Aspects of Water Sensitivity of PVAc Latex Films

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Aspects of Water Sensitivity of PVAc Latex Films

by

Zhijin Chen

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Dedication

To my loving wife and son
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**Figure 6.7:** Reprint from the Chemical Reaction Engineering book of the scheme of shrinking-core model for an isothermal spherical particle concentration profile with reaction time $t$. $C_{\text{Ag}}$, $C_{\text{As}}$ and $C_{\text{Ac}}$ are the gas-phase concentration in bulk layer, in ash layer (porous layer) and on particle surface of the unreacted core respectively. $C_{\text{B0}}$ is the mole density of the solid B.
Figure 6.8a: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength at 23 °C (latex with GTDA).

Figure 6.8b: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength at 50 °C (latex with GTDA).

Figure 6.8c: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength at 50 °C (latex with GTDA).

Figure 6.8d: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength of the GTDA-latex blend at 23 °C, 50 °C and 80 °C.

Figure 6.9: Particle size of latexes (GTDA/AAEM = 1.0): (A) Control; (B) 1 hour mixing time; (C) 2 hour mixing time and (D) 3 hour mixing time.

Figure 6.10: Level curves of the residual sum of square (RSS) response surface for the GTDA-latex reaction at 80 °C (see Figure 6.8c).

Figure A1.1: Shear stress vs shear rate (run with a Hercules HI-Shear Viscometer, HHSV) (fully-hydrolyzed PVEOH was used as stabilizer, the stabilizer/monomer ratio is 6%).

Figure A1.1: Impact of VV10 on water absorption (fully-hydrolyzed-PVEOH was used as stabilizer, the stabilizer/monomer ratio is 6%).

Figure A1.3: The impact of VV10 level on surface tension fully-dydrorized-PVEOH was used as stabilizer, the stabilizer/monomer ratio is 6%.

Figure A1.4: Impact of VV10 on Latex Film Modulus and T_g (VV10 level changes from 10% to 70% based on total monomer).

Figure A2.1: Oxygen permeability of GH- and GTDA-crosslinked latex films.

Figure A2.2: Impact of pressure on oxygen permeability of GH crosslinked latex films (top: permeability of 80 °C annealed film vs room temperature cured films; bottom: permeability of 340 KPa vs 200 KPa on 80 °C annealed films).

Figure A2.3: Optical micrographs of cross-section of GH-crosslinked latex films (A) 0%; (B) 5% GH; (C) 10% and (D) 15%. The master batch latex was used and all cured films were annealed at 80 °C before test.
**Figure A2.4:** Water sensitivity comparison of latex film W/O crosslinkers. Dotted line is the 80 °C annealed GH-latex film.

**Figure A2.5:** Optical micrographs of GH crosslinked latex films (60°C annealed, lower film surface was measured). (A) control 0% GH; (B) 5% GH; (C) 10% GH and (D) 15% GH.
Abstract

Crosslinking reactions between emulsion polymers and crosslinkers play a large role in influencing the water sensitivity of latex films. This research program focuses on aspects of the water sensitivity of poly(vinyl acetate)-based latex films. The functional monomer, acetoacetoxy ether methacrylate (AAEM), and water-soluble crosslinkers, glyoxal (GH) and glutaric dialdehyde (GTDA), were used in this study. The partitioning of crosslinkers in the aqueous phase was studied and it was found that 60% of the GH remained in the aqueous phase after mixing with latex, while 40% of GTDA partitioned into the aqueous phase.

Model reactions between the crosslinkers and model molecules, ethyl acetoacetate (EAA) and 1, 3-pentanediol (PD), have been studied in order to understand the crosslinking kinetics and their reaction mechanisms. Model reactions showed that GH and GTDA do react with EAA and PD at various temperatures and all of the reactions are assumed to be pseudo-first-order reactions. It was found the reaction between GH and PD is reversible and its reaction kinetics were studied fully. The model reactions and experimental data matched very well. The partitioning study and the results obtained from the model reactions are useful for understanding crosslinking reactions in real-world applications. AAEM functional monomer was assumed to be evenly distributed in the interior of the latex particles and the hydroxyl functional groups arising from the colloidal stabilizer (polyvinyl alcohol) that was used were present on the surface of the latex particles. The kinetics and mechanism obtained
from model reactions can be used to predict the competition reactions for latex systems. The GTDA prefers to react with hydroxyl functional groups present on the particle surfaces, while the GH prefers to react with acetoacetyl functional groups inside of the latex particles. The preferred crosslinking reactions from kinetic studies are ranked as:

\[ K_{GH-AEEM} \gg K_{GH-PVOH} \approx K_{GTDA-PVOH} \gg K_{GTDA-AEEM} \]

The diffusion coefficient of water into crosslinked latex films is independent of the level of crosslinker, and the value is 12-14 times higher than neat poly(vinyl acetate) films. The GH diffusion coefficient is 4-5 times lower than the diffusion coefficient of water due to higher resistance for GH to be leached out. All diffusion processes are entropy controlled.

