Doctoral Dissertations   Student Theses and Dissertations

Fall 2015

Application of colloidal unimolecular polymer (CUP) particles in coatings

Sagar Vijay Gade

APPLICATION OF COLLOIDAL UNIMOLECULAR POLYMER (CUP)

PARTICLES IN COATINGS

by

SAGAR VIJAY GADE

A DISSERTATION

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

In

CHEMISTRY

2015

Approved

Michael Van De Mark, Advisor

Thomas P. Schuman

Nicholas Leventis

Jeffrey G. Winiarz

John Myers

PUBLICATION DISSERTATION OPTION

This dissertation consists of the following two articles that have been submitted for publication as follows. This dissertation is formatted according to Missouri University of Science and Technology specification.

Pages 11-43 have been submitted to the PROGRESS IN ORGANIC COATINGS.

Pages 44-70 have been submitted to the JOURNAL OF COATING TECHNOLOGY RESEARCH.

ABSTRACT

Colloidal unimolecular polymer (CUP) particles were prepared by the process of water reduction on copolymers containing hydrophobic and hydrophilic monomers at definite ratio using free radical polymerization. The CUPs are formed by the effect of hydrophilic /hydrophobic interactions of the polymer with a change in the solvent environment around them. Once formed these colloidal particles are thermodynamically stable with collapsed hydrophobic groups forming a spheroidal core and hydrophilic charges on the surface stabilizing the particle by the charge repulsion. CUPs contain only the charged CUP particles, water and counterions with all the functionality on the surface for further chemistry. CUP suspension with amine functional groups on the surface can react with epoxy groups and therefore can be used as a crosslinker for 2K epoxy coating. The cured films had comparable properties with commercial amine crosslinker at reduced VOCs.

New regulations which reduce the level of volatile organic compounds (VOC) for architectural latex coatings usually necessitate a sacrifice in performance. The use of glycol has been shown to aid in both freeze thaw and wet edge retention. Loss of this VOC will therefore compromise both. With small particle size, CUPs offer a large amount of surface area with the large amount of non-freezable surface water. The presence of non-freezing surface water make CUPs a candidate as an additive for the wet edge retention and freeze thaw stabilizer for architectural paints. The use of CUP as wet edge retention additive and freeze thaw stabilizer is good alternative for the glycols used in paints and therefore lowers the VOC of architectural latex paints.

ACKNOWLEDGEMENTS

I would like to thank Dr. Michael Van De Mark for continuous his support, guidance, and encouragement through the course of pursuing my PhD. His creative and critical thinking and assessment improved my research skills and prepared me for future challenges.

I extend my gratitude to my committee members Dr. Thomas P. Schuman, Dr. Nicholas Leventis, Dr. Jeffrey G. Winiarz, and Dr. John Myers for their time and help with my graduate study and research work.

I would like to thank my former and current lab members, Dr. Ming Han Chen, Dr. Jigar Mistry, Dr. Ameya Natu, Cynthia Riddles, Catherine Hancock, Yousef Dawib, Peng Geng and all undergraduates for their help and expertize for the completion of my research work. Further, I would like to thank Missouri S&T Coatings Institute and Department of Chemistry, Missouri University of Science and Technology for financial support and instrumentation. I am thankful to all teaching and non-teaching staff, and students of department of chemistry for their help for course work and making my stay comfortable at Missouri University of Science and Technology.

Sincere gratitude and respect to my parents, Vijay Laxman Gade and Vaishali Vijay Gade for their unconditional love, inspiration, patience and financial support. My deepest gratitude must be given to my wife, Bhagyashree for her constant love, understanding and encouragement.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Page

LIST OF TABLES

NOMENCLATURE

CUP	colloidal unimolecular polymer
MEK	Methyl ethyl ketone
EEW	epoxy equivalent weight
VOC	Volatile organic compounds
THF	tetrahydrofuran
MMA	methyl methacrylate
MAA	methacrylic acid
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
MADQUAT	[2-(methacryloyloxy)ethyl]trimethylammonium chloride
EA	ethyl acrylate
AA	acrylic acid
BMA	butyl methacrylate
2EHMA	2-ethylhexyl methacrylate
AIBN	2,2′-azobis(2-methylpropionitrile)
ASTM	American Society for Testing and Materials
GPC	Gel permeation chromatography
TDA	triple detector array
DSC	Differential scanning calorimetry
Tg	glass transition temperature
MFFT	Minimum Film Forming Temperature
FT-IR	fourier transform infrared spectroscopy
^{1}HNMR	proton nuclear magnetic resonance spectroscopy
EA-AA	ethyl acrylate – acrylic acid copolymer
EA-AA-AZ	aziridine adduct of ethyl acrylate – acrylic acid copolymer

Mn	number average molecular weight
DLS	dynamic light scattering
BP	boiling point
F/T	freeze thaw
SEM	scanning electron microscope
MEK	methyl ethyl ketone
AV	acid value
ASTM	American Society for Testing and Materials
KHP	potassium hydrogen phthalate
w/w	weight percent
RPM	revolutions per minute
% NV	percent non volatile
Wt/Gal	weight per gallon
Lbs	pounds
% Solids (Wt)	percent solids by weight
% Solids (Vol)	percent solids by volume
PVC	pigment volume concentration
P(MMA/MAA)	methyl methacrylate – co – methacrylic acid copolymer
ϕ_{max}	maximum packing volume fraction
η	fraction of bound water
T_{1b}	relaxation rate of bound water
T_{1f}	relaxation rate of free water
$[\eta]$	dimensionless intrinsic viscosity of suspension

1. INTRODUCTION

1.1. POLYELECTROLYTES

Polyelectrolytes are defined as "A macromolecule species bearing a large number of charges or chargeable groups that upon being placed in water or other ionizing polar solvent dissociates into a highly charged polymeric molecule. Such dissociation is typically accompanied by oppositely charged smaller counter ions which tend to neutralize the charge on the repeat units of the macromolecule preserving electroneutrality." [1] One specific class of polyelectrolytes is amphiphilic polyelectrolyte. [2] In recent years, amphiphilic polymers have been of increased academic as well as industrial interest due to their potential applications. Amphiphilic polyelectrolytes possess both charges and hydrophobe along or pendent to the polymer backbone. They have attracted attention mainly because of their self-assembling properties and their nanostructure. These amphiphilic polyelectrolytes undergo hydrophobically driven self-association to form well-defined spatial nanometer scale structures when placed in water, depending on their macromolecular architecture. The type of nanostructure depends on whether hydrophobic associations occur within the same or different chains of polymer in solution, which strongly depends on the macromolecular architecture. Thus, one can prepare an amphiphilic polyelectrolyte of given properties by designing the polymer. [3]

Practical interest in amphiphilic polyelectrolytes rises from their potential application in a variety of commercial applications such as polymeric surfactants for personal care products [4-7], as drug delivery systems [8-12] biocompatible materials for biomedical field [13-16] humidity and optical sensors [17-19] application as surfactant[20], flocculants [21-24], associative thickners [25], rheology modifiers [26-28] emulsifiers [29, 30] and

other applications. The properties of these materials in solution are sensitive to change in external environment such as ionic strength, shear stress, temperature, pH and solvent composition around them. [7] Amphiphilic polyelectrolytes are synthesized by different methods such as random copolymerization, block copolymerization, alternating copolymerization, chemical modification, micellar copolymerization, interfacial copolymerization, homogeneous or ultrasonic copolymerization, living anionic polymerization, GTP (group transfer polymerization). [6,7] In particular, random copolymerization has received interest as the synthesis protocol due to its ease and wide range of monomers selection available to articulate the polymer. When the hydrophilic ionic monomers and hydrophobic monomers are prepared by free radical polymerization to produce random copolymer, the sequence distribution of the monomer units is an important factor to influence their association behavior. Such homogenious polymers can be synthesized with statistical sequence distribution depending on monomer reactivity ratios.

Hydrophobic association in such polymers occurs competing with electrostatic repulsion between ionic sites in the same polymer and / or different polymer chains. The balance of these opposing interactions is primarily a function of the ratio of hydrophobes and charges in polymer chains as well as the size of the hydrophobic monomers present on the polymer.

Amongst these amphiphilic polymers, one particular class offers the specific advantage of allowing the formation of intramolecular aggregates to produce unimolecular particle in dilute solution of water. The corresponding highly hydrophobic micro domains essentially come from the macromolecule folding. These highly collapsed conformations have

properties closely related to those of micelles obtained from simple molecular surfactants at nanoscale. Therefore, they are most commonly known as pseudo-micelles or intra-chain micelles, though there is a quasi-absence of a critical micellar concentration.

The polymer chains in solution take different types of configuration depending on their chemical structure and solubility parameters of solvent composition. In good solvent they act as a random coil while in bad solvent they collapse to form nanoparticles with hydrophobic core and hydrophilic ionic groups on the surface. The architecture of such polymers consists of the hydrophilic- hydrophobic balance, the chemical structure of the backbone and the spatial arrangement of hydrophilic charges along the polymer chain. Morishima developed unimolecular micelles by random copolymerization of sodium 2-(acrylamido)-2- methylpropanesulfonate and methacrylamides bearing cyclododecyl groups and reported unimer particle with a mean hydrodynamic radius of 5.5nm at Mw = 5.1 X 10^5 molecular weight for synthesized polymer. [31]

1.2. COLLOIDAL UNIMOLECULAR POLYMERS (CUP)

One of the best methods to prepare nanoparticle suspension in water is to collapse single isolated polymer chains which are stabilized by charge repulsion and/or steric hindrance. Many aspects have to be considered to design such polymers, such as the balance of hydrophilic/hydrophobic groups of the polymer. The excess hydrophobicity allows aggregation of the collapsed chains, while the excess hydrophilicity does not allow collapse and keeps the polymer chains in chain-like conformation in water. With favorable conditions including concentration, temperature, pH, solubility of polymer in the solvent and charge fraction on the polyelectrolyte, the polyelectrolyte chains can collapse into a single isolated compact globule at a favorable solvent composition.

After numerous designs and synthesis, Dr. Van De Mark's group was able to develop the stable collapsed polyelectrolyte which has been termed colloidal unimolecular polymer (CUP). The name was deduced as these polyelectrolyte particles are solid particles suspended in the aqueous media and each particle is made up of single polymeric molecule. Colloidal Unimolecular Polymer (CUP) technology is a recent addition to true nanoscale amphiphilic materials which are not soluble in aqueous environment. Significant work has been published in the last decade on CUP technology, synthesizing CUP particles using different acrylates and methacrylates, understanding the science [32-37] and finally the application of CUP in a variety of fields. [38-44]

The CUPs are formed by the effect of hydrophilic/hydrophobic interactions of the polymer with a change in the solvent environment around them. The CUP particles are formed at critical solvent environment when the polymer - polymer interaction is greater than the polymer - solvent interaction and is entropically favored by release of the water analogously to form micelle with hydrophilic or charged groups on the surface and hydrophobic groups collapsed to form core creating the sphere-like shape. The CUP particles are stabilized by the charge repulsion of hydrophilic charged groups on the surface. Once formed these colloidal particles are thermodynamically stable and contains only the charged CUP particles, water and counterions. CUPs are free of surfactant and the preparation procedure is quite simple and the size and charge density can be easily varied. The CUP can find its application area in coating, drug delivery, catalyst matrix, etc. Having all the functionality on the surface for further chemistry, the application of CUP as crosslinker for epoxy coating is discussed in this dissertation. With small particle size CUPs have a large amount of surface area with large amount of non-freezable surface water

which make CUPs a candidate as an additive for wet edge retention and freeze thaw stabilizer for architectural paints which is also discussed in the dissertation.

1.3. SURFACE WATER AND BULK WATER

Analogues to typical hydrogels, the CUP particles in water have polar, hydrophilic groups on the surface hydrated by water, which is called 'primary bound water' and the exposed hydrophobic groups near surface interact with water through hydrophobic interaction called 'secondary bound water'. Together, primary and secondary water is called the total bound water or the surface water. The rest of the water in the system is called 'bulk water'.

Analogues to various thermodynamic properties of water around polyelectrolytes, water around CUPs can be differentiated as non-freezable surface water and freezable free water. The state of water in CUP has been measured quantitatively by differential scanning calorimetry (DSC) [45] and spin-lattice relaxation (T1) NMR experiments. [46, 47] From DSC data, water is classified as freezable and non-freezable water, whereas from NMR experiments it's classified as free and bound water.

1.4. VOLATILE ORGANIC CONTENT (VOC)

Global concerns of environmental pollution and greenhouse gas (GHG) emission has led growing legislative stringency to reduce VOC and other hazardous components. Increased consumer/user awareness towards green and sustainable chemistry is a demanding factor for major coatings and raw material suppliers to direct their efforts, either in the area of reformulating their existing product formulations or adopt new approaches to meet the requirements. Architectural coatings occupy around 55% portion of the total

global coating consumption. Ultra low and Zero VOC coatings with low odor are the need of the hour for sustaining the business as well as the future of the coating industry.

The coating industry follows the following various definitions of VOC in standard practice which are emitted during the application of paints.

The US definition is "Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity. [48]

The European Union definition is based on evaporation into the atmosphere rather than the reactivity. The EU "Paint Directive" 2004/42/EC defines a VOC as an organic compound having an initial boiling point lower than or equal to 250 ^{O}C at an atmospheric pressure of 101.3 kPa. [49]

The GS 11 definition is "Any organic compound which participates in atmospheric photochemical reactions as defined by the U.S. EPA in 40 CFR 51.100 (s) and has an initial boiling point lower than or equal to 280°C measured at standard conditions of temperature and pressure."

Why is VOC a major concern? Emission of VOCs from paints may not always necessarily give rise to health or environmental problems. However, they react with nitrogen oxides from automotive and industrial exhaust in the presence of heat or sunlight to form ozone at ground level - which is the primary source of 'Photochemical Smog'.

1.5. FREEZE THAW STABILITY

A variety of latex dispersions are utilized as binder resin for interior and exterior paint application. Many of these latex dispersions in the paint are stabilized using glycols, otherwise they will lack freeze thaw stability during transportation and storage in cold temperature. The freeze–thaw stability is one of the major *In Can* properties of the architectural paint. The mechanism for the process of freezing and thawing, destabilization of latex polymer structures has been of interest since 1950. [50]

Blackley [51] has given a comprehensive review of colloidal destabilization of latexes by freezing, where the work of Talalay is reported. The effect of pH, temperature and duration of freezing, chemical constitution of carboxylate soap and polymer hardness on freeze thaw stability is discussed.

When the temperature of latex paint is lowered, the water in the paint formulation starts freezing which leads to the nucleation of ice crystals. The formed ice crystals grow which increases the concentration of the latex particles in the unfrozen water. As the time progresses, the latex particles are forced to come in contact with each other due to the pressure of the expanding freezing water. The low Tg latex particles starts aggregating and hence coagulate, while the latex with high Tg do usually recover after the thawing process.

To achieve better free thaw stability of latex dispersions, addition of antifreeze such as glycol is necessary. [52]. The glycols incorporated as antifreeze decrease the freezing point of the water and hence protect the waterborne formulation from gelation and aggregation due to freezing. The glycols used as antifreeze are ethylene glycol (BP 197 ^{O}C), diethylene glycol (BP 244-245 ^{O}C) and propylene glycol (BP 188 ^{O}C). The glycols used as antifreeze are very effective freeze thaw stabilizers allowing paint to be useful even after 5+ freeze

thaw cycles, but with strict environmental legislation with respect to VOC on coatings, they are becoming undesirable. To achieve low levels of VOC in paint means the amount of glycols used in coatings formulation has to be reduced or eliminated completely.

To make freeze thaw stable latex paint, various antifreeze agents have been developed and utilized over the past few decades. Cheng-Le Zhao et al. [53] synthesized the latex polymers containing alkoxylate monomers and claimed that the paint formulation derived from it have excellent freeze thaw stability at lower VOC levels. Rajeev Farwaha et al. [54, 55] developed a polymerizable amphoteric surfactants and claimed that the utilization of the same in latex copolymer preparation improved the freeze–thaw stability to the latex paints. The other work report in literature contains polymerizable polar monomers [56-58] polar surfactants [59] or new additives [60, 61] used in latex synthesis or in the paint formulation improving the freeze thaw stability of the paint. None of the approaches have been applicable to resin systems over a broad range of coatings.

1.6. WET EDGE RETENTION

Wet edge and open time is very important issue for all the waterborne coatings. The problem of limited open time in water-borne paints has already been identified in the literature in the early days of dispersion paints by, for example, Fischer and Washburn in 1969 [62], and by Rohm & Haas in a patent back in 1964 [63]. In the literature [64], wet edge time (also referred to as lapping time) has been defined as the period of time during which no edge marks are produced when a freshly applied paint film is lapped over a previously painted area.

Drying is quicker at the edges of the film and this is the origin of a water and particle flux that creates a drying front perpendicular to the surface. This phenomenon has been

described the first time by Hwa [65] and analyzed among others by Deegan [66], Winnik and Feng [67] and Ming [68] and the drying process at the edges has a direct and important impact on the open time. [69]

Typically for conventional water-borne coatings, the open time will be the order of about 15 min, and the wet edge time is even shorter at about 2–6 min. For solvent-based alkyds, the open time is typically around 45 min, with a wet edge time of about 25 min.

Many attempts have been made to improve the open time and wet edge time of water-borne dispersion paints. Initially, literature and patents focused on addition of organic solvents to the water-borne dispersion paints, to control the rheology of the paint and to delay the total evaporation of liquids [70-72]. Andrews [73] and Croll [74] studied the effect of ethylene glycol and propylene glycol on the drying of latex paints and found ethylene glycol is more hydrophilic than propylene glycol, it evaporates more slowly after the majority of the water has evaporated. Sullivan [75] found that the hydrophilic solvents tend to partition into the aqueous phase and diffuse out of the coating rapidly compare to hydrophobic coalescent, which largely partitions to the latex polymer. Winnick and Feng [76] found that the high Tg latexes dry more rapidly than low Tg latexes, they also found some blends of the high and low Tg latexes dry more slowly than either of the individual latexes. Other techniques aimed at delaying the evaporation of water ranges from grafting very hydrophilic compounds into or onto latex particles [77-79] to keep water in between the particles for a longer period of time to make a completely water soluble polymeric system [80]. The addition of a surface-active evaporation suppressing agent, such as eicosanol, has been described [81] as one of the solution for short open times. In such case,

a hydrophobic barrier is formed at the air–water interface, which retards the evaporation of water to a certain extent.

