in Chapter III and IV. The urethane functionality showed significant effect on the film formation, and the mechanical properties of the latex films. In Chapter V, the carbon nanofiller epoxy coating systems aiming for anticorrosive applications were investigated.

In Chapter III, a series of urethane functional methacrylate monomers were synthesized and incorporated into latexes by emulsion polymerization. These urethane monomers were synthesized through a non-isocyanate route and characterized by $^1$H, $^{13}$C NMR, FT-IR and MS. It was found that the new urethane methacrylates (from methyl to octyl substitution) can be easily copolymerized with MMA and BA to achieve almost 100% conversion under the monomer-starved semibatch polymerization. No secondary or coagulative nucleation was evidenced since the uniform particle sizes were close to the theoretical values and the number of particles remained constant. This indicated the emulsion polymerization processes for all non-isocyanate urethane functional latexes proceeded under the control of Smith-Ewart theory. The glass transition temperature and the film properties of poly(MMA/BA/UMA) decreased with the increasing chain length of urethane methacrylate monomers due to the increasing flexibility of side chains. The ability
of film formation, represented by the difference between $T_g$ and MFFT, was improved by the presence of urethane functionality. This was attributed to the plasticizing effect of water by forming additional hydrogen bonding with the urethane groups. Higher tensile modulus, tensile strength, storage modulus and elongation were observed from urethane functional latexes. Such behavior was attributed to the increasing particle interaction by forming hydrogen bonding among urethane groups.

Furthermore, the effect of the urethane functional methacrylate monomers on the urethane functional latex in terms of the polymer composition, the location and the concentration of the functionality were investigated in Chapter IV. The urethane functional methacrylate monomer (BEM) was used to prepare the urethane functional latexes by copolymerization with MMA and BA. It was observed that batch and semibatch reactions resulted in the heterogeneous and relatively homogeneous polymer composition, respectively. The difference in polymer composition was further indicated from the narrow and broad glass transition of the polymers derived from semibatch reaction and batch reaction, respectively. Higher tensile modulus, tensile strength and storage modulus were obtained from the polymer from batch reaction than that from semibatch reaction. This was attributed from the difference in the polymer composition; a rigid block rich in MMA and BEM existed in the latex derived from the batch reaction. Homogeneous and core-shell morphology were observed for urethane functional latexes derived from single and two-stage monomer-starved polymerization reactions, respectively. This was further confirmed from single and two clearly separated glass transition for single and two-stage reaction. The study of molecular dynamics by SS-NMR was consistent with these results. It was found that mechanical properties, i.e. Young’s modulus, tensile strength and elongation-
at-break, were improved with increasing concentration of urethane functionality, regardless of location. The storage modulus also showed ascending trend with increasing concentration of urethane functionality. The latexes with the urethane located in the shell gave the best overall properties. This was because of the improved polymer interaction among particles due to the higher concentration of urethane present in the continuous phase.

In Chapter V, the carbon nanofiller filled epoxy coating systems aiming for anticorrosive applications were investigated. The nanocomposite coating systems were fabricated by the solution mixing method with ultrasonic dispersion of six types of conductive fillers into the alkoxyisilane modified epoxy coatings. It was found that the storage modulus and crosslink density increased and tan δ decreased with the increase of filler content below 0.8 wt% loading. The decreased film properties at higher loading were presumably due to the presence of aggregation. The increased elongation-at-break indicated the improvement of toughness. This improvement in toughness was the result of the distorted crack propagation path resulted from the decreasing of the cleavage planes and the increasing of the surface roughness. It was postulated that the nanofiller interacted with the siloxane layer formed near the substrates. Poor pull-off adhesion properties were attributed to the interaction between nanofillers and siloxane layer formed near the substrates. It was found that the most efficient material to enhance the electrical conductivity and anticorrosive properties of the nanocomposite coating system is fullerene CNTs.
REFERENCES


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187. Li, J.; Isayev, A. I.; Ren, X.; Soucek, M. D., Modified Soybean Oil-Extended SBR Compounds and Vulcanizates Filled with Carbon Black. Polymer 2015.