A second order chemical reaction, i.e., a “Shrinking-Core Model” (SCM) equation was derived in detail, and it fits well with the experimental data obtained from the reaction time-conversion curves. The reaction constants \( (k_r, \text{Lmol}^{-1} \text{s}^{-1}) \) calculated from the SCM was similar to the experimental values. It was assumed the crosslinker (GTDA) diffusion coefficient, \( D_e \), in the GTDA-latex system could be calculated from the SCM as well. Indeed it was found that the calculated \( D_e \) predicted from SCM agreed with reported literature values.

Scaling theory was used to explain the latex film formation. The analytical control factor, \( \alpha \), based on scaling theory was derived and this control factor was compared with experimental data.
Chapter 1

Background and Motivation for the Study “Aspects of Water Sensitivity of Poly(vinyl acetate) Latex Films”

1.1 Background of Vinyl Acetate (VAc) Monomer and PVAc Emulsion Polymer

Vinyl acetate monomer was first recognized by Klatte in 1912 based on the liquid-phase reaction of acetylene and acidic acid where the vinyl acetate was a by-product in the preparation of ethylidene diacetate. Klatte at el. also were the first to obtain patents for the polymerization of VAc, although the polymers were described as being too soft for use in plastic articles. There have been three major manufacturing processes to prepare of VAc in history: 1) the first process used for the manufacture of VAc was ethylidene diacetate pyrolysis which was described in a patent issued to British Celanese in 1947. The Celanese British plant first used this process to manufacture VAc monomer; 2) the second method was the acetylene and acidic acid vapor reaction process which was first used in 1964 by Borden Chemical Company, Du Pont and some other companies; 3) the third process was the reaction of ethylene and acidic acid practiced in 1967. In 1967, there were several methods for VAc manufacture from ethylene available for licensing. The VAc monomer manufacturers were all likely considering the possibility of changing from older processes to use ethylene feed stock. The driving force for the technology changes was due to the
advanced petroleum refining process of ethylene monomer and the low cost of ethylene compared to acetylene. In 1967, ethylene was only 3.25 cents per pound while acetylene was 10 cents per pound. However, the manufacturing process did not change immediately due to the high cost of the reaction catalyst. The changeover process from older technology to ethylene feed stock was gradually precipitated by the solving of engineering problems and lower cost of catalyst and acidic acid².

The contemporary bulk price of pertinent monomers is listed in Table 1.1 below:

Table 1.1: Common Monomer Market Price*

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Bulk price ($/lbs)</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate (VAC)</td>
<td>0.40</td>
<td>Ethylene+acidic acid with catalyst</td>
</tr>
<tr>
<td>Styrene (St)</td>
<td>0.50</td>
<td>Dehydrogenation from ethylbenzene; ethylbenzene is made from ethylene and benzene</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>1.35</td>
<td>The BASF Route: Hydroformylation of ethylene to propionaldehyde, condensation with formaldehyde to methacrolein, followed by oxidation and esterification. The first and only company to commercialize with this route is BASF.</td>
</tr>
<tr>
<td>n-Butyl acrylate (nBA)</td>
<td>1.10</td>
<td>Esterification reaction of Acrylic acid and butanol</td>
</tr>
<tr>
<td>2-ethylhexyl methacrylate (2-EHA)</td>
<td>1.12</td>
<td>Esterification reaction of Acrylic acid and 2-ethylhexyl alcohol</td>
</tr>
</tbody>
</table>

*The bulk price as of November 05, 2011.

The VAc and styrene monomer global production were 12.3 billion pounds in 2007⁷ and 15 billion pounds 2005⁸ respectively. VAc monomer is a building block used to manufacture a variety of polymers, such as lamination adhesives (e.g. Hot-melt
ethylene-vinyl acetate (EVA)), plastic, paper coatings (e.g. VAc homo-polymer); building construction (e.g. homo and copolymers); textile finishing and non-woven binders, finishing and impregnation materials (e.g., homopolymers); elastomers (e.g., copolymers), and emulsion polymers for paints (e.g. vinyl acrylic emulsion) and emulsion polymer for adhesives (e.g., homo-polymer based). The 83% of VAc production is used in PVAc emulsions and resins\textsuperscript{9,10}. It should be emphasized that 70% of PVAc-based emulsions were used in adhesives in 2008\textsuperscript{11}. The features of the PVAc emulsion include great adhesion to porous substrates including wood, paper and fibers, good adhesion to metal and porcelain and more color stability than other adhesives. PVAc emulsions are also odor-free and inexpensive compared to other emulsion polymers. The VAc monomer can be copolymerized with many other monomers to form a copolymer which will extend its application such as vinyl-acrylic copolymers for latex paints, binders and architecture coatings; or vinyl-ethylene copolymers for adhesives used in wood working, packaging and hot-melts. Thus, PVAc-based polymers are very important due to their wide scope of application areas.