While a significant amount of literature has been published on the processes related to film formation and coalescence, there has been less focus on fundamental mechanisms related to the impact of glycols and other additives on the workability of waterborne architectural paints.[82]

Numerous techniques to characterize open time, wet edge, and viscosity build during cure have been described in recent publications. The common techniques utilized for evaluation of open time and wet edge is to drawn down a paint film on a sealed chart using a 3 mil Bird bar and make a series of 'X' marks as mentioned in ASTM D7488-11. [83] After fixed number of minutes, paint is brushed back and forth across the film for four cycles. The time at which the edge of the drawdown can no longer be worked into the body of the paint is referred to as the wet edge time, while the time at which the 'X' begins to show through the paint is deemed the open time. [84, 85]

In this research a partial replacement of the latex resin by a CUPs was explored. With small particle size, the CUP particles have a large surface area with a larger amount of surface / bound water. During drying the large weight fraction of the surface water around the CUP particles creates a gel structure. We hypothesis that this gel structure restricts the diffusion of water in latex paint and slower its evaporation. We also hypothesis that, It can prevents the coalescence of the latex resin until enough water is lost improving the wet edge retention.

PAPER

I.   SYNTHESIS OF AMINE FUNCTIONAL COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES AND THEIR USE AS CROSS-LINKER FOR EPOXY COATING

Sagar Vijay Gade, Michael Van De Mark*

Missouri University of Science and Technology | 1870 Miner Circle, Rolla, MO 65409

*Corresponding Author. mvandema@mst.edu
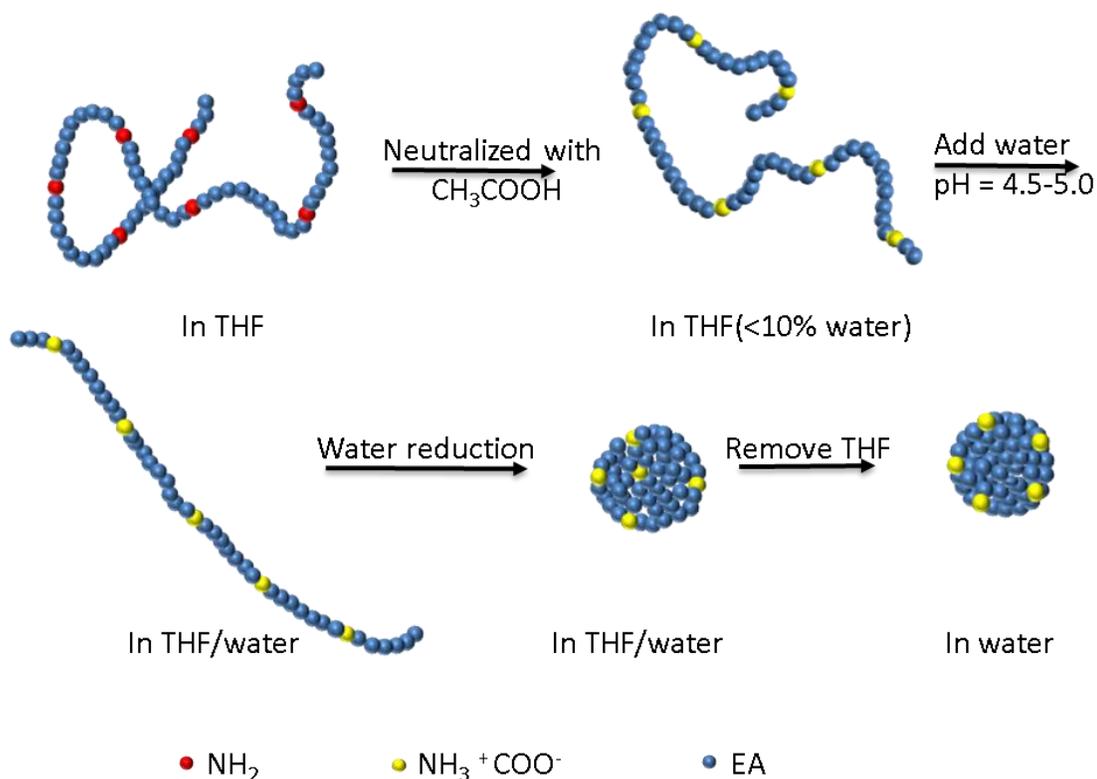
ABSTRACT

A copolymer of ethyl acrylate and acrylic acid with ratio 9: 1 was synthesized in THF. The carboxylic acid functionality was then reacted with 2-methylaziridine to produce amine functionality on the copolymer. The polymer was isolated, water-reduced with pH

modification with acetic acid and solvent stripped using rotovap to produce Colloidal Unimolecular Polymer (CUP) with ammonium functionality on the particle surface. These particles are typically 3-9 nanometers in diameter depending upon the molecular weight. They were then utilized as cross linking agent for crosslinking an epoxide resin. The formed coatings were evaluated for MEK resistance, adhesion, hardness, gloss, flexibility, wet adhesion, abrasion and impact resistance properties and were compared with traditional amine cross linkers. These new amine functional acrylic CUPs were solvent free (low or no VOC).

1. INTRODUCTION

Solvent borne epoxy systems have been produced for many years due to their excellent properties [86]. With increasing environmental regulations, switching to water borne systems [87] was inevitable and many industries and research groups have developed environmentally friendly water borne epoxy systems.[88-90] Water borne epoxy resins are typically prepared by an emulsifiable amino resin or by an emulsifiable epoxy or in recent years, both an emulsifiable amino resin and emulsifiable epoxy. [91-94]

Compared to solvent borne epoxy systems, the physical and mechanical properties of water borne epoxy are in a developing phase because many of the aspects such as pot life, pigmentation, cure time and crosslink density are not yet meeting the needs of the customer. There are two fundamental types of the waterborne epoxy coatings. Type I epoxy are based on liquid bisphenol A or bisphenol F chemistry with an epoxy equivalent weight (EEW) less than 250 and Type II epoxy are based on solid higher molecular weight dispersed resins.

The curing agent in Type I systems not only crosslinks, but also acts as the emulsifier in the liquid state. As a result, the emulsion particles contain both curing agent and epoxy resin after mixing, although some amine is left in the aqueous phase. This process gives the advantage of less phase separation during drying. With low molecular weight, good coalescence is achieved due to high rates of diffusion with uniform film morphology. These systems can be formulated to near zero VOC, as liquid epoxy resins exhibit good flow and film formation properties without added coalescent aid. The concentration of epoxide groups in the liquid resin is high due to the lower molecular weight. The high concentration of epoxide in the close proximity of the active amine-hydrogen from the curing agent leads

to rapid reaction. This shortens the pot life to typically 2 hrs. Liquid epoxy with its short rigid backbone yields coatings with high hardness but low flexibility and impact resistance. [95]

Type II systems are based on higher molecular weight solid epoxy resins and are pre-dispersed in water and co-solvent, utilizing an emulsifier. The flow and coalescence of solid epoxies can be improved by adding glycol ether into the dispersions, which add VOC to the formulations. For the crosslinking reaction to occur, the curing agent has to migrate from the aqueous phase into the dispersed resin particles containing solid epoxy resin, which increases the pot life of the system. During coalescence, the films tends to develop heterogeneous film morphology with amine rich particle boundaries and un-reacted epoxy resin in the particle cores. [95]

A Colloidal Unimolecular Polymer is a colloidal system with a solid polymer phase consisting of a single polymer strand in a spheroidal configuration with a continuous water phase. Colloidal unimolecular polymers (CUP) are typically polymers containing hydrophilic groups and a hydrophobic backbone. They are generally synthesized by copolymerizing hydrophilic and hydrophobic monomers in a definite ratio by the mechanism of free radical polymerization but can be produced by any typical method. The ratio of hydrophilic to hydrophobic monomer plays a key role in water reduction process. The polymer is dissolved in solvent (generally 10-20% solids depending upon molecular weight), followed by addition of acid or base to neutralize the pendent base or acid groups present on polymer backbone forming ionic groups. To this solution, pH modified deionized water is added using a peristaltic pump, followed by stripping of the organic solvent, to produce CUPs. In Figure 1 particle size comparison of latex (100nm), urethane

(25nm) and CUP (4nm) is shown, CUPs produce clear solutions compare to latex and PUDs. It should be noted that these polymers are water insoluble and are only dispersed due to the process. [96]

Latex, ~100nm   Dispersion, ~25nm   CUPs, 3 – 8 nm

Figure 1. Particle size comparison for waterborne particulate coating resins

Colloidal unimolecular polymer (CUP) is one of the solutions to reduce VOC emission with distinct advantages. Figure 1 shows three different water borne resin systems (a) latex, (b) emulsion and (c) CUP particles. The most significant difference between these particles is their size. The diameter of the CUP particle is typically 3-9 nm, whereas latex is typically 100 nm and in urethane emulsions are approximately 25 nm.

The formation of CUP particles with nano size (3-9 nm) could potentially decrease film formation time and reduce VOC. Water reducible resins have been utilized for over 50 years but still require high VOC resulting from the use of high boiling water loving solvents in the reduction process. To avoid chain entanglement during the reduction

process, as the molecular weight is increased, it is necessary to have more solvent to dilute the polymer before reduction. The CUP approach reported here utilizes low boiling, water loving solvents such as THF which can be readily stripped from the solution to prepare a polyamine curing agents for epoxy. These colloidal unimolecular polymers, CUPs, could be made with near zero VOC and very low viscosity.

Significant work has been published in last 10 years on this new CUP technology, synthesizing CUP particles using different acrylates and methacrylates, understanding the science and finally the application of CUP in a variety of fields. CUP particles based on methyl methacrylate – methacrylic acid (MMA-MAA), [96-98] methyl methacrylate - 2-acrylamido-2-methylpropane sulfonic acid (MMA-AMPS) [99], methyl methacrylate - [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MMA-MADQUAT) [100], ethyl acrylate – acrylic acid (EA-AA) [101, 102], methyl methacrylate – butyl methacrylate – ethyl acrylate (MMA-BMA-EA), methyl methacrylate – butyl methacrylate – ethyl acrylate – 2-ethylhexyl methacrylate (MMA-BMA-EA-2EHMA) [103] have been successfully synthesized. The rheology [104], surface tension [105], gel point behavior [106], electroviscous effects [107], electrokinetics [99], surface and bulk water [108] in CUP system, effect of molecular weight and functionality on particle size of CUP has been studied. MMA-BMA-EA and MMA-BMA-EA-2EHMA systems have been used in the aziridine-cured acrylic CUPs coatings, and MMA-AMPS systems have been used as CUP acid catalyst for melamine cure. In this research, EA-AA copolymer was synthesized and amino functionality was introduced by reacting carboxyl groups of acrylic acid with 2-methylaziridine. The formed polymer was water reduced to produce EA-AAZ amino

functional CUP particles. EA-AAZ CUPs were used as the crosslinker for water borne epoxy systems to produce no/low VOC clear coats.

Aziridines are nitrogen containing three-membered ring compounds. Aziridine, which is also called ethyleneimine was first prepared in 1888 by Gabriel. [109] Commercial production of ethyleneimine began in Germany in 1938. Aziridine and its derivatives are commercially used in coatings to synthesis homopolymer, in aziridine-modified polymers and as polyfunctional aziridines which are used as a crosslinker. Aziridine-modified polymers are synthesized by grafting aziridine on carboxyl functionality on the polymer backbone to produce aminoalkyl esters of carboxylic acid polymers. [110, 111] Such products give improved adhesion of the polymer to anionic and hydroxyl group containing substrates. Substances derived from aziridines with no residual aziridine ring are normally of low toxicity except for being alkaline. [112]

A new approach for crosslinking the waterborne epoxy coatings is reported here that overcomes many of the traditional limitations. By covalently attaching aziridine to carboxyl functional acrylate polymer, polyfunctional amines are formed that are efficient cross-linkers for epoxy resins. The use of new colloidal unimolecular polymer, CUP, systems with amino groups offers a new approach to the crosslinking of epoxy resins. Experimental work and testing demonstrated the suitability of this technology as a zero / low VOC cross-linker for epoxy systems.

2. EXPERIMENTAL

2.1. MATERIALS

Ethyl acrylate (EA), acrylic acid (AA), 2,2′-azobis(2-methylpropionitrile) (AIBN), 1-dodecanethiol and 2-methylaziridine were purchased from Aldrich. The water dispersible epoxy resin, EPI-REZ™ Resin 5522-WY-55 and amino cross-linker EPIKURE 8290-Y-60 were received from Momentive. Ethyl acrylate (EA) was purified by washing with a 10% solution of sodium bicarbonate in water, followed by rinsing with de-ionized water, and brine. The product was dried over magnesium sulfate and filtered. CuBr was added as an inhibitor, and simple distillation with a positive flow of nitrogen was carried out. Acrylic acid (AA) was purified by distillation with CuBr under reduced pressure. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. Tetrahydrofuran (THF) was purchased from J.T.Baker and methyl ethyl ketone (MEK), and benzene were purchased from Fisher Scientific, and all were distilled prior to use.

2.2. INSTRUMENTATION AND METHODS

Acid value was measured by ASTM D974; modified by using potassium hydrogen phthalate (KHP) for standardization and THF as the solvent. Amine value was measured by ASTM D2074 modified by using THF as the solvent.

The absolute molecular weight of the copolymers was measured using Viscotek GPC Max with TDA 305 detector equipped with refractive index detector, low and right angle light scattering detector and viscosity measurement (Malvern Corp.) at THF flow rate of 0.5ml/min, and the injection volume 100μl. The polymer was dried at 50°C in a drying pistol under reduces pressure overnight prior to measurement.

Viscosity was measured by Ubbelohde viscometer. The solids content was measured by ASTM D2369. Particle size was measured using a Nanotrac 250 Particle Size Analyzer from Microtrac with solution concentration of 10% (w/w) using the solution viscosity. [113]

DSC analysis was conducted on a DSC Q 2000 from TA Instruments and the data was processed via Universal Analysis 2000 software. Twenty milligram of EA-AA polymer was weighed out in crimped closed hermetic aluminum pan. DSC was run in modulated mode, modulate at +/- 0.53°C every 100 seconds. To determine Tg, sample was cooled to -40°C, and then the temperature was raised at 2^{O}C/min up to 25°C. The Tg was determined using the second scan after cooling at 10°C/min of the DSC. DSC analysis was conducted under a nitrogen environment.

Gloss of the formed film was measured by ASTM D513 using Byk-Gardner Micro-Tri-Gloss meter. The film gloss which corresponds to specular reflection was measured on chromate treated aluminum Q-panels in accordance with ASTM D523. The averages of 5 readings for 20° and 60° gloss were reported with the standard deviations.

Minimum Film Forming Temperature (MFFT) was measured using Rhopoint MFFT bar 90. The flexibility of coating was measured by ASTM D522 using a Gardner mandrel set. Intrusion and extrusion impact was measured by ASTM D2797 using a Gardner impact tester. Adhesion was measured by ASTM D3369 and ASTM D4541. Pencil hardness was measured by ASTM D3363. Indentation hardness of formed coating was measured by Fischerscope HM2000 S microindenter using Vickers indentation tip using standard application by increasing and decreasing 8mN load over the period of 20 seconds.

2.3. POLYMER SYNTHESIS

A three-necked round bottom flask was fitted with a magnetic stirrer, thermometer, and reflux condenser with a drying tube containing anhydrous calcium chloride on the top and an argon gas bubbler to allow a positive flow of argon throughout the polymerization. To the flask were added 90.2g (0.9 mole) of freshly distilled ethyl acrylate, 7.2g (0.1 mole) of purified acrylic acid, 194.6g of purified THF and 0.1198g (0.073 mole% of monomers) of recrystallized AIBN and 0.0898g (9.95×10^{-4} mole) butanethiol, chain transfer agent. The reaction temperature was then raised to $70 \pm 2\,^O$C for 24 hours. The polymer was then precipitated in ice water at high shear. The polymer was separated by decanting the water. Benzene was added to the precipitated polymer and residual water was removed azeotropically at $70\,^O$C. The polymer was dried under vacuum for 4 days at ambient temperature, followed by further drying at $50 \pm 5\,º$C under vacuum (~1mmHg) for 24 hours to ensure complete removal of solvent from the polymer. The weight of the dried polymer, EA-AA-2 was 77.9 g (80% recovered yield). The polymer was characterized by FT-IR, ^{1}HNMR, GPC for absolute molecular weight, particle size, and acid number. Polymers EA-AA 1 was also synthesized as per the above-mentioned protocol except 0.1040g (11.53×10^{-4} mole) butanethiol was added as chain transfer agent.
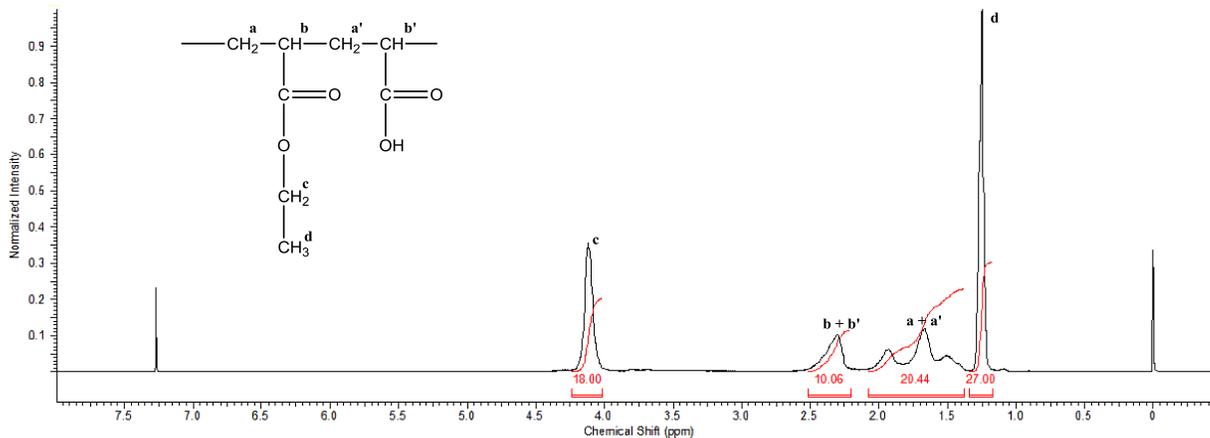
Figure 2. 1H NMR of ethyl acrylate – acrylic acid 2 copolymer

^{1}H NMR (400MHz, Chloroform-d) δ = 4.10 (m, 18 H), 2.29 (br. s., 10 H), 2.07-1.38 (br. s., 20 H), 1.33 - 1.17 (m, 27 H)

The FTIR spectrum of EA-AA 2 polymer shows strong band at 1732 cm^{-1} which are characteristic of the carbonyl of ester, 1258, 1161 cm^{-1} for C-O stretching of ester. Bands were observed at 2981, 2938 and 2874 cm^{-1} for C-H stretching, 1447 and 1379 cm^{-1} are C-H bend and rock. The IR band at 3250, 931cm^{-1} were attributed to the broad CO$_2$H stretch and bend from acrylic acid present in the polymer. All these bands support the proposed structure in the reaction scheme.