APPENDIX

The Mass spectra, FT-IR spectra and NMR spectra of UMAs were shown in Figure A1, Figure A2 and Figure A3, respectively.

(a) MA-EC-MAA

(b) EA-EC-MAA
(c) BA-EC-MAA

(d) HA-EC-MAA
Figure A1. The Mass spectra of UMA monomers: (a) MA-EC-MAA, (b) EA-EC-MAA, (c) BA-EC-MAA, (d) HA-EC-MAA and (e) OA-EC-MAA.

Figure A2. The FT-IR spectra of UMA monomers.
Figure A3. The NMR spectra of UMA monomers: (a) MA-EC-MAA, (b) EA-EC-MAA, (c) BA-EC-MAA, (d) HA-EC-MAA and (e) OA-EC-MAA.
GC analysis was based on the external standard calibration with known concentration. The calibration curves of MMA, BA and UMAs were shown in Figure A4. The calibration standard solutions were prepared as follows: A known amount of each specific monomer was dissolved into HPLC grade THF; a precise volume of the solution was introduced using a micropipette in a 10-25-50 ml volumetric flasks and the volume made up with THF to get standard solutions. The unknown solution point can be determined by using the calibration curves.
Figure A4 The calibration curves of (a) MMA, (b) BA and UMAs: (c) MA-EC-MAA, (d) EA-EC-MAA, (e) BA-EC-MAA, (f) HA-EC-MAA and (g) OA-EC-MAA.

The theoretical glass transition temperature was calculated based on Fox equation\textsuperscript{208}; for the systems, we have

\[
\frac{1}{T_g} = \frac{w_{\text{MMA}}}{T_{g,\text{MMA}}} + \frac{w_{\text{BA}}}{T_{g,\text{BA}}} + \frac{w_{\text{BEM}}}{T_{g,\text{BEM}}}
\]  

(A1)

where \(T_g\) represents the overall \(T_g\) of the blend; \(T_{g,\text{MMA}}, T_{g,\text{BA}}\) and \(T_{g,\text{BEM}}\) are \(T_g\)s of the homopolymer of MMA, BA and BEM, respectively (with \(T_{g,\text{MMA}}=105^\circ\text{C}, T_{g,\text{BA}}=-54^\circ\text{C}\) and \(T_{g,\text{BEM}}=26.5^\circ\text{C}\); \(w_{\text{MMA}}, w_{\text{BA}}\) and \(w_{\text{BEM}}\) are weight fractions of components MMA, BA and BEM, respectively. The BFL10\% and SBFL10\% latexes was designed with \(T_{g,\text{overall}}=0^\circ\text{C}\). The heat flow curves of BFL10\% and SBFL10\% were compared in Figure A5. The core-shell latex was designed with \(T_{g,\text{overall}}=0^\circ\text{C}, T_{g,\text{core}}=20^\circ\text{C}\) and \(T_{g,\text{shell}}=-20^\circ\text{C}\). The latexes with homogeneous structure were designed with \(T_g=0^\circ\text{C}\), the same as the overall \(T_g\) of core-shell latexes. The heat flow curves of FLC-S, C-FLS and FLH series were shown in Figure A6.
Figure A5 DSC thermograms of BFL and SBFL10% latexes

Figure A6 DSC thermograms for core-shell and homogeneous latexes

Variable temperature $^{13}$C CP MAS experiments of latexes with 10% urethane functionality from -40 to 60 °C, was shown in Figure A7 and Table A1.
Figure A6 $^{13}$C CP MAS spectra of latexes with 10% urethane functionality from -40 to 60 $^\circ$C

Table A1 Typical resonance fitting half widths for latexes with 10% urethane functionality at variety of temperatures

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