Vinyl acetate emulsion polymers can be stabilized with surfactants (such as anionic or non-ionic surfactants) or with colloidal stabilizers such as poly(vinyl alcohol) (PVOH). Surfactant-stabilized VAc homopolymers or its copolymers are typically used in coatings and binders, while PVOH-stabilized emulsions are usually used as adhesives.
Poly(vinyl acetate) has been available commercially in the United States since about 1930\textsuperscript{1}. The VAc polymerization can be easily carried out at 55 °C to 85°C with proper initiators. The popular process for adhesive or binder applications is to use PVOH as a stabilizer. Partially-hydrolyzed PVOH is very common in such applications. A typical production process is illustrated in Figure 1.1. The solid PVOH is pre-dissolved in heated water and then the PVOH solution and VAc monomer are pumped into the reactor for polymerization at a designed reaction temperature profile. The process is a semi-batch process and the finished emulsion polymer is pumped to a holding tank for post additions such as coalescing agents or other additives\textsuperscript{15}.

Semi-batch emulsion polymerization can be carried out using different feed types. Two main types of feeds have received the greatest attention\textsuperscript{12}: neat monomer feed and monomer emulsion feed. Monomer emulsion feeds may vary between an emulsified monomer solution\textsuperscript{13} and an emulsion recipe containing all ingredients\textsuperscript{14}.
Using PVOH as a stabilizer usually enhances adhesion to wood and related substrates when compared to the use of typical anionic or nonionic surfactants. However, when the polymer emulsion is prepared with surfactants or with conventional partially-hydrolyzed PVOH, the polymer film has highly sensitivity to water or exhibits poor water resistance; the bonded substrates cannot be used under wet conditions including building construction sealants, millwork, or wood-related outdoor features. Surfactants and PVOH both contribute negatively to the water resistivity of dried latex films because these stabilizers that are present on the particle surfaces exhibit high sensitivity to moisture. The PVAc backbone also has high affinity of water compared to
most organic polymers, and it can easily hydrolyze to form water-soluble PVOH, thus losing its water resistance (see figure 3.1). Chapter 3 gives more detail on the water sensitivity of PVAc latexes.

1.2 Overview of VAc Based Emulsion Polymers and Their Water Sensitivity

1.2.1 Water Sensitivity of VAc Homopolymers

Like all other polymers, the preparation of PVAc may be divided into four types of processes: emulsion, bulk, solution and suspension. The PVAc emulsion polymerization process is most important among these since it is easy in practice and easy to scale up in industry due to good heat transfer in the aqueous phase during polymerization. The homopolymer of PVAc is called “white glue” such as “school glue” which is widely used in the paper industry, the packaging industry and furniture assembling industry where water resistance is not required. PVAc homopolymer usually is very water sensitive due to two reasons: 1) the backbone of PVAc is subjected to hydrolysis in water, especially in alkaline media; its hydrolysis is shown in Scheme I; 2) the latex when stabilized with PVOH will exhibit an abundance of hydroxyl functional groups on the latex particle surface and these -OH groups will remain on the latex film surface when dried. Hence the latex surface will show high sensitivity to moisture (Figure 1.2).
Scheme I: Hydrolysis of poly(vinyl acetate) homopolymer.

Figure 1.2: Surface of latex particles with hydroxyl functional groups, which are provided by the colloidal stabilizer (PVOH).
1.2.2 Water Sensitivity of VAc Copolymers

Copolymerizations of VAc with secondary monomers are often used to reduce latex film water sensitivity. Such latex will have a lower $T_g$ ($<\text{ambient temperature}$) than PVAc homopolymer ($T_g = 35\, ^\circ\text{C}$). The predominant co-monomers include ethylene, n-butyl acrylate, 2-ethylhexyl acrylate and ethylene$^{16}$. However, many other monomers have been successfully copolymerized with VAc monomer for desired properties. Tokita$^{17}$ studied ethylene-vinyl acetate copolymer dispersions for thermal recording medium applications due to improved low water sensitivity of ethylene-vinyl acetate copolymer. Poly(vinyl acetate-co-ethylene) is an important copolymer which has been widely used in glue-lap applications (carton box packaging), wood adhesives and coating applications. Iovine$^{18}$ reported a copolymer use of acrylate-(dimethylamino)ethyl methacrylate-vinyl acetate copolymer as particle core and acrylic acid-butyl acrylate-vinyl acetate copolymer as the shell in adhesive application. Rigsby$^{19}$ reported up to 50% styrene monomer was incorporated with VAc monomer in a core-shell structure for heat and water resistance studies. However, Rigsby found that the water resistance did not improve with this structure. Use of castor acrylated monomer (CAM) in vinyl-acrylic latexes was reported by Brister$^{20}$. The CAM monomer contains 22 carbons, making it the largest co-monomer used in emulsion polymerization. With incorporation of CAM in the polymer backbone, the latex demonstrated improved alkaline resistance and water resistance.
The reactivity of VAc monomer with other monomers is shown in Table 1.2. Their physical parameters are shown in Table 1.3.