2.4. AZIRIDINE MODIFICATION OF POLYMER

To a 250ml round bottom flask equipped with a magnetic stirrer and reflux condenser were added 40.0 g (0.0411 mole of –CO$_2$H) of EA-AA 2 copolymer and 40.0 g of THF. After dissoution 2.35g (0.0411mole) of 2-methyl aziridine was added slowly over a period of 5 minutes utilizing a glass syringe, followed by 5.0 g of THF and allowed to react overnight at 25°C under stirring. Isolation of the product was done via vacuum removal of THF and any unreacted 2-methylaziridine.

Figure 3. 1H NMR of aziridine adduct of ethyl acrylate – acrylic acid 2 copolymer

^{1}H NMR (400MHz, Chloroform-d) δ = 4.10 (br., m, 20 H), 3.46 (br., m, 1H), 2.29 (br., m, 10 H), 1.65 (br., m, 20 H), 1.30 - 1.01 (br., overlap, m, 32 H).

The reaction of the acrylic acid in the EA-AA polymer with 2-methyl aziridine can also potentially produce the isomer with primary amine showed in the figure 4. The NMR results indicate formation of the secondary amine as the major product shown in figure 3, which is consistent with the findings of Roesler and Danielmeier. [114]

Figure 4. Another possible aziridine adduct of ethyl acrylate – acrylic acid copolymer

The FTIR spectrum of EA-AAZ 2 shows similar peaks associated with carbonyls of ester and C-H stretch, bend and rock. No peak was observed indicating presence of carboxylic acid. The IR band at 3377, 1662 and 917cm^{-1} were attributed to the primary amine stretch, bend and wag from aziridine modification of polymer. All these bands support the proposed structure in the reaction scheme.

2.5. PREPARATION OF CUP (EA-AAZ CUP)

Amino functional EA-AAZ polymers were water reduced to form CUP. A 20% polymer solution was made by dissolving 10g polymer in 40g tetrahydrofuran (THF) and stirred overnight. The acetic acid was added to the solution to neutralize all the amino groups according to its amine number and 90g pH modified water (pH = 4.5 -5.0 pH adjusted with the acetic acid) was added by a peristaltic pump at a rate of 1.24g/minute. THF was stripped in-vacuo to produce a clear 10% solids colloidal unimolecular polymer (CUP) with ammonium ion functionality on the particle surface in water. EA-AAZ CUP solution was then filtered through 0.45μm Millipore membrane.

Carboxyl functional EA-AA polymers were also reduced using similar protocol except ammonium hydroxide was used to neutralize carboxylic groups according to acid number on polymer and pH modified water (pH = 8.0-9.0 pH adjusted with ammonium hydroxide) was used during water reduction.

2.6. PREPARATION OF EA-AAZ CUP – EPOXY SYSTEM

Technical information for EPI-REZ Resin 5522-wy-55 epoxy and EPIKURE 8290-Y-60 crosslinker is given in Table 1. EPI-REZ Resin 5522-wy-55 epoxy contains a modified 1002 type epoxy resin in water and 2- propoxyethanol which act as co-solvent / plasticizer

for solid epoxy resin. The EPIKURE 8290-Y-60 crosslinker contains 60% solution of proprietary polyethylene polyamine adduct in 2-propoxyethanol.

Table 1. Typical properties of EPI-REZ Resin 5522-wy-55 epoxy and EPIKURE 8290-Y-60 crosslinker [115,116]

	Phase	Particle size	% solids	Epoxy Equivalent	Amine Equivalent
EPI-REZ Resin 5522-wy-55	Solid	200-700 nm	52 – 55 %	550-700	-
EPIKURE 8290-Y-60	Liquid	-	59 – 61 %	-	360-420

The EA-AAZ CUPs were utilized as a cross-linker for the epoxy resins. To 28.32g of EA-AAZ CUP solution (equivalent weight 534, amine value 105.9) and 3.41g of control EPIKURE 8290-Y-60 were added 5.43g of EPI-REZ™ Resin 5522-WY-55. Extra water was added to control the systems % solids. Compared to 0.63lbs/gallons of VOC for the control coating, the CUP cured system had 0.14lbs/gallon of VOC. For CUP cured system the VOC contribution was mainly from EPI-REZ Resin 5522-wy-55 from 2-propoxyethanol and only trace was from the acetic acid used to form the CUP salts.

Table 2. Epoxy coating composition

	Coating 1	Coating 2	Coating 3
EPI-REZ™ Resin 5522-WY-55	5.43 g	5.43 g	5.43 g
EA-AAZ 10K CUP	28.32 g	-	-
EA-AAZ 37K CUP	-	28.32 g	-
EPIKURE 8290-Y-60	-	-	3.41 g
Water	-	-	24.91 g

Surface preparation of the aluminum panels was done by rinsing with distilled acetone to remove any organic processing oil present, followed by drying in air. The coatings were on A-36 aluminum Q-panel and R-46 steel Q-panel using #30 wire wound bar. The panels were coated and dried in air for 2hrs followed by heating in a 60^0C oven for 12 hours. To confirm the crosslinking of epoxy resin, solvent tests were performed using MEK double rub. The cured coatings were tested for gloss and mechanical properties including flexibility, impact, hardness and adhesion.

3. RESULTS AND DISCUSSION

The 9:1 molar ratio of EA:AA was based on typical surfactants having approximately 16-22 carbon atoms comprising the hydrophobic portion of the chain to one hydrophilic group and previous success with carboxylate and QUAT based CUPs. [96-103] Slightly higher or lower ratios were found to water-reduce into CUP particles without difficulties. [96, 98] The hydrophobicity of the monomer, length of alkyl group, and the length of the backbone between hydrophilic groups determine the number of acid or base groups needed to stabilize the CUP particle. Due to the random nature of the polymerization mechanism, it was not possible to place one AA monomer at every 10th position. The combination of controlling the monomer feed and the random placement of the acid groups during polymerization was sufficient to produce the CUP particles. Particle size of these CUP particles can be in the range of 3-9 nm depending on the molecular weight of polymers. [97]
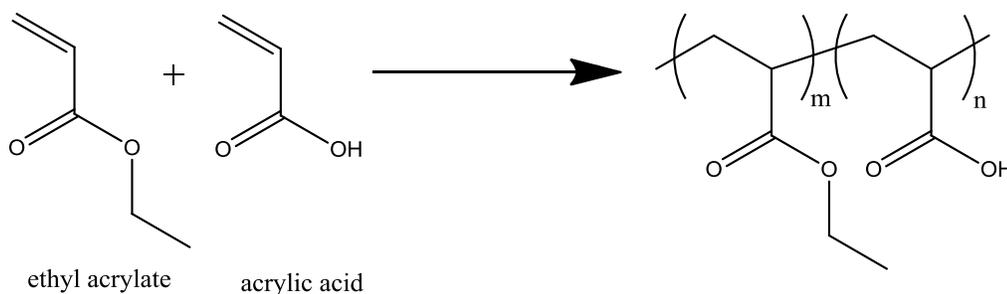
Figure 5. Synthesis of EA-AA copolymer

3.1. CHARACTERIZATION OF EA-AA POLYMER

In Table 3 are listed the values for acid number and percent yield for the synthesized polymer. The measured acid value of polymers was in good agreement with the calculated acid value based on monomer composition of ethyl acrylate and acrylic acid in the polymers. Molecular weight and the polydispersity index for both the polymers are also listed in Table 3.

Table 3. Monomer composition, polymer yield, acid value, molecular weight and particle size of synthesized polymer

Polymer	EA:AA	Yield[a] (%)	Acid value Theo.	Acid value Expt.	Mn	PDI[b]	CO_2H / chain
EA-AA 1	9:1	80	56.29	56.35	10.5K	1.66	10.55
EA-AA 2	9:1	85	56.29	56.87	37K	1.57	37.51

a) Yield is the precipitated and dry isolated yield, b) PDI – polydispersity index

DSC was conducted to determine the glass transition temperature (Tg) of EA-AA copolymer and co-relate it with the calculated value (-15°C) using the Flory Fox equation. The glass transition temperature measured by DSC of the synthesized ethyl acrylate and acrylic acid copolymer EA-AA 1 and EA-AA 2 were -16.17^{O}C and -16.62^{O}C respectively. These polymers exhibits cold flow and would not require a co-solvent. Therefore, the synthesized polymers potentially could produce a near zero VOC cross-linker and near zero VOC coatings.

3.2. POLYMER-AZIRIDINE ADDUCT

2-Aminoester containing copolymers were prepared by addition of 2-methylaziridine to the ethyl acrylate-acrylic acid copolymers. The acrylic acid on polymer backbone reacts with the 2-methylaziridine by protonation of the basic 2-methyaziridine nitrogen atom followed by a nucleophilic attack of the carboxylate anion likely through a 6 membered transition state to form an ester linkage which yields a terminal amine group. [117, 118] The reaction is shown in Figure 6.
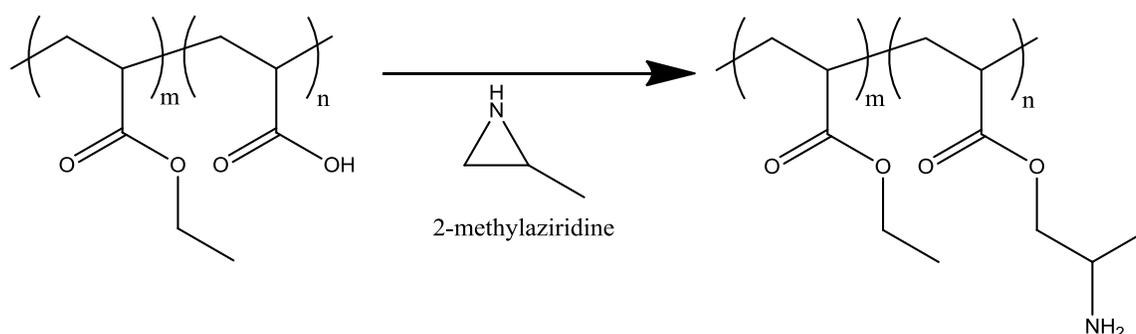
Figure 6. Synthesis of EA-AA and methylaziridine adduct (EA-AAZ)

The measured glass transition temperature by DSC of the polymers EA-AAZ 1 and EA-AAZ 2 were -27.5^{O}C and -26.6^{O}C respectively. By knowing the Tg of the polymer, weight fraction of ethyl acrylate monomer and aziridine modified acrylic acid unit in the polymer, the theoretical Tg of the new amino monomer was calculated using the Flory Fox equation as -49.88^{O}C, which has a value close to n-butyl acrylate (-54°C) [119] as expected.

Table 4. Characterization of EA-AAZ polymer

Polymer	EA:AA	Amine value Theo./ Expt.	Mn	Amine hydrogen per chain	Equivalent weight
EA-AAZ 1	9:1	112.7 / 105.9	11.1K	19.82	529.75
EA-AAZ 2	9:1	113.7 / 106.8	39.1K	70.44	525.28

The measured amine values of polymer was in good agreement with the calculated amine value (based on the previously measured acid value) and indicates that 94% of the acid groups on the polymer reacted with 2-methylaziridine. The introduction of amino functionality on polymer was based upon the acid number being converted to an amine value. The percent conversion was calculated by equation 1.

$$\% \ conversion = \frac{moles \ of \ amine/_{chain}}{moles \ of \ acid/_{chain}} \times 100 \qquad \text{Equation 1}$$

3.3. WATER REDUCTION OF EA-AAZ POLYMERS TO FORM CUPS

The 2-methyl aziridine adduct of polymer 1 and 2 were dissolved in THF (dielectric constant = 7.58 at 25°C). The polymer chain acts as a random coil in THF. When acetic acid was added to the solution, the amino groups on polymer chain formed ion pairs of R-NH_3^+ and $CH_3CO_2^-$. With addition of pH modified water (pH = 4.5-5.0) using a peristaltic pump, the ion pairs become solvated and separate further apart in the THF-water solvent mixture. Positively charged amino groups on same polymer chain repel each other with

the increasing dielectric of solvent mixture caused by the addition of water (dielectric constant = 78.39 at 25°C) and the polymer chain conformation changes to approach a rigid rod which cause an increase in the viscosity. With further addition of pH modified water, at a critical point in the water – THF composition, these polymer chains collapse. The amino groups, being hydrophilic, orient outward to the water phase organizing to produce maximum separation of the positive charges and the collapsed hydrophobic polymer chain forms the spheroidal CUP particle. The unimolecular collapse was found to be dependent on the molecular weight and the concentration of collapsing polymer in THF/water mixture. At high concentrations aggregation was observed but not at the concentration used in this study.

3.4. COLLOIDAL UNIMOLECULAR POLYMERS AND COLLOIDAL AGGREGATED POLYMERS

In previously reported work, the unimolecular collapse is not favorable for molecular weight below 13000 because of insufficient stability by way of electrostatic repulsion on the surface of particle. This leads to some degree of aggregation of polymer chains at the collapse transition which increases the particle diameter of CUPs as compared to the theoretical particle size. The polymers with a molecular weight of 13000 and above form CUPs with stable particle size which was consistent with the theoretical particle size.[96] For polymer EA-AA-1, with Mn = 10.5K, it was observed that the average particle size was larger than that of the theoretical particle size, indicating a degree of agglomeration, shown in figure 7. For polymer EA-AA-2, with Mn = 37K, the measured particle size by DLS was in agreement with the theoretical particle size, indicating unimolecular collapse, shown in figure 8. Both the polymers had particles size of ~4nm and were utilized for

crosslinking epoxy resin to compare the effect of a slightly aggregated CUP but with lower

molecular weight.

Table 5. % solids, viscosity and particle size of CUP particles

Polymer samples	% Solids	Viscosity (cP) at 21° C	Viscosity (cP) at 30.5^{O}C	Measured Particle Size (nm)	Theoretical Particle Size* (nm)
EA-AAZ 1 CUP	10.28%	6.59	5.45	4.2	3.0
EA-AAZ 2 CUP	9.37%	4.24	3.34	4.3	4.5

*Theoretical particle size is based on GPC molecular weight and calculated density
which has been found to agree well with DLS particle size. [96]
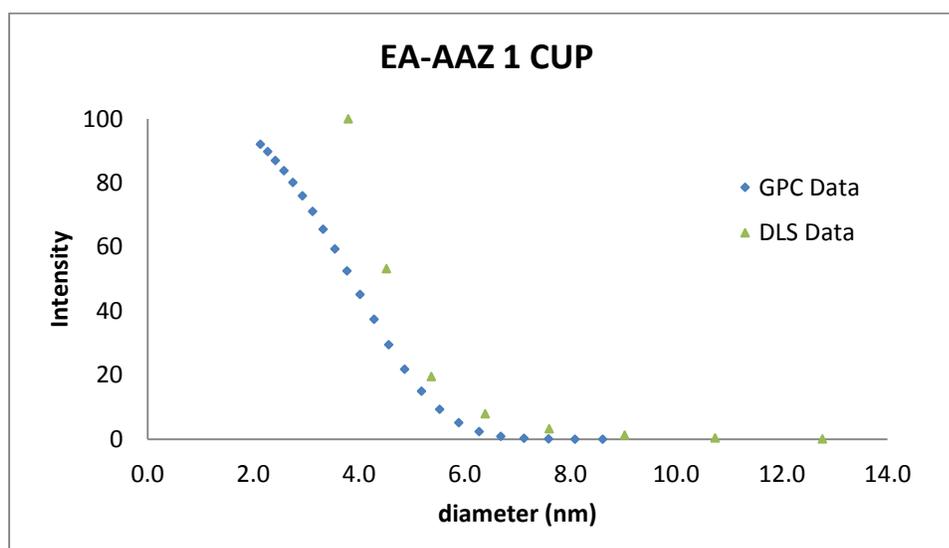
Figure 7. Particle size distribution comparison of EA-AAZ 1 CUP
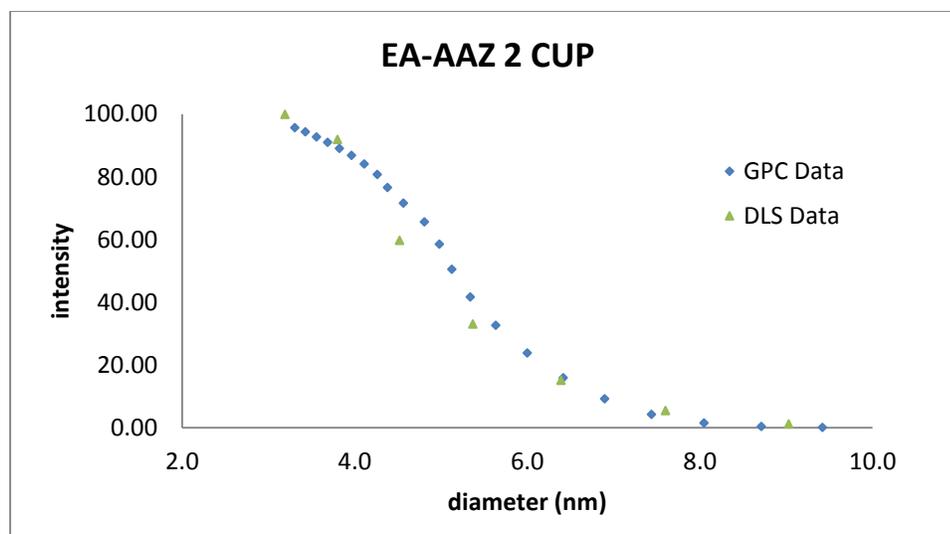
Figure 8. Particle size distribution comparison of EA-AAZ CUP particles

3.5. AMINO FUNCTIONAL AZIRIDINE MODIFIED ACRYLATE – EPOXY SYSTEM

The CUPs work reported in this paper were evaluated for their ability to enhance coating technology by addressing the need for near VOC free coatings. This research leads to the potential of amino functionalized CUPs that are relatively high in functionality, resulting in highly cross linked epoxy resins that can be transparent, high gloss coatings or highly pigmented coatings due to the increased surface area of the nano sized particles. The conversion of the carboxylate CUP particle into an amino functionalized CUP hardener is not limited to 2-methylaziridine. Aziridine derivatives such as n-butyl aziridine can also be grafted onto the polymer. The ability to coalesce at ambient temperature due to the CUP's low Tg offers the prospects of a coating without the need of an additional co-solvent or coalescing aid. These coatings share the same properties that make water borne epoxy

resins attractive to industry such as a simple curing process, low shrinkage on cure, good mechanical properties, and outstanding adhesion.

3.6. TESTING OF THE CUP COATS

In the 2K water borne epoxy coatings, the process of cohesive strength development consist of the molecular interdiffusion of polymeric chains from one particle into another, interfacial crosslinking and residual crosslinking. The interdiffusion of the polymer chains of latex particles depend on the molecular weight. Low molecular weight ensures facile diffusion of polymeric chains from one particle into the other in the coalescing phase, which helps but is not restricted to the development of the cohesive strength.