Table 1.2: Reactivity of Vinyl Acetate Monomer with Other Monomers

<table>
<thead>
<tr>
<th>Monomer 1 (M1)</th>
<th>Monomer 2 (M2)</th>
<th>Reactivity ratio $r_1=k_{11}/k_{12}$</th>
<th>Reactivity ratio $r_1=k_{22}/k_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate</td>
<td>n-Butyl acrylate CH$_2$CHCOOC$_4$H$_9$</td>
<td>0.018</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td>2-Ethylhexyl acrylate CH$_2$=CHOOC$_3$H$_7$</td>
<td>0.10</td>
<td>9.20</td>
</tr>
<tr>
<td></td>
<td>Ethylene CH$_3$=CH$_2$</td>
<td>1.49</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>VeoVa 9 Vinyl ester (at 60 °C) CH$_2$=CHOOC(CH$_3$)$_2$R$_1$R$_2$ Total 8 carbons in R$_1$ and R$_2$</td>
<td>0.93</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>VeoVa 10 Vinyl ester (at 60 °C) CH$_2$=CHOOC(CH$_3$)$_2$R$_1$R$_2$ Total 9 carbons in R$_1$ and R$_2$</td>
<td>0.99</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Vinyl butyrate CH$_2$=CHOOC$_3$H$_7$</td>
<td>1.00</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Methyl methacrylate (MMA) CH$_2$=C(CH$_3$)$_2$COOCH$_3$</td>
<td>0.81</td>
<td>137.5</td>
</tr>
<tr>
<td></td>
<td>Acrylic acid (AA) CH$_2$=CHCOH</td>
<td>0.021</td>
<td>8.66</td>
</tr>
<tr>
<td></td>
<td>N-Isobutoxymethyl acrylamide (IBMA) CH$_2$=CHCONHCH$_2$OCH$_2$CH(CH$_3$)$_3$</td>
<td>0.015</td>
<td>34</td>
</tr>
</tbody>
</table>

It is shown that VAc has very different reactivity with other monomers. In the case of VAC-VeoVa 10 copolymerization, the latex can form very random copolymer since their reactivity ratios are nearly equal. The same conclusion can be reached for
VAc-VeoVa 9 and VAc-vinyl butyrate copolymers. However, when n-butyl acrylate (nBA) is polymerized with VAc, the reaction has to be very slow in order to achieve instantaneous conversion for both monomers during polymerization. The normal process time for this copolymerization is over the span of hours. It has to be noted that the reactivity ratio of VAC-nBA was only used as a reference since the data were recorded from solution polymerization. The actual emulsion polymerization is carried out in an aqueous phase with surfactant or colloidal stabilizer, hence, the loci of reaction are totally different from solution polymerization. In fact, the polymerization of VAC-nBA should be a lot easier than expected if judged by their respective reactivities. Due to the large difference in reactivity between these monomer pairs, the latex structure of the copolymer composition will be varied. It is to be expected that the copolymer may consist of blocks of individual monomer segments in acrylate-VAc backbone. Martin\textsuperscript{22} used differential scanning calorimetry (DSC) to study the $T_g$ of vinyl acetate copolymers. The $T_g$ curve for VAc-nBA copolymers exhibited two transitions while the curves of VAc-2-EHA showed three transitions (curves not included here). However, the VAC-VeoVA10 copolymer prepared from emulsion showed only one transition since the two monomers have similar reactivities and the structure of the copolymer tends to be random as mentioned above. The commercially available second monomers for VAc copolymerizations are shown in Table 1.3.
Table 1.3: Commercially-Available Monomers for Emulsion with Vinyl Acetate

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Structure</th>
<th>( T_g ) ((^{\circ})C) of homopolymer</th>
<th>B.P. ((^{\circ})C) monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate (VAc)</td>
<td>( \text{CH}_2=\text{CHOOCCH}_3 )</td>
<td>32</td>
<td>72</td>
</tr>
<tr>
<td>n-Butyl acrylate (nBA)</td>
<td>( \text{CH}_2\text{CHCOOC}_4\text{H}_9 )</td>
<td>-40</td>
<td>145</td>
</tr>
<tr>
<td>2-Ethylhexyl acrylate (2EHA)</td>
<td>( \text{CH}_2=\text{CHOOCC}_3\text{H}_7 )</td>
<td>-85</td>
<td>216</td>
</tr>
<tr>
<td>Ethylene</td>
<td>( \text{CH}_2=\text{CH}_2 )</td>
<td>-78 (LDPE)</td>
<td>-103.7</td>
</tr>
<tr>
<td>VeoVa 9 Vinyl ester (at 60 °C)</td>
<td>( \text{CH}_2=\text{CHOOCC} (\text{CH}_3)_2 \text{R}_1 \text{R}_2 ) Total 8 carbons in ( \text{R}_1 ) and ( \text{R}_2 )</td>
<td>-3</td>
<td>185-200</td>
</tr>
<tr>
<td>VeoVa 10 Vinyl ester (at 60 °C)</td>
<td>( \text{CH}_2=\text{CHOOCC} (\text{CH}_3)_2 \text{R}_1 \text{R}_2 ) Total 9 carbons in ( \text{R}_1 ) and ( \text{R}_2 )</td>
<td>70</td>
<td>133-136</td>
</tr>
<tr>
<td>Vinyl butyrate</td>
<td>( \text{CH}_2=\text{CHOOCC}_3\text{H}_7 )</td>
<td>-5</td>
<td>116</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>( \text{CH}_2=\text{C(} \text{CH}_3\text{)COOCH}_3 )</td>
<td>105</td>
<td>101</td>
</tr>
<tr>
<td>Acrylic acid (AA)</td>
<td>( \text{CH}_2=\text{CHCOH} )</td>
<td>193</td>
<td>141</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>( \text{CH}_2=\text{CHCl} )</td>
<td>82</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Copolymerization of two or more monomers during free radical polymerization is an effective way of altering the polymer properties. Farwaha et al.\textsuperscript{21} studied the scrub and alkali resistance of VAc-VeoVA10, VAc-2EHA and VAc-nBA copolymers and found that the VeoVA10 containing copolymer exhibited much higher scrub resistance than 2EHA and nBA (Figure 1.3). Wet scrub resistance is a test wherein a brush is literally rubbed over a prescribed film of latex paint until the film “fails” and rubs off. It is measured in brush cycles. Higher brush cycles indicate a more durable latex paint. The alkali resistance is a measure of the hydrolysis resistance of the polymer itself.
This is also referred to as the saponification number of latex film. The lower the saponification number, the more suitable is the copolymer for use in paints for masonry with highly alkaline surfaces. Figure 1.2 also shows a much stronger alkali resistance for the copolymer of VAc-VeoVa10.

**Figure 1.3:** (Reprinted from Farwaha, R.; Sousa, L. D. *Coating Tech*, 2010, 36) Comparison of VAc/Co-monomer emulsions at a ratio of 73%/30% by weight.

It is reasonable to assume that copolymers of vinyl acetate prepared with long chain second monomer could reduce latex water sensitivity due to the presence of hydrophobic monomers in the polymer backbone. An example of the water uptake of VAc-VeoVA10 copolymer from latex is shown in Figure 1.4 (see Appendix 1 for detail). It can be seen that increasing the quantity of VeoVa10 (VV10) in the
copolymer structure results in a general decrease in the latex film water sensitivity. However, the lower limit of water absorption was reached when the polymer contained about 30% VV10. No further impact was obtained when higher VV10 is used. Figure 1.4 shows a plateau for minimum water absorption at about 30% by weight after eight hour of water absorption of the film.

**Figure 1.4:** Water absorption vs. VeoVa10 level in copolymer (fully-hydrolyzed poly(vinyl acetate-co-ethylene) was used as a stabilizer; the stabilizer/monomer ratio is 6%-see Appendix 1 for detail).
1.2.3 Water Sensitivity of VAc with Functional Monomers

The VAc monomer can also be copolymerized with functional monomers, such as acetoacetoxy ether methacrylate (AAEM)\textsuperscript{23}, acrylic acid, and methyl acrylic acid\textsuperscript{24}, N-methylol acrylamide (NMA) or N-isobutoxymethyl acrylamide (IBMA)\textsuperscript{25}. It was reported that the AAEM-Vinyl acetate-VeoVa10 terpolymer latex can be used as a wood adhesive with enhanced water resistance when crosslinked with diamines\textsuperscript{26}.

Cylink N-methylolacrylamide (NMA) and N-isobutoxymethyl acrylamide (IBMA) are commonly used as crosslinkers for emulsion polymers; both demonstrate self-cross-linking properties in a copolymer backbone. Acid or aluminum ion (e.g., aluminum chloride) is often employed as catalyst to accelerate the crosslinking reactions of NMA- or IBMA-containing latexes. The mechanism of self-crosslinking NMA monomer is shown in Scheme II. The vinyl group in NMA enables the NMA to be readily incorporated into the polymer structure with VAc or other monomers. The methylol group in NMA can be triggered to undergo crosslinking with itself and other functional groups in the polymer, such as hydroxyls or amines, or with cellulosic substrates. The bi-functional feature of NMA in the latex makes the latex more stable to separation due to its water affinity. The NMA-containing latex usually has good wet strength, tear strength and solvent resistance after crosslinking. The self-crosslinking mechanism of NMA is shown in Scheme II\textsuperscript{27}.
Scheme II: NMA self-crosslinking mechanism (Cytec NMA technical procedure, PRT-789-B)\textsuperscript{27}.