In tradition epoxy- crosslinker systems, the diffusion of the crosslinking agent into the epoxy particles is crucial to achieve a homogeneously crosslinked film. After coalescence of the particles, a relatively high concentration of reacting functionality is present on the interface of the particles resulting in a densely crosslinked film at the interface. This reduces mobility of polymer chains and crosslinker across the interface, resulting in inhomogeneous crosslinking and hindering the residual crosslinking to some extent. Presence of 2-propoxyethanol, which act as co-solvent / plasticizer, in both epoxy (8%) and conventional crosslinker (40%) reduces the MFFT and enhances the mobility of chains. This helps in the residual crosslinking and hence improves the film formation but increases the VOC of coating system.

In the epoxy – CUP system, after evaporation of water, 4nm CUP crosslinker particle change conformation to a random coil chain. The low Tg crosslinker polymer chains can defuse within the core of the 200nm solid epoxy particles plasticized with 2-

propoxyethanol giving improved residual crosslinking. The hardness of crosslinked epoxy films not only depend on the crosslinking density but also on the glass transition temperature, molecular weight and molecular mobility of polymer chains. The reptation time of the chains during curing depend on the molecular weight. The low molecular weight (Mn = 10.5K) polymer chains will have higher reptation diffusion compare to the high molecular weight (Mn = 37K) polymer chains during curing.

The test results from Table 6 indicate the molecular weight of synthesized EA-AAZ polymers has no significant effect on the crosslinking. As each amine group reacts with 2 epoxy groups to form crosslink, the higher number of amine functionalities per chain length on the crosslinker may hinder the residual crosslinking. The EA-AAZ 1 CUP and EA-AAZ 2 CUP have about 20 and 70 amine hydrogens per chain, well separated by about 9 units of low Tg ethyl acrylate monomers in the random copolymer giving more mobility during crosslinking.

Table 6. Gloss, flexibility, impact resistance, dry and wet adhesion resistance, MFFT, pencil hardness and indentation hardness of epoxy clear coats

		Coating 1	Coating 2	Coating 3
Gloss	20°	88.5 ±1.0	88.2 ±1.2	87.9 ±2.2
	60°	104.4 ±0.1	101.0 ±0.2	99.9 ±0.0
Flexibility	¼ inch mandrel	Pass	Pass	Pass
Impact resistance	Forward (extrusion)	100 in.lbs	100 in.lbs	140 in.lbs
	Reverse (intrusion)	140 in.lbs	140 in.lbs	140 in.lbs
Adhesion	(ASTM D3359)	5B	5B	4B

Table 6. Gloss, flexibility, impact resistance, dry and wet adhesion resistance, MFFT, pencil hardness and indentation hardness of epoxy clear coats (cont.)

Wet adhesion		5B	5B	2B
Puck adhesion	(ASTM D 4541)	1041PSI	1033 PSI	1108 PSI
	Failure mode: a/b*	80% / 20%	80% / 20%	30% / 70%
Pencil Hardness	(ASTM D 3363)	HB	HB	HB
Microindenter Hardness	(ASTM E 2546)	193 N/mm^2	200 N/mm^2	233 N/mm^2
Indentation Modulus	(ASTM E 2546)	7605 MPa	6072 MPa	5331 MPa

**Failure mode: a - cohesive coating failure, b - adhesive substrate to coating failure

3.6.1. Gloss. The 20°/ 60° gloss for the experimental (EPI-REZ™ Resin 5522-WY-55 - EA-AAZ CUP system) and the control (EPI-REZ™ Resin 5522-WY-55 - EPIKURE 8290-Y-60), all produced high gloss coatings. The experimental coatings with the CUP cross-linker produced higher 20°/ 60° gloss than the control. Higher gloss of both EA-AAZ CUP crosslinked epoxy coating can be attributed to good flow and no phase separation in crosslinked epoxy films.[120, 121] The low Tg of CUP cross-linker imparts better mobility than the control polyethylene polyamine adduct at room temperature as well as elevated temperature during curing may also aid in gloss enhancement.

3.6.2. Mandrel Flexibility and Impact Resistance. Test Results Mandrel flexibility and impact resistance of clear coats formulated from epoxy EPI-REZ Resin 5522-WY-55 with prepared cross-linker EA-AAZ CUP and control EPIKURE 8290-Y-60 were tested in accordance with ASTM D522-93A on aluminum Q-panels and ASTM D2797-93 on steel Q-panels respectively. The coating on the substrate gets elongated

when the substrates are bent during manufacturing or abused during service. The elongation / flexibility test measures the ability of the coating on the substrate to be flexed and to resist cracking when elongated. Also, coatings can get damaged by sudden impact during their service. The impact test measures the performance of coating for its ability to resist cracking caused by impact which again is controlled by the coating ability to be elongated and retain adhesion. Better flexibility and impact resistance can be achieved by using a polymer with better elongation to break and good tensile strength. Optimum crosslinking and adhesion promoters can aid performance, with lower crosslinking resulting in poor film properties, while with the higher crosslink density, the coating can become brittle.

The control polyethylene polyamine curing agent has an equivalent weight of 163 compared to the equivalent weight of 534 dalton of the experimental EA-AAZ CUP cross linkers, which have more aliphatic hydrocarbon chain inbetween two consecutive functional groups. Both epoxy clear coats, with the experimental (EA-AAZ CUP systems) and the control (EPIKURE 8290-Y-60) cross-linker, passed 1/8 inch mandrel (i.e. ~28% elongation) flexibility test and forward and reverse impact rating of 140 in-lbs. This excellent flexibility and impact resistance for both control and experimental cross linker cured epoxy coatings can be attributed to the higher equivalent weight of epoxy used. The control EPIKURE 8290-Y-60 crosslinker has 2-propoxyethanol as a solvent which helps yielding better film by aiding coalescence during curing. The EA-AAZ CUP cross linker has a lower glass transition temperature with no added solvent, however due to all the amine being on the surface, reaction is rapid since diffusion is only over a short distance with the nano resin.

3.6.3. Dry and Wet Adhesion Test Results. Dry and wet adhesion tests were done according to ASTM D-3359 using the multiblade cutter on the coated aluminum Q panels. Two sets of scribes were made perpendicular to each other on the coated specimens to create a grid of 10×10 small squares of paint. Once the specimen was scribed, the adhesive tape was cut to lengths of 75 mm, and applied. The tape was then peeled close to an angle of 180°. The grid area was inspected for removal of coating from the substrate. Semi-quantitative rating of the paint adhesion was done according to ASTM D-3359. Table 6 shows the results of dry and wet adhesion tests on all the samples.

The puck adhesion test was done according to the ASTM D-4541 on the coated aluminum Q panels by prepping the coating with sandpaper #320, and wiping with the chemwipe. The grit blasted pucks where glued onto the coating with a 3M Scotch-Weld epoxy adhesive DP 460 NS, and allowed to cure for 24 h. A digital torque wrench ComputorQ-II was used to measure the torque required for the failure and the failure type. The torque reading was measured in inch-pound units and was reported in PSI units by using appropriate conversion and an average of two readings in Table 6. It was observed that both of the CUP cured epoxy clear coats had coating failure comparable to the control, all coatings showed good adhesion of polymeric film to the aluminum Q-panels.

3.6.4. Minimum Film Forming Temperature (MFFT). MFFT was performed using Rhopoint MFFT bar 90 using 75 μm square bar applicator. The MFFT of all the epoxy coatings are listed in Table 7 along with the measured glass transition temperature of EPI-REZ 5522-WY-55 epoxy resin, EPICURE 8290-Y-60 crosslinker, and the EA-AAZ CUPs and the cured coatings. The results indicate that the lower Tg of the EA-AAZ

CUPs and Tg of plasticized epoxy resin allow the coatings to form films at lower temperature compare to the control crosslinker.

Eckersley and Rudin found that the MFFT was proportional to the number average particle diameter of the particle. They also found that larger diameter particles have smaller contact radii and so the degree of coalescence is lowered. Jensen and Morgan found that as the latex particle size decreased by a factor of seven, the MFFT was reduced by approximately 10 ^{O}K. Larger voids are formed when larger particles come in contact with each other. This prolongs the time for the voids to be filled by particle deformation reducing the efficiency of coalescing. In contrast, smaller particles form better packing with smaller voids improving the rate of coalescence. Sperry found the MFFT increases with increasing particle size and concluded a correlation of a simple viscous flow model stating longer time is required for the larger interstitial voids to shrink to a size resulting in visually transparent films. The results in Table 7 are consistent with the findings of Eckersley and Rudin [122], Jensen and Morgan [123], and Sperry [124]. After evaporation of water, low Tg EA-AAZ CUP particles change conformation of random coil chains and with smaller interstitial voids, defuse faster yielding lower MFFT.

Table 7. Minimum film formation temperature and glass transition temperature of Epoxy resin, crosslinkers and final coating

	MFFT (^{O}C)	Tg (^{O}C)
EPI-REZ 5522-WY-55	-	5.85
EA-AA-AZ 1	-	-27.59
EA-AA-AZ 2	-	-26.65

Table 7. Minimum film formation temperature and glass transition temperature of Epoxy resin, crosslinkers and final coating (Cont.)

EPICURE 8290-Y-60	-	-17.50
Coating 1	4.7	36.07*
Coating 2	4.6	39.64*
Coating 3	11.3	51.04*

* Glass transition temperature of cured coatings

The final Tg of the cured coating is critical factor controlling the completion of crosslinking reaction. As the crosslinking progresses, the Tg of the curing film approaches a limiting temperature. The rate of crosslinking is then limited to the mobility of the epoxy and crosslinker chains rather than their reactivity. For CUP crosslinkers, as the polymer chains can diffuse further and aid mobility for further residual crosslinking due to lower Tg compare to control crosslinker.

3.6.5. Drying Time and Pot Life. Mechanical dry time of the EA-AAZ 2 CUP cured and the EPICURE 8290-Y-60 cured epoxy coatings was measured according to ASTM D5895-13 using a Gardener straight line drying time recorder. This study determines the different stages of the drying of the coating. The results are shown in Table 8. Coatings 2 had faster tack free time and hard dry time compare to coating 3. The initial rate of reaction of liquid polyethylene polyamine of EPICURE 8290-Y-60 crosslinker is faster compare to CUP crosslinker. The slower film formation of the control system can be attributed to higher percentage of the slow evaporating high boiling solvent 2-propoxyethanol (BP 150 ^{O}C).

Table 8. Stages of drying using straight line drying time recorder for coating 2 and coating 3

Stages of drying	Coating 2	Coating 3
Set to touch	20 min	30 min
Tack free time	1 hr	2.5 hr
Dry hard time	3 hr	12.5 hr
Dry though time	5 hr	13.5 hr

It is important to know the time frame in which the epoxy coatings can be used after are mixed with the crosslinker. The pot life gives an estimate of the time after which the coating becomes less effective. Preliminary testing indicates both EA-AAZ CUP and EPICURE 8290-Y-60 cured epoxy coatings have 4 -6 hr pot life. Further investigations would be required to fully validate these results.

3.6.6. Pencil Hardness and Micro Indenter Hardness. Pencil hardness of the coatings was determined by ASTM D 3363 using standard pencils of hardness of 6B to 5H. All the films showed gouge hardness of HB which was comparable for all three coatings. The test results are qualitative and depend on operator and preparation of pencil lead tip. For quantitative measurement of hardness, a microindenation method was utilized which measures the indentation modulus and indentation hardness. The use of a high precision mechanical indenter increases the quantitative aspect and type of information of the polymeric coating. [125, 126]

Indentation moduli and indentation hardness were evaluated from load versus indentation depth for all three coating films. The reported data was the mean of 5 measurements at different locations. The Vicker indentation tip was used in this study to

measure indentation modulus and indentation hardness. In Figure 8, the indentation patterns are shown for three different coatings: control amine-cured epoxy, and EA-AAZ CUPs-cured epoxies. The indentation moduli (E_{IT}) of these three coatings obtained from microindentation tests are 5331.3 ± 140.2 MPa for control amine-epoxy, 7605.2 ± 939.6 MPa for EA-AAZ 1 CUP-epoxy, and 6072.0 ± 83.42 MPa for EA-AAZ 2 CUP-epoxy. The indentation hardness (H_{IT}) values of these three coatings are 232.9 ± 3.3 N/mm^2 for control amine-epoxy, 193.3 ± 28.42 N/mm^2 for EA-AAZ 1 CUP-epoxy, and 200.1 ± 14.9 N/mm^2 for EA-AAZ 2 CUP-epoxy. The values of E_{IT} and H_{IT} are shown in Table 6.
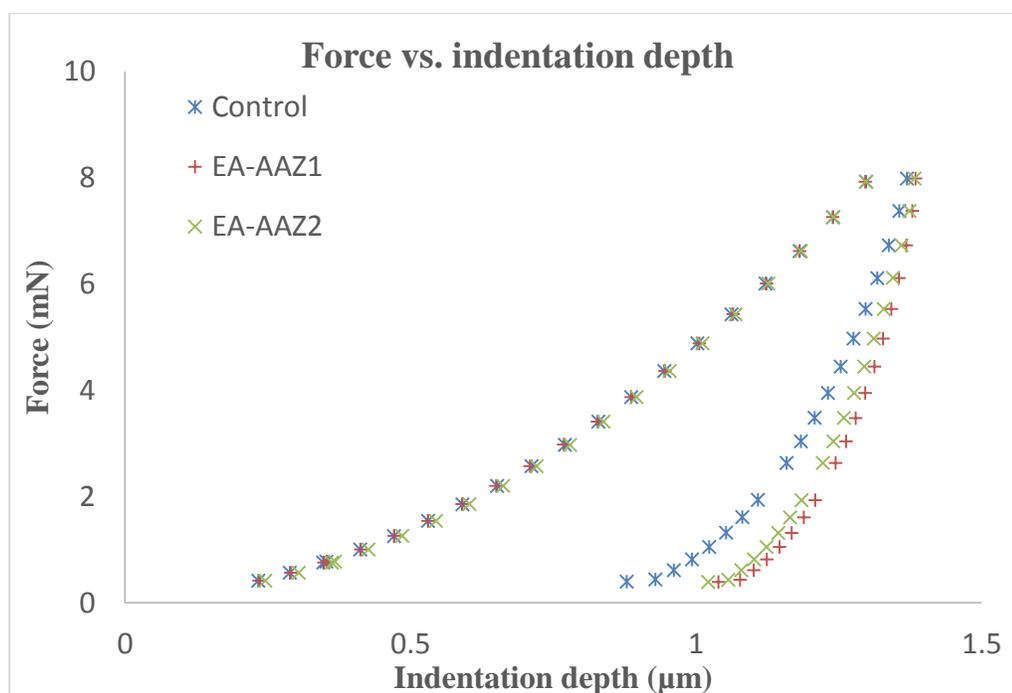
Figure 9. Load versus indentation depth

The results have clearly demonstrated the effects of the cross-linker on the surface mechanical properties of the epoxy coating. Among the three cross-linkers used, the control

produced a relatively harder film compared to EA-AAZ 1 and EA-AAZ 2 cross-linkers. The ability of the thermoset epoxy to deform under indentation were limited by its cross-linked density, structure and the Tg of crosslinked coating. Crosslinking density, glass transition temperature and viscoelastic properties are often considered to be the most important parameters influencing the scratch resistance hence the hardness of coatings. [127] From the glass transition temperature data from Table 7, with higher Tg of EPIKURE 8290-Y-60 yield high Tg coating yielding better hardness to the coating. The low Tg of EA-AAZ CUP yield lower Tg coating with slightly lower values of hardness. The EA-AAZ CUP coatings were more flexible and slightly softer compare to control EPIKURE 8290-Y-60 made up of the polyethylene polyamine adduct. The higher equivalent weight (534) of CUPs is due to higher volume fraction of hydrophobic ethyl acrylate in CUP cross-linker which makes the films more flexible and slightly softer compare to equivalent weight (163) of control EPIKURE 8290-Y-60 cross-linker.

4. CONCLUSION

Multifunctional 4nm EA-AAZ CUPs were prepared with zero volatalie organic content (VOC). EA-AAZ CUPs and EPIKURE 8290-Y-60 were tested as crosslinker for coatings based on a waterborne epoxy. The minimum film-forming temperatures for the EA-AAZ CUPs cured coatings were lower than the reference croslinker containing solvent. The incorporation of EA-AAZ CUPs in epoxy systems enables the coating formulation to have reduced volatile solvent content, therefore contributing to decrease VOC emissions.

Evaluation of properties of EA-AAZ CUPs crosslinked coatings revealed that the low Tg CUP nano crosslinker was an innovative approach to reduce the VOC and have performance comparable to the control. Amine crosslinkers based on CUP technology are not restricted to epoxy coatings but can be suitable for a variety of applications.

II.   SYNTHESIS OF ETHYL ACRYLATE - ACRYLIC ACID COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES AND THEIR USE AS FREEZE THAW STABILIZER AND WET EDGE RETENTION ADDITIVE IN LATEX PAINT

Sagar Vijay Gade, Yousef Dawib, Peng Geng, Minghang Chen,

Michael Van De Mark*

Missouri University of Science and Technology | 1870 Miner Circle, Rolla, MO 65409

*Corresponding Author. mvandema@mst.edu

Keywords. colloidal unimolecular polymer (CUP), latex, freeze thaw, paint

ABSTRACT

New regulations which reduce the level of volatile organic compounds (VOC) for architectural latex coatings usually necessitate a sacrifice in performance. The use of glycol has been shown to aid in both freeze thaw and wet edge retention. Loss of this VOC will therefore compromise both. The new additive technology presented here replaces 8-15% of the resin with a new additive resin technology. The freeze thaw stability goes from poor to excellent and with excellent wet edge retention. The paper will cover the science and application of the technology as well as the additives preparation. Viscometry, NMR and DSC data will be presented to explain the science of this new technology.

1. INTRODUCTION

In the past several decades, the use of waterborne coatings has increased over solvent borne formulations. Several parameters are responsible for this shift, but one of the primary motivations was to make more environmentally friendly coating formulations. The waterborne formulations still utilize supplementary VOC co-solvents to improve properties like freeze thaw stability, wet edge retention, coalescence etc. The glycols were incorporated as antifreeze, which depress the freezing point of the water and hence protect the waterborne formulation from gelation and aggregation due to freezing and it allows the evaporation of water during drying inhibiting film formation which helps in wet edge retention. Volatile coalescent aids like 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate and 2-ethylhexyl benzoate have been used to depress the glass transition temperature of the latex polymers which allow for film formation at lower temperatures but yield hard final film properties for better performance of final coating by evaporating.