An example of the water sensitivity of NMA crosslinked latex is shown in Figure 1.5. The haziness is a measure of water sensitivity when the latex film is immersed in water. The higher the amount of the NMA in latex, the lower the haziness of the cured film observed during a 30 minute boiling water immersion test.
Figure 1.5. (Reprinted from Cytec technical brochure PRT-707-C)\textsuperscript{46}. Haze developed in latex polymer films containing various amounts of N-methylolacrylamide (Vinyl acetate/ethyl acrylate/N-methylolacrylamide/itaconic acid tetrapolymer, ethyl acrylate =25\%, itaconic acid =1.0\%).

However, NMA can also lead to premature crosslinking or gel formation during emulsion polymerization and storage. The crosslinking reaction releases free formaldehyde as the NMA undergoes crosslinking to form the methylene-bis-acrylamide (MBA) bridge (see Scheme II). Both the NMA and IBMA crosslinking mechanisms are similar and copolymers prepared with them are not considered as “green” materials since free formaldehyde is released during the self-crosslinking reaction.

Aluminum ion (\textit{Al}^{3+}) and some transition metal salts such as zirconium and titanium halide or other organo-metallic complexes have been reported as crosslinkers.
For example, Kuo et al.\textsuperscript{28} reported use of acetoacetate-functional polymers for aldehyde removal with aluminum ion acting as crosslinker.

Common crosslinkable or functional monomers are shown in Table 1.4. The crosslinking mechanism and approaches differ for functional monomers, thus, specific crosslinking conditions are needed for specific system for particular functional monomers.
<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetoacetoxy ether methacrylate (AAEM)</td>
<td>CH₂=C(CH₃)COO(CH₂)₂OOCCH₂ COCH₃</td>
<td>Polymerizes T_g =18 °C</td>
</tr>
<tr>
<td>Glycidyl methacrylate</td>
<td>CH₂=C(CH₃)COOCH₂ (CH(O)CH₂)</td>
<td>189</td>
</tr>
<tr>
<td>4-Hydroxybutyl acrylate glycidylether (4-HBAGE)</td>
<td>CH₂=CHCOO(CH₂)₄ OCH₂(CH(O)CH₂)</td>
<td>120</td>
</tr>
<tr>
<td>4-hydroxybutyl acrylate (4-HBA)</td>
<td>CH₂=CHCOOCH₂ CH₂ CH₂CH₂OH</td>
<td>230</td>
</tr>
<tr>
<td>Diacetone acrylamide (DAAM)</td>
<td>CH₂=CHCONHC(CH₃)₂ CH₂ COCH₃</td>
<td>120/8 mm Hg</td>
</tr>
<tr>
<td>Polyethylene glycol Dimethacrylate (RS210)</td>
<td>CH₂=C(CH₃)COO(CHCHO)₄ OOC(CH₃)C=CH₂</td>
<td>N/A</td>
</tr>
<tr>
<td>Vinyltriisopropoxysilane A-1706</td>
<td>CH₂=CHSi[OCH(CH₃)₂]₃</td>
<td>150</td>
</tr>
<tr>
<td>Gamma-Methacryloxypropyl-trimethyloxy Silane A-174NT</td>
<td>CH₂=C(CH₃)COO(CH₂)₃ Si[OCH(CH₃)₂]₃</td>
<td>255</td>
</tr>
<tr>
<td>Methacryloxypropyl-tris-(2-propoxy)silane A-1757</td>
<td>CH₂=C(CH₂)COO(CH₂)₃ Si(OCH₃)₂OCH₃</td>
<td>&gt;300</td>
</tr>
<tr>
<td>N-Methylol acrylamide (NMA)</td>
<td>CH₂=CHCONHCH₂ OH</td>
<td>M.P. 74-75</td>
</tr>
<tr>
<td>N-Isobutoxymethyl acrylamide (IBMA)</td>
<td>CH₂=CHCONHCH₂OCH₂CH(CH₃)₃</td>
<td>108</td>
</tr>
<tr>
<td>2-Hydroxyethyl acrylate</td>
<td>CH₂=CHCOOCH₂CH₂OH</td>
<td>90-92/12 mmHg</td>
</tr>
<tr>
<td>Methacrylic acid (MAA)</td>
<td>CH₂=CHCOOH</td>
<td>163</td>
</tr>
<tr>
<td>Acrylic acid (AA)</td>
<td>CH₂=CHCOOH</td>
<td>139</td>
</tr>
</tbody>
</table>
1.2.4 Other Approaches to Latex Film Water Sensitivity

Various other approaches have been taken to improve the water resistance of PVAc emulsion adhesives. Crosslinked latex films usually show higher tensile storage modulus and higher $T_g$ as well as higher gel fraction when the internal crosslink density increases. Blending of PVAc emulsions with melamine/urea/formaldehyde resins improved the water resistance considerably. This latex film has a higher tensile storage modulus because of the formation of an interpenetrating network-type structure\textsuperscript{29}. Such products often exhibit improved heat resistance, but not initial water soak resistance, because melamine/urea/formaldehyde resins usually require relatively high heat to be properly cured. However, applying heat is not always possible in many industrial production processes.