To make freeze thaw stable latex paint, various antifreeze agents have been developed and utilized over the past few decades. The mainstream antifreezes are glycols which allow paint to be useful even after 5+ freeze thaw cycles. Mainstream glycols used as antifreeze are ethylene glycol (BP 197 ^{O}C), diethylene glycol (BP 244-245 ^{O}C) and propylene glycol (BP 188 ^{O}C). [128]

A variety of latex dispersions are utilized as binder resin for interior and exterior paint application. Many of these latex dispersions in the paint are stabilized using glycols, otherwise they will lack freeze thaw stability during transportation and storage in cold temperature. The glycols, which are used as antifreeze are very effective freeze thaw stabilizers, but with strict environmental legislation with respect to VOC on coatings, they

are becoming undesirable. With higher boiling point, glycols also evaporate slowly as the coating dries. To achieve low levels of VOC in paint means the amount of glycols used in coatings formulation has to be reduced or eliminated completely.

Blackly gave a review of colloidal destabilization of latex polymers during freezing. In a latex paint formulation, when the paint freezes, the freezing process initiates the formation of ice crystals. As ice crystals grow the volume solids of the dispersion increases, it forces the latex particles to pack closer together. As the initially formed ice will be pure ice excluding all components, the electrolyte concentration in the remaining cold liquid water increases, which compresses the protective double layer of electrostatically stabilized lattices. The synergistic effects of these factors can reduce the stability of latex and lead to particle-to-particle contact. If the stability of these latex particles is not sufficient under these conditions, this aggregation is irreversible upon thawing and results in undesirable coagulation and the coalescing of latex particles results in a solid lump of latex resin. Since polymer flow and particle coalescence can occur at these low-temperature conditions, this situation is further intensified with the lower Tg or softer binders utilized in many low-VOC paints. The use of small amount of the glycol will inhibit part of water from freezing which maintains a small layer of non-freezing fluid of high dielectric around each latex particle thus stabilizing the coating. Many low-VOC waterborne paints fail to provide sufficient freeze/thaw (F/T) stability. [129]

Yue Ma studied the microstructure development in drying latex coatings by cryo-SEM for simple mono-disperse and bimodal latex coatings. The mechanism of latex film formation was followed visually at different stages of latex film formation, targeting the effects of key parameters such as polymer glass transition temperature, dispersion

composition, and coating drying rate on the drying process. [130] Farwaha synthesized amphoteric surfactant copolymer latex improving the freeze thaw stability of the latex paint. Latex paints destabilizes on repeated freeze-thaw cycles as the anionic surfactants used in latex paints tend to desorb from the latex particles, which increases the ionic strength of the aqueous phase resulting in coagulation. The use of amphoteric surfactants in paints improves the freeze-thaw stability due to its zwitterionic character, with desorption from latex surface, the ionic strength of the aqueous phase does not change and hence delayed the paint coagulation or eliminated it entirely. [131] Farwaha also found that incorporation of a monomer with a long polyethylene glycol groups in latex synthesis improve the freeze thaw stability of the final paint formulation. During the freezing cycle the contact between latex particles is minimized by a hydration layer resulting from the surface-bound polar groups, such as the polyethylene glycol functionalities. [132, 133]

Zhao disclosed the use of polymerizable alkoxylated surfactants in latex polymers for aqueous paint and paper coating compositions to reduce the VOC content with excellent freeze-thaw stability of these compositions. Use of polymerizable alkoxylated surfactants in latex preparation gives the lattice stabilization through steric mechanisms, improving electrolyte and freeze thaw stability. [134, 135] Masayoshi Okubo disclosed the use of unsaturated (poly)oxyalkylene glycol monomer in a resin composition for an aqueous paint which contains substantially no VOC. The paint had excellent freezing-thawing stability and low temperature film-formability with excellent anti-blocking property and water resistance. [136] Adam developed new additive technology (trade name FT 100) to improve freeze thaw stability of low/zero VOC latex paint along with improved gloss, better pigment dispersion and improved stain resistance. [137] Butler synthesized acrylic

acid –methyl methacrylate latex using nonyl phenyl ethoxylate surfactants with ethoxylate lengths of 30 and 50 along with electrosteric stabilizers. They studied its effect on shelf-life, freeze–thaw stability and mechanical stability of coating formulation derived from it. [138] Rodriguez studied the use of propylene oxide based glycol ethers as coalescing solvent and they revealed its improved effect on freeze thaw stability of the latex paint formulation. [139] Most of the work report above contains polymerizable polar monomers or polar surfactants used in latex synthesis which help by adding a thicker layer of hydration on the surface of latex particles. The layer of hydration minimizes the contacts between the particles during freezing cycle.

Open time is another very important issue for all the waterborne coatings. The water-borne paints having a problem of limited open time has already been known for the dispersion paints [140], for example by Rohm & Haas Company back in 1964 [141]. In the literature [142], wet edge time (also referred to as lapping time) has been defined as the period of time during which no edge marks are produced when a freshly applied paint film is lapped over a previously painted area.

Drying is quicker at the edges of the film and this is the origin of a water and particle flux that creates a drying front perpendicular to the surface. This phenomenon has been described the first time by Hwa [1143] and analyzed by Deegan [144], Winnik and Feng [145] and Ming [146] and the drying process at the edges has a direct and important impact on the open time. [147]

Typically for conventional water-borne coatings, the open time will be the order of about 15 min, and the wet edge time is even shorter at about 2–6 min. For solvent-based alkyds, the open time is typically around 45 min, with a wet edge time of about 25 min.

Many attempts have been made to improve the open time and wet edge time of water-borne dispersion paints. Initially, literature and patents focused on addition of organic solvents to the water-borne dispersion paints to control the rheology of the paint and to delay the total evaporation of liquids [148-150]. Andrews [151] and Croll [152] studied the effect of ethylene glycol and propylene glycol on the drying of latex paints and found ethylene glycol is more hydrophilic than propylene glycol, it evaporates more slowly after the majority of the water has evaporated. Sullivan [153] found that the hydrophilic solvents tend to partition into the aqueous phase and diffuse out of the coating rapidly compare to hydrophobic coalescent aids, which largely partitions to the latex polymer. Winnick and Feng [154] found that the high Tg latexes dry more rapidly than low Tg latexes. They also found some blends of the high and low Tg latexes dry more slowly than either of the individual latexes. Other techniques aimed at delaying the evaporation of water ranges from grafting very hydrophilic compounds into or onto latex particles [155-157] to keep water in between the particles for a longer period of time. The addition of a surface-active evaporation suppressing agent, such as eicosanol, has been described [158] as one of the solution for short open times. In this case, a hydrophobic barrier is formed at the air–water interface, which will retard the evaporation of water to a certain extent. Controlling the rheology of the drying paint is obviously key if the open time of a water-borne paint is to be extended.

While a significant amount of literature has been published on the processes related to film formation and coalescence, there has been less focus on fundamental mechanisms related to the impact of glycols and other additives on the workability of waterborne architectural paints. [159]

The colloidal unimolecular polymer particles have a diameter ranging from 3-9 nanometers and therefore have a large surface area (16,600 m^2/g for 3nm diameter particles). The particles are suspended in water with a large amount of "surface water" which is non-freezing. The large surface area per gram yields a larger weight fraction of surface water around these particles compare to latex systems. In this research a partial replacement of the latex resin by a CUP polymer solution was explored. The surface water of the CUP could substantially improve the freeze thaw stability and the wet edge retention by controlling evaporation and coalescence rates. The study involves application of CUP technology in architectural paint as VOC free freeze thaw stabilizer and relating this performance to the freezable and non-freezable water fraction found in differential scanning calorimetry (DSC) [160], viscometry [161] and a *T1* NMR relaxation methods [162].

2. EXPERIMENTAL

2.1. MATERIALS

Ethyl acrylate (EA) was purchased from Alfa Aesar and acrylic acid (AA) was purchased from Aldrich. EA was purified by washing with a 10% solution of sodium bicarbonate in water, followed by rinsing with de-ionized water, and brine. Ethyl acrylate was then dried over magnesium sulfate and filtered. Inhibitor CuBr was added and simple distillation with a positive pressure of argon was carried out. AA was purified by distillation with CuBr under reduced pressure. AIBN was purchased from Aldrich and was re-crystallized from methanol, and 1-butanethiol was purchased from Aldrich and was used as received. Tetrahydrofuran (THF) was purchased from J.T.Baker and methyl ethyl ketone (MEK), and benzene were purchased Fisher Scientific and distilled before use. Encor 379G, a vinyl acrylate latex resin was purchased from Arkema. Kronos 2101 TiO_2 pigment was received from Kronos. The rheology modifier RM825, dispersant Tamol 731A, pH modifier AMP 95 and surfactant Triton X-100 were received from Dow. BYK 22 defomer was obtained from BYK, a member of Altana. All paint additives were used as supplied by the manufacturer.

2.2. INSTRUMENTATION

The polymer was characterized for absolute molecular weight, particle size, Tg and acid number. Particle size was measured using a Nanotrac 250 Particle Size Analyzer from Microtrac with solution concentration of 10% (w/w). Absolute number average molecular weights (Mn) were measured by gel permeation chromatography (GPC) in THF at $25^{O}C$ on a Viscotek GPCmax from Malvern Instruments coupled with a triple detector array TDA305 (static light scattering, differential refractometer, and intrinsic viscosity). Glass

transition temperature (Tg) was measured on TA Instruments Q2000 by using differential scanning calorimeter (DSC) method at a scan rate of 10^OC/min. The Tg was determined at the second scan after cooling at 10^OC/min of the DSC. Acid values (AV—reported in mg of KOH/g of polymer sample) for polymer was measured by titration method ASTM D-974, which was modified by using potassium hydrogen phthalate (KHP) and THF as the solvent. Viscosity was measured by Ubbelohde viscometer. The solids content followed ASTM D2369.

The T_1 experiments were carried out on Bruker MiniSpec 20 MHz NMR spectrophotometer in 10mm NMR tube at constant temperature. The freeze thaw stability testing was performed according to ASTM standard test method 2243-95. The temperature of thawed paint was measured and the thawed paint was subjected to mixing by hand.

2.3. POLYMER SYNTHESIS

A three-necked round bottom flask was fitted with a mechanical stirrer, thermometer, and reflux condenser with a drying tube containing anhydrous calcium chloride on the top and a nitrogen gas bubbler to allow a positive pressure of nitrogen throughout the polymerization. Then 90.1g (0.9 mole) of freshly distilled ethyl acrylate, 7.1g of purified acrylic acid (0.1 mole), 250g of purified THF, 0.1362g of recrystallized AIBN (0.83 mmole) and 0.0898g butanethiol (0.99 mmole) as a chain transfer agent were added to the flask respectively. The reaction temperature was then raised to 70 ± 2ºC. The reaction was carried out at this temperature for 24 hours. The polymer was precipitated in ice water at high shear using high speed dispermat. The polymer was then separated by decanting the water and dried under vacuum for 4 days at ambient temperature, followed by further drying at 50 ± 5ºC under vacuum (~1mmHg) for 24 hours to ensure complete removal of

solvent and unreacted monomers from the polymer. The weight of the dried polymer was 77.6 g (80% isolated yield). ^{1}H NMR spectra were consistent with proposed polymer structure.

2.4. CUP PREPARATION

Synthesized polymer was dissolved in THF (20% w/w) and stirred overnight. Ammonium hydroxide was added to neutralize the carboxylic acid groups. De-ionized water, pH modified to 8.1 to 8.5 with ammonium hydroxide was added using a peristaltic pump at 1.24g/minute, diluting the solution to a 10% (w/w) polymer/water solution. After addition of water, the THF was stripped off in-vacuo using rotovap. CUP solutions were then filtered with a 0.45 micron filter then viscosity and particle sizes were measured. The CUP solution was further concentrated to 23.5% before using it in the paint formulation.

2.5. PAINT FORMULATION

To avoid variation of raw materials in the paint formulations, a master batch was prepared shown in Table 1 and formulated with CUP, water and Encor 379G added according to Table 2 at low shear (800RPM) and mixed for 20 minutes. All the testing was done after at least 24h after preparation of the paint formulations. Use of freeze-thaw stabilizer and coalescing aid was deliberately avoided to check the true effect of CUP on the paint formulations. The U.S. Environmental Protection Agency has officially removed AMP 95 from the Clean Air Act's list of VOCs making these paints truly zero VOC systems. [163]

Coating Compositions

Table 1. Grind master batch

% NV	Wt/Gal	Material	Formula		Solids	
			Pounds	**Gallons**	**Pounds**	**Gallons**
0	8.33	Water	229.60	27.56	0.00	0.00
0	7.85	AMP 95 pH Modifier	2.00	0.25	0.00	0.00
100	8.83	Triton X-100	3.76	0.43	3.76	0.43
100	8.33	Byk 22 defoamer	1.33	0.16	1.33	0.16
60	8.90	Tamol 731A	28.20	3.17	16.92	1.81
100	33.32	Kronos 2101 TiO_2	250.00	7.50	250.00	7.50
25	8.70	RM 825	12.00	1.38	3.00	0.30
		Total	526.89	40.45	275.01	10.2

Table 2. Let down

Table 2.1. Control without CUP

% NV	Wt/Gal	Material	Formula		Solids	
			Pounds	**Gallons**	**Pounds**	**Gallons**
		Base	526.89	40.45	275.01	10.20
55.0	9.00	UCAR 379G	436.36	48.48	240.00	24.91
0.0	8.33	Water	92.12	11.06	0.00	0.00
		TOTAL	1055.37	100.00	515.01	35.11

Table 2.2. 20 lbs polymer per 100gallon

		Base	526.89	40.45	275.01	10.20
55.0	9.00	UCAR 379G	400.00	44.44	220.00	22.84
0.0	8.33	Water	46.10	5.52	0.00	0.00
23.5	8.89	CUP	85.10	9.57	20.00	1.76
		TOTAL	1058.09	100.00	515.01	34.79

Table 2.3. 30 lbs polymer per 100gallon

		Base	526.89	40.45	275.01	10.20
55.0	9.00	UCAR 379G	381.83	42.43	210.01	21.80
0.0	8.33	water	23.20	2.77	0.00	0.00
23.5	8.89	CUP	127.65	14.36	30.00	2.64
		TOTAL	1059.57	100.00	515.01	34.64

Table 2.4. 40 lbs polymer per 100gallon

		Base	526.89	40.45	275.01	10.20
55.0	9.00	UCAR 379G	363.63	40.40	200.00	20.76
0.0	8.33	water	0.00	0.00	0.00	0.00
23.5	8.89	CUP	170.20	19.15	40.00	3.51
		TOTAL	1060.72	100.00	515.00	34.48

Weight per gallon was measured using a weight per gallon cup, % solids by weight was measured by ASTM D1259, % solids by volume was calculated by taking ratio of volume of dry paint and total volume paint, pigment volume concentration (PVC) was calculated by taking ratio of volume fraction of pigment in dry paint over total volume of dry paint as shown in Table 3.

Table 3. WPG, % solids by weight, % solids by volume, and PVC

	Control with no CUP	20 lbs polymer /100gal	30 lbs polymer /100gal	40 lbs polymer /100gal
WPG	10.55	10.58	10.59	10.61
% Solids (Wt)	48.80	48.67	48.61	48.55
% Solids (Vol)	35.11	34.79	34.63	34.47
PVC	21.37	21.56	21.66	21.76

3. RESULTS AND DISCUSSION

3.1. EA-AA POLYMER

The monomers EA and AA were chosen at a molar ratio of 9:1 for this study to produce a polymer with glass transition temperature lower than ambient to allow film formation without added solvent. The polymer had a hydrophobic backbone of ethyl acrylate while the hydrophilic ionic stabilizer was acrylic acid. The polymer should follow the monomer composition since the reactivity ratio of ethyl acrylate and acrylic acid is 1.02: 0.91. [164] The molecular weight (Mn 31K) chosen here is only one example. Polymers with molecular weights ranging from 15,000 to 153,000 have been successfully reduced to form CUPs with particle size ranging from 3-8 nm. The measured acid value (56.35 mg KOH/gm) of the synthesized polymers was found to be comparable with the theoretical acid value (56.29mg KOH/gm) as shown in Table 4. The precipitated and dry isolated yield was 80% for the synthesized polymer.

3.2. EA-AA CUP

When the polymer is in a good solvent, THF (dielectric constant, 7.5), it acts as a random coil. The measured values of the Mark–Houwink parameters, "a" and "log K" are 0.619 and -3.612 respectively for EA-AA copolymer-THF system. With addition of ammonium hydroxide, the carboxylic acid groups on polymer chain form carboxylate anions and ammonium cation pairs. With addition of pH modified water (dielectric constant 80.0), the polymer chains, which are in a state of random coils, undergoes a conformational change with the changing solvent environment around the polymer. In addition, with increasing volume fraction of water in the system, carboxylate anion and ammonium cation pair gets solvated and anions on the polymer chain start repelling each

other further extending the conformation of polymer chains more like a rigid rod. At a critical concentration, polymer-polymer interaction overcomes polymer-solvent interaction and the entropically favored collapse of polymer chains to produce a collapsed spheroidal like conformation occurs. When the concentration of polymer in the solution is dilute the polymer chains collapse unimolecularly and these CUPs are stabilized by the carboxylate groups by means of electrostatic repulsion.

Table 4. Yield, acid number, molecular weight of EA-AA polymer

| Polymer | EA:AA | % yield* | Acid value | | Mn | CO_2H / chain |
			Theo.	Expt.		
EA-AA	9:1	80	56.29	56.35	31K	31.82

*Yield is the precipitated and dry isolated yield

The kinematic viscosity of 10% water-reduced EA-AA CUP was measured at two different temperatures (19.4^{O}C and 30.7^{O}C) utilizing a Ubbelohde viscometer to be 3.10cSt and 2.30cSt respectively, as shown in Table 5. These viscosities were utilized to measure particle size, as the DLS measures the diffusion coefficient of the CUP particles in the media, and utilizes it to calculate the particle size by the Stokes-Einstein equation which requires the viscosity of suspension.[34] The measured glass transition temperature of EA-AA polymer in CUP solution was -16.17 ^{O}C.

Table 5. % solids, zero shear viscosity and particle size

| Polymer | % solids | Ubbelohde Viscosity | | Particle Size (nm) | | Tg |
		19.4^{O}C	30.7^{O}C	DLS	GPC	DSC
EA-AA	10%	3.10 cSt	2.30 cSt	4.12	4.4	-16.17 ^{O}C

The measured particle diameter from DLS was in good agreement with the theoretical particle diameter calculated from the molecular weights of fractions from the GPC, assuming the density of the CUPs was the same as that of bulk polymers. This data confirmed the unimolecular collapse during water reduction of the CUP as shown in Figure 1.
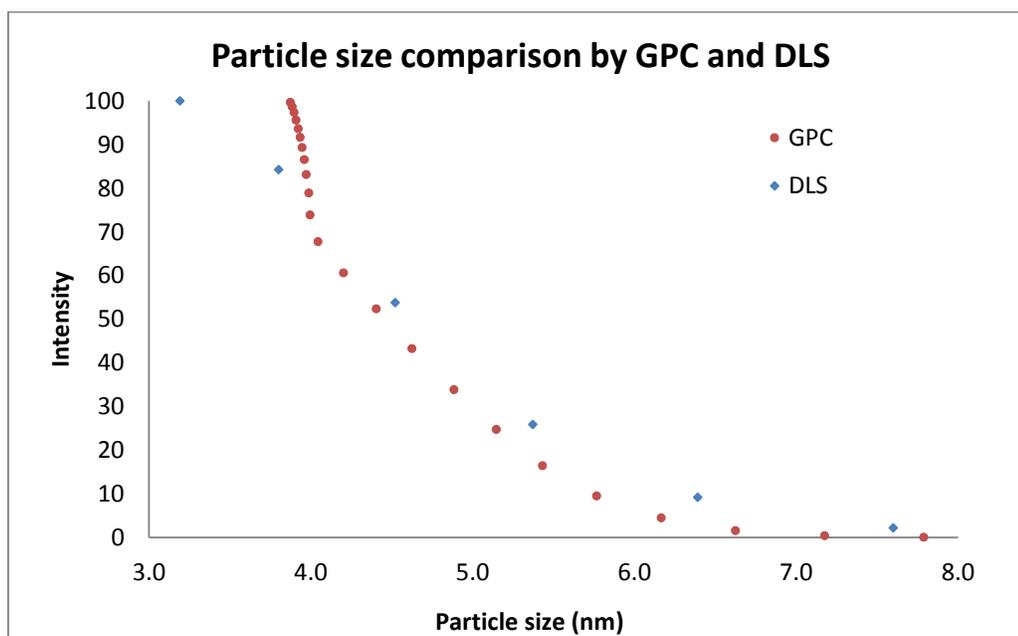
Figure 1. Particle size comparison on EA-AA CUP by GPC and DLS

3.3. FREEZE THAW STABILITY OF PAINT

Figure 2. Control and CUP modified paint formulation after 1st freeze thaw cycle

Table 6. Freeze Thaw Stability (KU Viscosity)

	Initial	FT Cycle 1	FT Cycle 2	FT Cycle 3	FT Cycle 4	FT Cycle 5
w/o CUP	67	Failed	-	-	-	-
20 LBS	60	62	65	86	115	-
30 LBS	58	58	58	58	60	60
40 LBS	58	58	58	58	58	58

The evaluation of CUPs as an additive to prevent freeze thaw instability was studied by adding CUP solution to a freeze thaw unstable latex formulation and then evaluating the paint. The results are shown in Table 6. The control paint formulation without CUP,

along with paint formulations with different levels of EA-AA CUP, were subjected to freeze–thaw cycles according to ASTM 2243-95. The control paint formulation without CUP coagulated during first cycle resulting in a "cottage cheese-like" consistency as shown in Figure 2. With the addition of EA-AA CUP, the freeze–thaw stability was improved from 0 to 5 cycles. Different loading levels were evaluated to find a minimum usage level. The paint with the lowest level (20lbs) of CUP failed on the 2nd freeze–thaw cycle but did not coagulate. The viscosity of the paint with medium level (30lbs) remained stable up to 3rd freeze thaw cycle and increased by only 2 KU. The viscosity of the paint with the highest level (40lbs) remained stable through all 5 freeze–thaw cycles. It was observed that the higher loadings of EA-AA CUP make it possible to stop the viscosity increase during the freeze–thaw process.

The number of CUP particles around an individual latex particle can be statistically calculated to ~9800 CUP particles per latex particles assuming 70% packing density based on Kepler conjecture for hexagonal close packing. This number can be calculated by knowing the volume fractions, volume solids, and particles size and hence the volume of CUP and latex particle. The extra CUP particles, if available would fill the voids between the latex particles. For the coating with 40lbs CUP, there are approximately ~16,000 CUP particles present around each latex particle. Negatively charged CUP particles in paint repel each other and space the coating. As the water freezes the volume of free water decreases forcing the particles closer together and manning condensation starts to reduce the repulsive force but only to a limited extent. The CUP particles keep the latex particles from coming into contact through this spacing effect and the bound water layer which does not freeze. The number of CUP particles agree well with the required number based upon

the coverage and void occupied by the CUP particles to meet the Kepler conjecture spacing. It should be noted that at lower temperatures the CUP particle is a solid well below its glass transition state which means that it too cannot flow together and become aggregated. CUP particles can be put into contact, as in drying, without becoming irreversibly aggregated provided that the temperature is below the Tg and the carboxylates remain as the salt. P(MMA/MAA) copolymer CUP particles as the sodium or potassium salt have been dried and are freely dispersed when placed back in water.

3.4. WET EDGE RETENTION

Latex paints dry very quickly which often causes difficulty in final appearance of painted areas, especially paints formulated below 100g/L VOC where lower amounts of solvents are in the formulated latex paint. [165]

The evaluation of CUPs as an additive to improve wet edge retention was studied on the same paint formulations with and without CUP solution. The control paint formulation without CUP, along with paint formulations with different levels of EA-AA CUP were subjected to wet edge test according to ASTM D7488-11. A 3 mil draw down of control paint was carded on an AG-5390 Leneta card and stop watch was started. Immediately 7 consistent 'X' marks were made on the drawdown using the wide curved end of a paint brush. The paint brush was dipped into the control paint and excess paint was removed by lightly scraping both the sides of the brush across the top edge of the can to keep the brush wet. After every 2 minute interval, according to ASTM D7488-11, paint is brushed back and forth across the film for ten cycles. The paint formulations with different levels of EA-AA CUP were also tested as per the above-mentioned protocol. After drying the cards overnight horizontally, each panel was observed to determine the wet edge and open time.

The time at which the edge of the drawdown can no longer be worked into the body of the paint is referred to as the wet edge time, while the time at which the 'X' begins to show through the paint is deemed the open time. The results are shown in Table 7. [165]

Table 7. Wet edge retention and open time

	Wet edge (minutes)	Open time (minutes)
w/o CUP	4	6
20 LBS	6	8
30 LBS	6	8
40 LBS	8	10

The addition of CUP particles causes a direct and consistent effect on the wet edge behavior. Although the test method is subjective and of low resolution it does validate that CUP particles can control the interfacial loss of water.

After application of the test paint on the substrate, water starts evaporating. With loss of water at the edge of the paint film near the paint-air interface, the latex particles come closer and start coalescing. This process makes it difficult to rework after first few minutes of drying. With addition of the high boiling solvents evaporation can be delayed to achieve good wet edge retention and open time. The addition of the high boiling solvent increases the VOC of the coating. When the paint with the CUP additive is applied on the substrate, the water starts evaporating. At the initial stage of evaporation of the water, at the edge of the paint film near paint-air interface, the latex particles along with the CUP particle come closer together. The CUP nano particles with bound water on the surface act as spacers

between the latex particle and delay the process of coalescence. With smaller particle size and substantial amount of bound water of the CUPs compared to the latex particles, the gel point of paint film at the interface approaches at much lower solids content than regular paint increasing the viscosity. [161] The increase in the viscosity at interface reduces the water diffusion thus slowing evaporation. This keeps the latex particles within the drying paint layer separated for a larger time. Therefore at the beginning stage of the drying of the paint film, the addition of the CUPs in the paint formulation improves the wet edge retention and open time. With further loses of the bound water, the CUP particles change conformation from solid particle to random coil chain. The experimental CUP polymer has a low Tg, and therefore will have faster reptation diffusion rate, the more rapid diffusion rate aids theearly step of coalescence of the latex particles. The use of CUP technology can therefore substantially reduce the VOC of the paint formulation.

4. MECHANISM OF ACTION

4.1. VISCOMETRY AND KEPLERS CONJECTURE

In an earlier report, a CUP copolymer of methyl methacrylate-methacrylic acid was synthesized with molar ratio of 9:1 and a particle size 6.5 nm. [161] The Krieger-Dougherty equation was applied to zero-shear viscosity of CUP solution and the value of maximum packing volume fraction was determined.

$$\eta_r = [1 - \frac{\phi}{\phi_{max}}]^{-[\eta]\phi_{max}} \qquad \text{Equation (2)}$$

Here ϕ_{max} is the packing volume fraction where viscosity of suspension diverge and $[\eta]$ is the dimensionless intrinsic viscosity of suspension. The relative viscosities of the CUP solutions were measured by cone-and-plate rheometer and plotted against volume fractions, and it was found that the data fit with Krieger-Dougherty equation. The maximum packing volume fraction (ϕ_{max}) was calculated to be 0.3940 and $[\eta]$ was 14.1. The value of ϕ_{max}=0.3940 was very low compared with other reported maximum packing volume fractions [166], which can be explained by the possibility of a large amount of bound or surface water on the CUP particles. Assuming the CUPs are spherical and the surface water forms a homogeneous layer on the spherical CUP particle and the CUP particles, along with surface water, reach random close packing when the actual volume fraction of CUP is 0.394. The thickness of water layer was found to be 0.57 nm and the density of surface water calculated to 1.0688g/ml at 25^OC. The water on the surface of the CUP particles was more compact than the bulk water and as diameter of one water molecule is 0.28nm, and then there will be 2 layers of surface water surround CUP particles. With data analysis, for the CUP with diameter of 6.6, the additional volume fraction was calculated to ~61% of the volume of CUP particle. For common latex

particles, if we assume the same thickness of surface water, for diameter of 300 nm, the ratio of surface water to latex was only 1.14%. [161] It should be noted that the same approach applied to a urethane, 25nm particle and a 77 nm latex produce "Gel point" of about 0.55 and 0.60 respectively [161]

During the freezing process the latex surface water offer very little nonfreezing water and the resultant ice crystals can force the particle together. If there was CUP particles, these can produce a buffer area of nonfreezing water which fills the voids between polymer particles and creates a protective layer around the latex.

If we assume 0.57 nm thick layer of water around both the latex and CUP particles. The Encor 379G has diameter of 300nm. The number of 4.12 nm CUP particles with surface water and assuming a packing density of approximately based upon the Kepler conjecture, it would require ~9,800 CUP particles to cover the latex surface. The finding of ~16,000 particles per latex is the highest CUP concentration used is only a modest amount above this and probably the excess most likely fills much of the voids between the latex particles.

4.2. T1 NMR EXPERIMENTS

The surface water of CUPs has been further investigated by T1 NMR experiments. [162] Surface and bulk water in the CUP system was investigated by spin-lattice relaxation measurements as function of CUP concentration. The water associated with CUP surface is termed as the bound water or the surface water with the remaining being bulk water. The properties of the bound water which differs from bulk water are lower vapor pressure, lower mobility, higher density (1.0688 gm/cc)*, and lower freezing point compare to bulk water.

The bound water is composed of a number of regions of lower molecular mobility compare to the mobility of bulk water and hence nuclear magnetic relaxation time is much faster than that of the bulk water. If we assume, two phase model for relaxation of total water in the CUP solution:

$$\frac{1}{T_1} = \frac{\eta}{T_{1b}} + \frac{1-\eta}{T_{1f}}$$ Equation (3)

Where, η is fraction of bound water, T_{1b} (relaxation rate of bound water) which is lower than T_{1f} (relaxation rate of free water). Shorter T_1 value of CUP solution than that of pure water indicates better structuring and partial immobilization of bound water molecules near surface of CUP.

By fitting the T1 values from the experiment to the model equations, bound water fraction and hence bound water layer thickness were calculated. The bound water layer thickness decreases with increasing concentration at constant temperature. For 111K MMA-MAA polymer at 5.30%-15.0% concentration the bound water layer thickness was found to be 0.67 for the lower concentration and 0.55nm for the higher concentration respectively, indicating approximately two water layers on the surface of CUP particle. These finding were in good agreement with the result calculated by viscometry and also illustrate Manning condensation of the charges as the concentration increases as shown by Chen in the rheology. [167]

4.3. DSC

The surface and free water content of CUP depends on both kinetics and thermodynamics parameters. At the surface, the most polar, hydrophilic carboxylates are hydrated first by water, which is called 'primary bound water'. Hydrophobic chains near the surface, which interacts with water through hydrophobic interaction are called

'secondary bound water' molecules. Together, primary and secondary water is called the total bound water, [169] the remaining water in solution is termed as 'free water' or 'bulk water'.

Water in a CUP solution may be present in three states. i) The non-freezable bound water (primary bound water) adsorbed on polymer surface which does not crystallize even when sample is cooled down to −100°C ii) the freezable bound water (secondary bound water) crystallizes at a temperature lower than 0°C, typically about -40°C or less and iii) the free water crystallizes at about 0°C. [169-170]

Differential scanning calorimetry (DSC) measurements were used in an earlier study to quantify the amount of freezable and non-freezable water in CUP solutions by measuring the heat of fusion of melting endotherms of water, which yields the amount of free water in CUP solution. [161] Total freezable bound water was obtained by subtracting calculated free water from total water content measured by % solids method ASTM D1259.

Surface water layer thickness can be calculated from volume of freezing water by knowing weight fraction of non-freezing water, density of non-freezing water (1.0688 g/cc), and surface area of CUP particles calculated by knowing average particle size. Surface water layer thicknesses for 111K polymer at various concentrations were found to give between 1.58nm for the high concentration and 0.83nm for the dilute concentration thick bound water layer did not freeze. The water layer is highly influenced by Manning condensation at the higher concentration.

It is obvious from the data that more water is "non-freezable" than the NMR or viscometry experiments show. This observation was not unexpected since each method

measures a different aspect of the water-CUP interface. Although the outer layers of water may not form ice, they may relax in the NMR and have mobility closer to that of free water in the absence of ice. The formation of an ice interface also will contribute to this "surface water" not freezing. It is this non-freezing water which helps prevent the latex particles from being forced into intimate contact and irreversibly gelling. Based upon this finding the amount of non-freezing water is obviously larger than with the rheological and NMR estimates.

The bound or surface water creates a gel structure as it dries. This gel structure restricts the diffusion of water and this slows its evaporation. It also prevents the coalescence of the latex resin until enough water is lost. The enhanced wet edge retention is clearly anticipated by this.

Both freeze thaw stability and wet edge retention will be highly dependent upon the charges on the surface and the particle size of CUP. As the number of charges increases or size decreases, the volume fraction water layer will increase. Thus these systems are highly tunable. The molecular weight should however be kept reasonably high to ensure adequate tensile strength in the final coating since the coating performance is the ultimate goal.

5. CONCLUSIONS

Colloidal unimolecular polymer particle based resins were found to make latex paint freeze thaw stable and enhance wet edge retention. The surface water surrounding these nano particles was found to control this behavior. The surface water does not freeze and helps keep the latex particles separated. The CUP particle act as spacers between the latex particles and also exhibits a gel point at a much lower solids content than latex which improves the wet edge retention and open time of the paint. This approach is zero VOC and should be able to be implemented cost effectively. This technology should be compatible with many different resin systems and easily adapted to improve other characteristics.

SECTION

2. SUMMARY

The CUPs are formed by the effect of hydrophilic/hydrophobic interactions of the polymer with a change in the solvent environment around them. During water reduction the CUP particles are formed at critical solvent environment when the polymer - polymer interaction is greater than the polymer - solvent interaction and is entropically favored by release of the water analogously to form micelle with hydrophilic charged groups on the surface and the hydrophobic groups collapse to form sphere-like core. These particles are stabilized by the charge repulsion of hydrophilic charged groups on the surface and are thermodynamically stable. The CUP suspensions contain only the charged CUP particles, water and counterions and are surfactant free. Therefore CUPs can find its application area in coating, drug delivery, catalyst matrix, etc.

Having all the functionality on the surface for further chemistry, application of the EA-AAZ CUP technology was found to be the new approach to crosslink the epoxy coatings. The formed coatings had properties comparable with the control crosslinker contributing to decreasing VOC emissions, making these coatings environment friendly.

With small particle size CUPs have a large amount of surface area with large amount of non-freezable surface water, which makes CUPs a candidate as freeze thaw stabilizer and an additive for wet edge retention for architectural latex paints. Partial replacement of latex resin with CUP suspension was found to be useful approach to make latex paint freeze thaw stable and enhance the wet edge retention without using glycol in the latex paint formulation. The CUP particle act as spacers between the latex particles and the non-freezing surface water surrounding these nano particles aids to improve freeze thaw

stability. During drying of latex paint, the CUP particle acts as spacers between the latex particles. With smaller particle size, the gel point of CUPs approaches at a much lower solids content. This helps in increasing in the viscosity of drying latex paint and reduces the further diffusion of water at interface, which helps improving the wet edge retention and open time of the paint.

REFERENCES

1.   Hassan H. Rmaile, Structure-property Relationships in the Design, Assembly and Applications of Polyelectrolyte Multilayer Thin Films, Thesis, pp 1 (2004).

2.   Lowe, Andrew B., McCormick, Charles L., "Stimuli responsive water-sol. and amphiphilic (co)polymers," ACS Symposium Series 780 pp 1-13 (2001).

3.   Morishima, Yotaro. Amphiphilic polyelectrolytes: characterization of associative properties and self-assembled nanostructures in water, ACS Symposium Series 937, pp 19-46 (2006).

4.   Llamas, Sara, Guzman, Eduardo, Ortega, Francisco, Baghdadli, Nawel, Cazeneuve, Colette, Rubio, Ramon G., Luengo, Gustavo S. "Adsorption of polyelectrolytes and polyelectrolytes-surfactant mixtures at surfaces: a physico-chemical approach to a cosmetic challenge," Adv. Colloid Interface Sci. (2014) In press.

5.   Vlachy, Nina, Touraud, Didier, Kogej, Ksenija, Kunz, Werner. "Solubilization of methacrylic acid based polymers by surfactants in acidic solutions," J. Colloid Interface Sci., Vol. 315, No.2, pp 445-455 (2007).

6.   Nichifor, Marieta, Stanciu, Magdalena Cristina, Simionescu, Bogdan C. "New cationic hydrophilic and amphiphilic polysaccharides synthesized by one pot procedure," Carbohydr. Polym., Vol. 82, No.3, pp 965-975 (2010).

7.   Kakran, Mitali, Antipina, Maria N. "Emulsion-based techniques for encapsulation in biomedicine, food and personal care," Current Opinion in Pharmacology, Vol 18, pp 47-55 (2014).

8.   Nichifor, Marieta, Stanciu, Magdalena Cristina, Ghimici, Luminita, Simionescu, Bogdan C. "Hydrodynamic properties of some cationic amphiphilic polysaccharides in dilute and semi-dilute aqueous solutions," Carbohydr. Polym., Vol. 83 No.4, pp 1887-1894 (2011).