Techniques to increase grafting are an important way to make the monomers graft to the stabilizer in a latex system\textsuperscript{30,31}. The high grafted latex will have an impact on heat and water resistance. As mentioned in section 1.2.2, long alkyl-chain monomers, such as isooctylacrylate and VV10 vinyl ester monomer, can be copolymerized with VAc for better water resistance. However, the glass transition temperature and heat resistance of the dry film are sacrificed. In fact, in most cases the copolymers do not show sufficient water resistance as needed with high demand from industry (e.g. Figure 1.4 and see Appendix 1).

One of the interesting polymer modifications reported is vinyl acetate-co-vinyltrimethoxysilane copolymer. The PVAc based emulsion is either used alone or
combined with additional crosslinking agents to further improve the water resistance\textsuperscript{32}. The vinyltrimethoxysilane structure is shown below.

\[
\text{H}_2\text{C}-\text{CH} \quad \text{CH}_2-\text{CH} \quad \text{CH}_2-\text{CH} \quad \text{H}_n \quad \text{OCH}_3
\]

Copolymerization with vinyl silane is a popular research topic because it provides enhanced adhesion to a variety of substrates for adhesives or coatings\textsuperscript{33}. More pertinently to this study, the inclusion of vinyl silane in copolymers provides enhanced water and scrub resistance. However, it is generally too expensive for many industrial applications, especially in the wood-related industries. As in the case of long-chain co-monomers, the silane will decrease the glass transition temperature, and thus has a negative impact on heat resistance.

Use of gamma radiation-initiated polymerization was reported for VAc monomer in emulsion systems. The performance of the emulsion prepared under such conditions was reportedly better than those prepared with gamma radiation methods\textsuperscript{34,35}. Higher molecular weight resulting from this initiation process may contribute to better water resistance compared to free-radical initiation. In conventional radical polymerization processes, very high molecular weight of PVAc is rarely achieved.
because of chain transfer reactions taking place between the colloidal stabilizer and reactive growing chains. However, the radical emulsion polymerization process still remains a much more practical and economical process.

Blending of more hydrophobic polymers, such as poly(vinyl chloride), with PVAc-based emulsion polymers has been often reported\textsuperscript{36}, but careful attention needs to be paid to polymer miscibility. The initial water absorption rate for immiscible emulsion blends was found to be significantly higher than the composite values derived from the constituents. This behavior is due to percolation networks in the blends where thermodynamic constraints prevent diffusion across the interface of bordering dissimilar particles. This leaves an interface enriched with water-sensitive species. Polyurethane dispersions seem to be more compatible with PVAc emulsions than other polymers such as acrylic latex. A minimum addition of 25% of polyurethane (PU) dispersion or its hybrid dispersion is usually required for a significant impact on performance, because a continuous interface is formed with a higher concentration of PU. For hybrid systems, polyurethane dispersions are often prepared in the presence of vinyl monomers such as acrylic or styrene monomers\textsuperscript{37}. This can be accomplished by the polycondensation reaction of polyurethane with monomer as the solvent, followed by a radical polymerization of the vinyl monomer. In-situ PVAc-PU hybrid polymerization has not been reported to date. The reasons may be that the VAc monomer is usually polymerized in acidic conditions, while the basic polyurethane dispersion media inhibits the radical polymerization.
The water sensitivity of the PVAc based latex can be improved by multi-step polymerizations. Mudge et al.\textsuperscript{38} reported that a water-resistant woodworking adhesive comprising PVAc was prepared from a two-stage polymerization procedure: (1) In the first stage VAc homopolymer is prepared; (2) in the second stage VAc is copolymerized with methyl methacrylate having a glass transition temperature within 50-120 °C, with a ratio of the first homopolymer to the second copolymer being 10:1-10:6.