9.   Cheng, Woei-Ping, Thompson, Colin, Ryan, Sinead M., Aguirre, Tanira, Tetley, Laurence, Brayden, David J. "In vitro and in vivo characterization of a novel peptide delivery system: Amphiphilic polyelectrolyte-salmon calcitonin nanocomplexes," J. Controlled Release, Vol. 147 No. 2, pp 289-297 (2010).

10. Zou, Liqiang, Peng, Shengfeng, Liu, Wei, Chen, Xing, Liu, Chengmei. "A novel delivery system dextran sulfate coated amphiphilic chitosan derivatives-based nanoliposome: Capacity to improve in vitro digestion stability of (-)-epigallocatechin gallate," Food Research International, Vol.69, pp 114-120 (2015).

11. Di Martino Antonio, Sedlarik Vladimir, "Amphiphilic chitosan-grafted-functionalized polylactic acid based nanoparticles as a delivery system for doxorubicin and temozolomide co-therapy," Int. J. Pharm., Vol 474, No.1-2, pp 134-145 (2014).

12. York, Adam W., Kirkland, Stacey E., McCormick, Charles L. "Advances in the synthesis of amphiphilic block copolymers via RAFT polymerization: Stimuli-responsive drug and gene delivery," Advanced Drug Delivery Reviews, Vol. 60, No.9, pp 1018-1036 (2008).

13. Cammas, Sandrine, Bear, Marie-Maud, Moine, Laurence, Escalup, Raphaele, Ponchel, Gilles, Kataoka, Kazunori, Guerin, Philippe. "Polymers of malic acid and 3-alkylmalic acid as synthetic PHAs in the design of biocompatible hydrolyzable devices," Int. J. Biol. Macromol., Vol. 25, No. 1-3, pp 273-282 (1999).

14. Alexander, Amit, Ajazuddin, Khan, Junaid, Saraf, Swarnlata, Saraf, Shailendra. "Polyethylene glycol (PEG)-Poly(N-isopropylacrylamide) (PNIPAAm) based thermosensitive injectable hydrogels for biomedical applications," European Journal of Pharmaceutics and Biopharmaceutics, Vol 88, No.3, pp 575-585 (2014).

15. Tian, Huayu, Tang, Zhaohui, Zhuang, Xiuli, Chen, Xuesi, Jing, Xiabin. " Biodegradable synthetic polymers: Preparation, functionalization and biomedical application," Prog. Polym. Sci., Vol. 37, No.2, pp 237-280 (2012).

16. Berger, J., Reist, M., Mayer, J. M., Felt, O., Gurny, R. "Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications," European Journal of Pharmaceutics and Biopharmaceutics, Vol.57, No.1, pp 35-52 (2004).

17. Yu, Haihu, Cao, Tong, Zhou, Lingde, Gu, Erdan, Yu, Dingshan, Jiang, Desheng. "Layer-by-Layer assembly and humidity sensitive behavior of poly(ethyleneimine)/multiwall carbon nanotube composite films," Sensors and Actuators, B: Chemical, Vol. 119, No.2, pp 512-515 (2006).

18. Baumgart, Tobias, Offenhausser, Andreas. "Lateral diffusion in substrate-supported lipid monolayers as a function of ambient relative humidity," Biophys. J., Vol.83, No.3, pp 1489-1500 (2002).

19. Meskath, Stephan, Urban, Gerald, Heinze, Jurgen. "Nanophase separated amphiphilic polymer co-networks as efficient matrices for optical sensors: Rapid and sensitive detection of NO_2," Sensors and Actuators, B: Chemical, Vol. 186, pp 367-373 (2013).

20. Martinez, A., Gonzalez, C., Porras, M., Gutierrez, J. M. "Nano-sized latex particles obtained by emulsion polymerization using an amphiphilic block copolymer as surfactant," Colloids Surf., A Vol. 270-271, pp 67-71 (2005).

21. Yang, Zhen, Shang, Yabo, Huang, Xin, Chen, Yichun, Lu, Yaobo, Chen, Aimin, Jiang, Yuxiang, Gu, Wei, Qian, Xiaozhi, Yang, Hu, et al. "Cationic content effects of biodegradable amphoteric chitosan-based flocculants on the flocculation properties," Journal of Environmental Sciences (Beijing, China), Vol. 24, No.8, pp 1378-1385 (2012).

22. Yang, Zhen, Wu, Hu, Yuan, Bo, Huang, Mu, Yang, Hu, Li, Aimin, Bai, Junfeng, Cheng, Rongshi. "Synthesis of amphoteric starch-based grafting flocculants for flocculation of both positively and negatively charged colloidal contaminants from water," Chem. Eng. J., Vol. 244, pp 209-217 (2014).

23. Yang, Zhen, Shang, Yabo, Lu, Yaobo, Chen, Yichun, Huang, Xin, Chen, Aimin, Jiang, Yuxiang, Gu, Wei, Qian, Xiaozhi, Yang, Hu, et al. "Flocculation properties of biodegradable amphoteric chitosan-based flocculants," Chem. Eng. J., Vol. 172, No.1, pp 287-295 (2011).

24. Zhang, Bingbing, Su, Haiquan, Gu, Xiaojun, Huang, Xiaoling, Wang, Huimin. "Effect of structure and charge of polysaccharide flocculants on their flocculation performance for bentonite suspensions," Colloids Surf., A, Vol. 436, pp 443-449 (2013).

25. Gosselet, Noelle Martine, Naranjo, Horacio, Renard, Estelle, Amiel, Catherine, Sebille, Bernard. "Association of poly-N-[tris(hydroxymethyl)methyl] acrylamide with a water soluble β-cyclodextrin polymer," Eur. Polym. J., Vol.38, No.4, pp 649-654 (2002).

26. Kastner, U. "The impact of rheological modifiers on water-borne coatings," Colloids Surf., A, Vol. 183-185, pp 805-821 (2001).

27. Karlson, L., Joabsson, F., Thuresson, K. "Phase behavior and rheology in water and in model paint formulations thickened with HM-EHEC: influence of the chemical structure and the distribution of hydrophobic tails," Carbohydr. Polym., Vol.41, no.1, pp 25-35 (1999).

28. K.C. Taylor, H.A. Nasr-El-Din. Chapter 24 – Rheology of water-soluble polymers used for improved oil recovery, Edited by Nicholas P Cheremisinoff. Advances in Engineering Fluid Mechanics Series: Advances in Engineering Fluid Mechanics: Multiphase Reactor and Polymerization System Hydrodynamics, Gulf Publishing Company, Houston, Texas pp 615–668 (1996).

29. Kato, Satoshi, Sato, Kazuhiro, Maeda, Daiharu, Nomura, Mamoru. "A kinetic investigation of styrene emulsion polymerization with surface active polyelectrolytes as the emulsifier. II: effects of molecular weight and composition," Colloids Surf., A, Vol. 153, no.1-3, pp 127-131, (1999).

30. Yan, Xiuhua, Xu, Wei, Rong, Sao, Tang, Lanqing, Ji, Yongxin. "Synthesis of polymerizable quaternary ammonium emulsifier and properties of its fiber crosslinking emulsion," Colloids Surf., A, Vol.443, pp 60-65 (2014).

31. Morishima, Yotaro, Nomura, Shigeki, Ikeda, Takahiro, Seki, Michiko, Kamachi, Mikiharu. "Characterization of Unimolecular Micelles of Random Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate and methacrylamides bearing bulky hydrophobic substituents," Macromolecules, Vol.28, No.8, pp 2874-81 (1995).

32. Chen, Minghan, Van De Mark, Michael R. "Rheology studies on colloidal unimolecular polymer (CUP) particles in absence and presence of NaCl," Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, POLY-21 (2011).

33. Van De Mark, Michael R., Chen, Minghang, Norman, Spencer G. "Surface tension of colloidal unimolecular polymer particles at air/water interface," Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium, 40th pp 292-301 (2013).

34. Chen, Minghang, Riddles, Cynthia, Van De Mark, Michael. "Gel point behavior of colloidal unimolecular polymer (CUP) particles," Colloid. Polym. Sci., Vol.291, No.12, pp 2893-2901 (2013).

35. Chen, Minghang, Riddles, Cynthia J., Van De Mark, Michael R. "Electroviscous Contribution to the Rheology of Colloidal Unimolecular Polymer (CUP) Particles in Water," Langmuir, Vol. 29, No.46, pp 14034-14043 (2013).

36. Natu, Ameya, Wiggins, Marcus, Chen, Minghang, Van De Mark, Michael R. "Electrokinetic, rheology, and surface tension behavior of colloidal unimolecular polymer (CUP) particles," Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, POLY-286 (2013).

37. Van De Mark, Michael, Dawib, Yousef, Gerald, Rex, II, May, Dave. "Surface and bulk water in colloidal unimolecular polymer (CUP) systems investigated by spin-lattice (T1) relaxation measurements," Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, POLY-625 (2014).

38. Riddles, Cynthia J., Zhao, Wei, Hu, Hua-Jung, Chen, Minghang, Van De Mark, Michael R. "Self-assembly of water insoluble polymers into Colloidal Unimolecular Polymer (CUP) particles of 3-9 nm," Polymer, Vol. 55, No.1, pp 48-57 (2014).

39. Van De Mark, Michael R., Natu, Ameya M., Gade, Sagar V., Chen, Minghang, Hancock, Catherine, Riddles, Cynthia. "Molecular weight (MN) and functionality effects on CUP formation and stability," 40th Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, LA, p 332-347 (2013).

40. Natu, Ameya, Wiggins, Marcus, Chen, Minghang, Van De Mark, Michael R. "Electrokinetic, rheology, and surface tension behavior of colloidal unimolecular polymer (CUP) particles," Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, POLY-286 (2013).

41. Natu, Ameya, Wiggins, Marcus, Van De Mark, Michael R. "Synthesis and characterization of cationic colloidal unimolecular polymer (CUP) particles based on a random copolymer of MMA and MADQUAT," 48th Midwest Regional Meeting of the American Chemical Society, Springfield, MO, United States, MWRM-25 (2013).

42. Behave, Mandar R., Hancock, Catherine E., Van De Mark, Michael R. "Near zero VOC low viscosity colloidal unimolecular polymer (CUP) epoxy hardener," PMSE Preprints (2011).

43. Gade, Sagar V., Hancock, Catherine, Van De Mark, Michael R. "Synthesis of amine functional colloidal unimolecular polymer (CUP) particles and their use as cross-linker for epoxy coatings," Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, POLY-330 (2013).

44. Mistry, Jigar K., Van De Mark, Michael R. "Aziridine cure of acrylic colloidal unimolecular polymers (CUPs)," J. Coat. Technol., Vol. 10, No.4, pp 453-463 (2013).

45. Geng, Peng, Van De Mark, Michael R. "DSC evaluation of free and surface water for colloidal unimolecular polymer (CUP) particles utilizing the heat of fusion,".49th Midwest Regional Meeting of the American Chemical Society, Columbia, MO, United States, MWRM-95 (2014).

46. Dawib, Yousef, Gerald, Rex E., II., Van De Mark, Michael R. "Isotope effect of deuterium on colloidal unimolecular polymer (CUP) surface and free water by T1," 49th Midwest Regional Meeting of the American Chemical Society, Columbia, MO, United States, MWRM-94 (2014).

47. Van De Mark, Michael, Dawib, Yousef, Gerald, Rex, II, May, Dave. "Surface and bulk water in colloidal unimolecular polymer (CUP) systems investigated by spin-lattice (T1) relaxation measurements," Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, POLY-625 (2014).

48. Code of Federal Regulations, 40: Chapter 1, Subchapter C, Part 51, Subpart F, 51100. http://cfr.vlex.com/vid/19784887 accessed March 15, 2015.

49. http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32004L0042 accessed March 15, 2015.

50.   Zong, Zhengang, Wall, Sarah, Li, Yi-Zhong, Ruiz, Jose, Adam, Herve, Badre, Chantal, Trezzi, Fabio. "New additives to offer freeze-thaw stability and increase open time of low/zero VOC latex paints," Prog. Org. Coat. Vol.72, No.1-2, pp 115-119 (2011).

51.   D.C. Blackley, Polymer Lattices: Science and Technology, vol. 1, 2nd ed., Chapman & Hall USA, New York (1997).

52.   S.F. Bosen, W.A. Bowles, E.A. Ford, B.D. Person, Antifreezes, Ullmann's encyclopedia of Industrial Chemistry, vol. A3, 5th ed., VCH Verlagsgesellschaft, Weinheim, (1985).

53.   Zhao, Cheng-Le, Cunningham, Terri A., Zhuo, Li, "Low-VOC aqueous coating compositions with excellent freeze-thaw stability and coating preparation," US Patent 2003022917 (2003).

54.   Farwaha, Rajeev, Currie, William, "Thermoplastic, aqueous latex paints having improved wet adhesion and freeze-thaw stability," US Patent 5399617A (1995).

55.   Farwaha, Rajeev, Phan, Lien, Currie, William, "Latex paints which are free of volatile coalescents and freeze-thaw additives," US Patent 5610225A (1997).

56.   Zhao, Cheng-Le, Cunningham, Terri A., Zhuo, Li, "Low-VOC aqueous coating compositions with excellent freeze-thaw stability and coating preparation," US Patent 20030229171A (2003).

57.   Richard J. Farn, Chemistry and Technology of Surfactants, Blackwell Publishing Ltd. Oxford, UK, (2006).

58.   Okubo, Masayoshi, Sakaguchi, Shinya, Takamatsu, Atsushi, Sasaki, Hiroharu, Tsuneta, Kazyoshi, "Containing particles obtained by emulsion polymerization as a binder, having an outermost phase formed of an unsaturated (poly)oxyalkylene glycol monomer, inner phase of unsaturated monomer, low temperature film forming, water resistance," US Patent 6410655 B2 (2002).

59.   Butler, Lauren N., Fellows, Christopher M., Gilbert, Robert G., "Effect of surfactants used for binder synthesis on the properties of latex paints," Progress in Organic Coatings, Vol. 53, No.2, pp 112-118 (2005).

60.   Zong, Zhengang, Wall, Sarah, Li, Yi-Zhong, Ruiz, Jose, Adam, Herve, Badre, Chantal, Trezzi, Fabio, "New additives to offer freeze-thaw stability and increase open time of low/zero VOC latex paints," Progress in Organic Coatings, Vol.72, No.1-2, pp 115-119 (2011).

61.   Rodriguez, C, Weathers, J, Corujo, B, Peterson, P, "Formulating water-based systems with propylene-oxide-based glycol ethers," Journal of Coating Technology, Vol. 72, No.6, pp 67-72 (2000).

62. A.E. Fischer, R.N. Washburn, J. Oil Col. Chem. Assoc. 53 (1970) 578–591, also presented at the Manchester Section Symposium on 24 September 1969.

63. Rohm & Haas Company, "A process for the preparation of water paints," NL Patent 6511518 (1966).

64. A.J. Reuvers, "Control of rheology of water-borne paints using associative thickeners," Proceedings of the International Conference on Organic Coating: Water-borne, High Solids, Powder Coating, 24th ed., New Paltz, NY (1998).

65. Hwa, J, "Mechanism of film formation from latices. Phenomenon of flocculation," Journal of Polymer Science Part A., Vol. 2, No.2, pp 785 (1964).

66. Deegan, R, Bakajin, O, Dupont, T, Huber, G, Nagel, S, Witten, T, "Contact line deposits in an evaporating drop," Physical Review E, Vol. 62, pp 756–765 (2000).

67. Winnik, M, Feng, J, "Latex Blends: An Approach to Zero VOC Coatings," Journal of Coatings Technology, Vol. 68, pp 39–50 (1996).

68. Ma, Yue, Davis, H. T., Scriven, L. E., "Microstructure development in drying latex coatings," Progress in Organic Coatings, Vol.52, No.1, pp 46-62 (2005).

69. Zong, Zhengang, Wall, Sarah, Li, Yi-Zhong, Ruiz, Jose, Adam, Herve, Badre, Chantal, Trezzi, Fabio, "New additives to offer freeze-thaw stability and increase open time of low/zero VOC latex paints," Progress in Organic Coatings, Vol.72, No.1-2, pp 115-119 (2011).

70. Cooke, P, Delatycki, O, Kershaw, R, Sang, W, "The brushing characteristics of latex paints," J. Oil Col. Chem. Assoc., Vol.55, pp 275–284 (1972).

71. M.J. Collins, J.W. Taylor, R.A. Martin, "Zero and near-zero VOC interior glossy architectural coatings," Proceedings of the 213th ACS National Meeting, San Francisco, (1997).

72. Storfer, S, DiPiazza, J, Moran, R, "Isoparaffins impart beneficial properties to coatings," Journal of Coatings Technology, Vol. 60, No.761, pp 37–43 (1988).

73. Andrews, M, "Influence of ethylene and propylene glycols on drying characteristics of latex paints," Journal of paint technology, Vol.46, No.598, pp 40-48 (1974).

74. Croll, S, "Drying of latex paint," Journal of paint technology, Vol. 58, No. 734, pp 41-49 (1986).

75. Sullivan, D, "Water and solvent evaporation from latex and latex paint films," Journal of paint technology, Vol. 47, no. 610, pp 60-67 (1975).

76.   M.A. Winnick, J. Feng, "Latex blends: an approach to zero VOC coatings," Journal of paint technology, Vol. 68, no. 852, pp 39-50 (1996).

77.   Adamson, L, Merritt, R, Nkansah, A, Lee, J, "Method for extending the open time of an aqueous coating composition," US Patent 5270380A (1993).

78.   Luebke, Gary, Benton, Kenneth Curtis, Letuchy, Yakov, "Starch graft copolymers and their preparation," PCT Int. Appl. WO 9909251 A1 (1999).

79.   Farwaha, Rajeev, Currie, William D., Humphreys, Robert W., Thomaides, John S., "Latex binders and coatings containing polymers derived from polymerizable saccharide monomers, freeze-thaw stable, even in the total absence of a volatile freeze-thaw additive," US Patent 5719244 A (1998).

80.   Taylor, Philip Louis, Gosling, Julian John, Bromley, Charles William Alfred, Nicks, Peter Francis, "Water-based autoxidizable coating composition containing partial ester of carboxylic acid film former," Eur. Pat. Appl. EP 425085 A1 (1991).

81.   Sperry, Peter R., Chung, Chao-Jen, "Aqueous polymer compositions containing surface-active evaporation suppressants," US Patent 4647610 (1987).

82.   McCreight, Kevin W., Stockl, Rebecca, Testa, Carlo, Seo, Kab Sik, "Development of low VOC additives to extend the wet edge and open time of aqueous coatings," Progress in Organic Coatings, Vol. 72, No.1-2, pp 102-108 (2011).

83.   ASTM Standard D7488 - 11, 2010, "Standard Test Method for Open Time of Latex Paints," ASTM International, West Conshohocken, PA, 2010, DOI: 10.1520/D7488–11, www.astm.org (Accessed on 11/18/14).

84.   G. Monaghan, JCT Coat.Vol.4, No.10, pp.30. (2007).

85.   J. Akkerman, M. Bosma, A. Berry, F. Fallani, R. Adolphs, D. Mestach, Surf. Coat. Aus. Vol.47, No.1/2, pp 13 (2010).

86.   R. Hill, "Resinous polymerization products," US 2121695 (1938).

87.   M. Okada, "Chemical syntheses of biodegradable polymers," Prog. Polym. Sci., Vol. 27, No.1, pp 87-133 (2002).

88.   W.J. Van Westrenen, J.R. Weber, G. Smith, C.A. May, F.A.T.I.P.E.C. Congr., Vol.8, pp 126-36 (1966).

89.   M. Gerlitz, "Water-thinned two-component epoxy paints for heavy corrosion prevention," Ochrona przed Korozja, Vol.47, No.9, pp 234-238 (2004).

90.   T.P. Takas, B.A. Naderhoff, "The chemistry and properties of unique curing agents in two-component waterborne epoxy coatings," 22nd Proc. of the Waterborne, High-Solids, and Powder Coatings Symposium, pp 110-118 (1995).

91. S. Kojima, T. Moriga, H. Gotoh, "Development of high performance, water-borne coatings for can coating application," 20th Proc. of the Waterborne, High-Solids, and Powder Coatings Symposium, pp 146-51 (1993).

92. F.H. Walker, O. Shaffer, "Film formation and morphology in two-component, ambient cured, waterborne epoxy coatings," ACS Symposium Series, Vol. 648, pp 403-417 (1996).

93. L. Qian, "Study on fast drying two-component water borne epoxy resin coating," Tuliao Gongye, Vol. 29, No.11, pp 30-32 (1999).

94. J. Liu, S. Liu, "Preparation of two-package water-borne epoxy anticorrosion coatings," Zhongguo Tuliao, Vol. 24, No.9, pp 44-46 (2009).

95. M. Rufo, D. Shah, W. Raymond, F.H. Walker, M. Lohe, A. Klippstein, M. Cook, "2K Waterborne Epoxy Systems: Technology Overview and New Developments," Air Products and Chemicals, Inc. http://www.airproducts.com/~/media/Files/PDF/industries/paints-coatings-2k-waterborne-epoxy-systems-technology-overview.pdf. (Accessed 9 May 2015).

96. Van De Mark, Michael R., Natu, Ameya M., Gade, Sagar V., Chen, Minghang, Hancock, Catherine, Riddles, Cynthia. "Molecular weight (MN) and functionality effects on CUP formation and stability," J. Coating Technol., Vol.11, No.2, pp 111-122 (2013).

97. Riddles, Cynthia J., Zhao, Wei, Hu, Hua-Jung, Chen, Minghang, Van De Mark, Michael R. "Self-assembly of water insoluble polymers into Colloidal Unimolecular Polymer (CUP) particles of 3-9 nm," Polymer, Vol. 55, No.1, pp 48-57 (2014).

98. Van De Mark, Michael R., Natu, Ameya M., Gade, Sagar V., Chen, Minghang, Hancock, Catherine, Riddles, Cynthia. "Molecular weight (MN) and functionality effects on CUP formation and stability," 40th Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, LA, p 332-347 (2013).

99. Natu, Ameya, Wiggins, Marcus, Chen, Minghang, Van De Mark, Michael R. "Electrokinetic, rheology, and surface tension behavior of colloidal unimolecular polymer (CUP) particles," Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, POLY-286.

100. Natu, Ameya, Wiggins, Marcus, Van De Mark, Michael R. "Synthesis and characterization of cationic colloidal unimolecular polymer (CUP) particles based on a random copolymer of MMA and MADQUAT," 48th Midwest Regional Meeting of the American Chemical Society, Springfield, MO, United States, MWRM-25 (2013).

101.   M.R. Behave, C.E. Hancock, M.R. Van De Mark, "Near zero VOC low viscosity colloidal unimolecular polymer (CUP) epoxy hardener," PMSE Preprints (2011).

102.   Gade, Sagar V., Hancock, Catherine, Van De Mark, Michael R. "Synthesis of amine functional colloidal unimolecular polymer (CUP) particles and their use as cross-linker for epoxy coatings," Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, POLY-330 (2013).

103.   Mistry, Jigar K., Van De Mark, Michael R. "Aziridine cure of acrylic colloidal unimolecular polymers (CUPs)," J. Coat. Technol., Vol. 10, No.4, pp 453-463 (2013).

104.   Chen, Minghan, Van De Mark, Michael R. "Rheology studies on colloidal unimolecular polymer (CUP) particles in absence and presence of NaCl," Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, POLY-21 (2011).

105.   Van De Mark, Michael R., Chen, Minghang, Norman, Spencer G. "Surface tension of colloidal unimolecular polymer particles at air/water interface," Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium, 40th pp 292-301 (2013).

106.   Chen, Minghang, Riddles, Cynthia, Van De Mark, Michael. "Gel point behavior of colloidal unimolecular polymer (CUP) particles," Colloid. Polym. Sci., Vol.291, No.12, pp 2893-2901 (2013).

107.   Chen, Minghang, Riddles, Cynthia J., Van De Mark, Michael R. "Electroviscous Contribution to the Rheology of Colloidal Unimolecular Polymer (CUP) Particles in Water," Langmuir, Vol. 29, No.46, pp 14034-14043 (2013).

108.   Van De Mark, Michael, Dawib, Yousef, Gerald, Rex, II, May, Dave. "Surface and bulk water in colloidal unimolecular polymer (CUP) systems investigated by spin-lattice (T1) relaxation measurements," Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, POLY-625 (2014).

109.   S. Gabriel, "Ethylamine derivatives," Ber. Dtsch. Chem. Ges., Vol.21, pp 566-575 (1888).

110.   E.M. Mazzarella, J. Fertig, M. Skoultchi, "Process for preparing salts of aminoalkyl esters of carboxylic acid polymers," US Patent 3372149 A, (1968).

111.   H. Endres, R. Fikentscher, W. Maurer, E. Scharf, U. Soenksen, "Cross-linked polyamide-imine polymer for papermaking," US Patent 3642572 A, (1972).

112.   D.N. Roark, B.C. McKusick, U. Steuerle, Ullmann's Encyclopedia of Industrial Chemistry, Published Online: 15 JUN 2000, DOI: 10.1002/14356007.a03_239

113. Chen, Minghan, Van De Mark, Michael R. "Rheology studies on colloidal unimolecular polymer (CUP) particles in absence and presence of NaCl," Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, POLY-21 (2011).

114. R.R. Roeslera, K. Danielmeierb, "Tris-3-(1-aziridino)propionates and their use in formulated products," Prog.Org. Coat. Vol.50, No.1, pp 1-27 (2004).

115. https://www.hexion.com/Products/TechnicalDataSheet.aspx?id=4133 (Accessed on 04/04/2015).

116. https://www.hexion.com/Products/TechnicalDataSheet.aspx?id=2698 (Accessed on 04/04/2015).

117. R.A. Potyrailo, E.J. Amis, High-Throughput Analysis: A Tool for Combinatorial Materials Science, Kluwer Academic Publication, New York, (2003).

118. O. Dermer, Ethylenimine and other aziridines: Chemistry and Applications, Academic Press Inc. New York, (1969).

119. Brandrup, J., Immergut, E, Polymer Handbook, Edition 3, John Wiley and Sons, New York, (1989).

120. S. Paul, Surface Coatings, Science and Technology, 2nd ed., Wiley, New York, (1996).

121. E. Sharmin, L. Imo, S.M. Ashraf, S. Ahmad, "Acrylic-melamine modified DGEBA-epoxy coatings and their anticorrosive behavior," Prog. Org. Coat. Vol. 50, No.1, pp 47-54 (2004).

122. S.T. Eckersley, A. Rudin, "Mechanism of film formation from polymer latexes," J. Coat. Technol. Vol.62, No.780, pp 89-100 (1990).

123. D.P. Jensen, L.W. Morgan, "Particle size as it relates to the minimum film formation temperature of latexes," J. Appl. Polym. Sci. 42 2845-2849 (1991).

124. R. Sperry, B.S. Snyder, M.L. O'Dowd, P.M. Lesko, "Role of water in particle deformation and compaction in latex particle film formation," Langmuir Vol.10, 2619-2628 (1994).

125. K.P. Chong, M.R. VanLandingham, L. Sung, "Advances in Materials and Mechanics," Proc. International Conference on Advances in Building Technology, Hong Kong, China, (2002).

126. M.R. VanLandingham, N.K. Chang, C.C. White, S.H. Chang, "Viscoelastic Characterization of Polymers Using Instrumented Indentation-I. Quasi-static Testing," J. Polym. Sci. Pol. Phys. Vol.43, No.14, pp 1794–1811 (2005).

127. Vu, O. Laferte, "All layers count. Silica nanoparticles in the optimisation of scratch and abrasion resistance of high performance UV multi-layer coatings," European Coatings Journal, Vol. 6, pp 34-36 (2006).

128. Basen, S, Bowies, W, Person, B, "Antifreeze," In: Ullmann's 5th Edition, volume 43, pp.22-23, VCH Verlag, Weinheim, Germany (1985).

129. Blackly, D, Polymer Lattice – Science and Technology, 2nd Edition, volume 1. Chapman and Hall, London, UK (1997).

130. Ma, Y, "Microstructure development in drying latex coatings," Prog. Org. Coat., Vol. 52, No.1, pp 46–62 (2005).

131. Farwaha, R, Currie, W, "Thermoplastic, aqueous latex paints having improved wet adhesion and freeze-thaw stability," US Patent 5,399,617 A, (1995).

132. Farwaha, R, Phan, L, Currie, W, "Latex paints which are free of volatile coalescents and freeze-thaw additives," US Patent 5,610,225 A, (1997).

133. Scriven, L, Zhao, C, Porzio, S, Smith, A, Ge, H, Davis. H, "Direct observation of freeze-thaw instability of latex coatings via high pressure freezing and cryogenic SEM," J. Coating Technol., Vol. 3, No.2, pp 109-115 (2006).

134. Zhao, C, Cunningham, T, Zhuo, L, "Low-VOC aqueous coating compositions with excellent freeze-thaw stability," US Patent 6,933,415 B2, (2005).

135. Farn, R, Chemistry and Technology of Surfactants, Blackwell Publishing Ltd. Oxford, UK, (2006).

136. Okubo, M, Sakaguchi, S, Takamatsu, A, Sasaki, H, Tsuneta, K, "Containing particles obtained by emulsion polymerization as a binder, having an outermost phase formed of an unsaturated (poly)oxyalkylene glycol monomer, inner phase of unsaturated monomer; low temperature film forming, water resistance," US Patent 6,410,655 B2, (2002).

137. Zong, Z, Wall, S, Li, Y, Ruiz, J, Adam, H, Badre, C, Trezzi, F, "New additives to offer freeze–thaw stability and increase open time of low/zero VOC latex paints," Prog. Org. Coat., Vol.72, No.1–2, pp 115–119 (2011).

138. Butler, L, Fellows, C, Gilbert, R, "Effect of surfactants used for binder synthesis on the properties of latex paints," Prog. Org. Coat., Vol. 53, No.2, pp 112-118 (2005).

139. Rodriguez, C, Weathers, J, Corujo, B, Peterson, P, "Formulating water-based systems with propylene-oxide-based glycol ethers," J. Coating Technol., Vol.72, no.6, pp 67-72 (2000).

140. Overbeek, A, Bückmann, F, Martin, E, Steenwinkel, P, Annable, T, "New generation decorative paint technology." Prog. Org. Coat., Vol.48, No.2-4, pp 125-139 (2003).

141. Rohm & Haas Company, "A process for the preparation of water paints," NL Patent 6511518 (1966).

142. Reuvers, A, "Control of rheology of water-borne paints using associative thickeners," Prog. Org. Coat., Vol. 35, No.1-4, pp 171-181(2006).

143. Hwa, J, "Mechanism of film formation from latices. Phenomenon of flocculation," J. Polym. Sci. Part A. Vol.2, No.2, pp 785 (1964).

144. Deegan, R, Bakajin, O, Dupont, T, Huber, G, Nagel, S, Witten, T, "Contact line deposits in an evaporating drop," Phys. Rev. E, vol. 62, No.1, pp 756–765 (2000).

145. Winnik, M, Feng, J, "Latex Blends: An Approach to Zero VOC Coatings," J. Coating Technol., Vol.68, No.852, pp39-50 (1996).

146. Ma, Y, Davis,H, Scriven, L, "Microstructure development in drying latex coatings," Prog. Org. Coat., Vol.52, No.1, pp 46-62 (2005).

147. Zonga, Z, X Walla, S, Lia, Y, Ruiza, J, Adama, H, Badrea, C, Trezzib, F, "New additives to offer freeze–thaw stability and increase open time of low/zero VOC latex paints," Prog. Org. Coat., Vol.72, no.1-2, pp 115-119 (2011).

148. Cooke, P, Delatycki, O, Kershaw, R, Sang, W, "The brushing characteristics of latex paints," J. Oil Col. Chem. Assoc. Vol. 55, pp 275–284 (1972).

149. Collins, M, Taylor, J, Martin, R, "Zero and near-zero VOC interior glossy architectural coatings," Proc of the 213th ACS National Meeting, San Francisco, (1997).

150. Storfer, S, DiPiazza, J, Moran, R, "Isoparaffins impart beneficial properties to coatings," J. Coat. Technol. Vol. 60, No.761, pp 37–43 (1988).

151. Andrews, M, "Influence of ethylene and propylene glycols on drying characteristics of latex paints," J. Paint Technol., Vol. 46, No. 598, pp 40-48 (1974).

152. Croll, S, "Drying of latex paint," J. Coat. Technol. Vol.734, No.58, pp 41-49 (1986).

153. Sullivan, D, "Water and solvent evaporation from latex and latex paint films," J. Paint Technol. Vol.47, No.610, 60-67 (1975).

154. M.A. Winnick, J. Feng, J. Coat. Technol. Vol 68, No.852, pp 39 (1996).

155.   Adamson, L, Merritt, R, Nkansah, A, Lee, J, "Method for extending the open time of an aqueous coating composition" US Patent 5270380A, (1993).

156.   Luebke, G, Benton, K, Letuchy, Y, "Starch graft copolymers and their preparation," PCT Int. Appl. WO 9909251 A1, (1999).

157.   Farwaha, R, Currie, W, Humphreys, R, Thomaides, J, "Latex binders and coatings containing polymers derived from polymerizable saccharide monomers, freeze-thaw stable, even in the total absence of a volatile freeze-thaw additive," US Patent 5719244 A, 91998).

158.   Sperry, P, Chung, C, "Aqueous polymer compositions containing surface-active evaporation suppressants," US Patent 4647610 A, (1987).

159.   McCreight, K, Stockl, R, Testa, C, Seo, K, "Development of low VOC additives to extend the wet edge and open time of aqueous coatings," Prog. Org. Coat., Vol.72, no.1-2, pp 102-108 (2011).

160.   Geng, P, Van De Mark, M, "DSC evaluation of free and surface water for colloidal unimolecular polymer (CUP) particles utilizing the heat of fusion," 49th Midwest Regional Meeting of the American Chemical Society, Columbia, MO, United States, (2014).

161.   Chen, Minghang, Riddles, Cynthia, Van De Mark, Michael. "Gel point behavior of colloidal unimolecular polymer (CUP) particles," Colloid. Polym. Sci., Vol.291, No.12, pp 2893-2901 (2013).

162.   Dawib, Y, Gerald, R, Van De Mark, M, "Isotope effect of deuterium on colloidal unimolecular polymer (CUP) surface and free water by T1," Abstracts, 49th Midwest Regional Meeting of the American Chemical Society, Columbia, MO, United States, November 2014

163.   Angus   AM   http://www.dow.com/angus/prod/amp_prod.htm   (Accessed   on 11/18/14).

164.   Brandrup, J., Immergut, E, Polymer Handbook, Edition 3, John Wiley and Sons, New York (1989).

165.   ASTM Standard D7488 - 11, "Standard Test Method for Open Time of Latex Paints," ASTM International, West Conshohocken, PA, 2010, DOI: 10.1520/D7488–11, www.astm.org (2010).

166.   de Kruif, C, Van Iersel, E, Vrij, A, Russel, W, "Hard sphere colloidal dispersions: Viscosity as a function of shear rate and volume fraction," J. Chem. Phys., Vol. 83, No.9, pp 4717-4725 (1985).

167. Chen, M, Van De Mark, M, "Rheology studies on colloidal unimolecular polymer (cup) particles in absence and presence of NaCl," Polymer Preprints Vol.52, No.2, pp 336-337 (2011).

168. Hoffman, A, "Hydrogels for biomedical applications," Adv. Drug Deliver Rev., Vol. 54, No.1, pp 3-12 (2002).

169. Cursaru, B, Stanescu, P, Teodorescu, M, "The states of water in hydrogels synthesized from diepoxy-terminated poly(ethylene glycol)s and aliphatic polyamines," U.P.B. Sci. Bull., Series B, Vol. 72, no.4, pp 99-114 (2010).

170. Baba, T, Sakamoto, R, Shibukawa, M, Oguma, K, "Solute retention and the states of water in polyethylene glycol and poly(vinyl alcohol) gels," J. Chromatogr. A. Vol. 1040, no.1, pp 45-51 (2004).

VITA

Sagar Vijay Gade was born in 1983 in Maharashtra, India. He received his Bachelor Degree in Paint Technology with a first class in May 2004 and Master Degree in Surface Coating Technology with first class with distinction in May 2006 from Institute of Chemical Technology (Formerly known as UDCT). Sagar worked in Masco Coatings Research Center (Behr Process Paints India Pvt. Ltd.) from June 2006 to July 2008 in Pune, India as senior chemist. In August 2008, Sagar joined the Missouri University of Science and Technology to pursue a Ph.D. degree in Chemistry. During the course of his Ph.D. work, Sagar worked as a Teaching Assistant for the Department of Chemistry and as a Research Assistant for Missouri S&T Coatings Institute. Sagar presented his research work in five conference articles, two posters, wrote three review articles for magazines and he has submitted two articles for publication. He received Shelby F. Themes best paper award in Feb. 2013 and was nominated for the same again in February 2015 for conference papers presented in waterborne symposium. He received outstanding graduate teaching assistant award twice in 2011 and 2013 from Chemistry Department, Missouri S&T. In August, 2015, Sagar received his Ph.D. in Chemistry from Missouri University of Science and Technology.