Power feed is a technique that can be used in copolymerization to integrate chemical composition changes into the polymer backbone\textsuperscript{39,40,41}. Emulsion copolymers prepared \textit{via} power feed have a very broad glass transition when compared with random copolymers. This is explained by the fact that the system synthesized through the power-feed method is an “alloy” of copolymers which are a continuous transition from monomer A-rich copolymers to monomer B-rich copolymers. The dynamic mechanical behavior of films cast from solution is almost the same as that of emulsion films. The power feed copolymer (MMA-co-nBA) was shown to maintain adhesive strength over a wide temperature range compared with random copolymers\textsuperscript{42}. However, there have been no reports in the literature investigating the power feed of VAc with long-chain monomer, such as Velva10. Furthermore, its practical application to achieve for high water resistance are questionable due to the concerns of the water sensitivity for the VAc-rich shell and lower $T_g$ of the soft monomer-rich core. In fact, Farwaha\textsuperscript{21} reported that in this case the water scrub resistance was much lower when using a
power feed method compared to feeding a fixed ratio of VAc/VV10 (65%/35%). It was explained that ester groups from VAc in the random copolymer is better protected by long-chains from the VV10 molecule in polymer structure.

Polyvinyl alcohol (PVOH) is a common colloidal stabilizer. The high degree of grafting of monomers onto PVOH makes the polymer film more water resistant. Emulsion polymers can be synthesized by graft copolymerization of corn starch and iso-octyl acrylate. Functional PVOH can also be used in emulsion polymerization, and the water sensitivity of the resulting latex films can vary depending on the structure of the modified PVOH. Qiao et al. summarized the different ways of modifying PVOH. Water resistance can be achieved by modified crosslinkable PVOH (such as acetoactylated PVOH, carboxylated or amine-containing PVOH) or using long side chain comonomers. The acetalization of PVOH is a simple, quick, and inexpensive way to enhance the water resistance and toughness of the PVAc emulsion. However, the extent of this enhancement is limited due to the need to retain a proportion of the hydroxyl groups in the stabilizer chains for stabilization of the latex. During film formation, the aldehyde-modified PVOH tends to separate from the polymer particles. As a result, the water resistance is lowered due to discontinuities and non-uniformities in the film. Acetoacetylated PVOH can be prepared by copolymerization of VAc and acetoacetoxyethyl methacrylate (AAEM). The copolymer is then subjected to hydrolysis to form an acetoacetylated PVOH. The acetoacetyl functional group - OCO(CH₂)COCH₃ can go through many reactions, similar to the AAEM monomer due
to the acidic active methylene groups in the monomer. One possible description of the behavior of the AAEM-modified PVOH during the polymerization is that the equilibrium between its keto and enol tautomers shifts to the enol form, which is favored in polar environments under polymerization conditions\textsuperscript{47}. No details were found both in the literature regarding the polymerization process or crosslinking studies to address the goal of reducing water sensitivity of the latex films. Ethylene-vinyl alcohol (EVOH) copolymers from Kuraray have been reported as good stabilizers for VAc latex polymerization (e.g. RS2117). The ethylene content in the EVOH structure can be as high as 15 molar percent. It is reported that latex made with this material exhibits very good water resistance\textsuperscript{44}. However, heat resistance is an issue because the EVOH is a much softer polymer in the latex film.

The methods of modifying PVOH depend on the desired target properties. Modified PVOH plays an important role in the improvement of the water resistance and other performance properties of latex films. The developing trend in PVOH modification is to introduce multiple functionalities to the stabilizers which will allow higher grafting and crosslinking during the PVAc polymerization process compared to conventional PVOH\textsuperscript{45}.

1.3 Objectives

PVAc-based latex films are very water sensitive. Copolymerization with hydrophobic monomer has been reported, but improvements on water sensitivity were
limited. The physical approaches, such as polymer blending, particle sizing packing and latex film annealing also displayed limited improvements in the performance of latex films since PVAc is easily hydrolyzed and the latex particle surfaces are sensitive to moisture. At present, there are no basic studies of the relationship between water sensitivity of VAc-based polymers and critical latex film performance. Most of the literature in this field is patent related to formulations and applications. The goal of this research is to establish a fundamental understanding between water sensitivity of latex films and their mechanical performance.

The motivation for the objective of this research is chemical crosslinking for PVAc-based latex to investigate the impact of water-soluble crosslinkers on water sensitivity of PVAc-based latex films. The aspects of those studies are:

1. To characterize the latex film water sensitivity.
2. To investigate partitioning of the crosslinkers in the latex.
3. To explore the kinetics and crosslinking mechanisms of crosslinkers in latex.
4. To determine the mechanical performance of the crosslinked latex films.
5. To analyze the crosslinking reaction kinetics using the second order reaction Shrinking-Core Model (SCM).
6. To compare SCM and scaling theory with experimental findings.

1.4 References


34. Li, J.; Wang, Q.; Department of Chemical Technology, Hebei University of Technology, *Zhanjie*, 1997, 18(5), 40.


Chapter 2

PVAc-Based Latex and Latex Film Water Sensitivity

2.1 Introduction

Water sensitivity of PVAc-based latex films can be improved in many different ways as discussed in Chapter 1, such as preparing ultra-high molecular weight PVAc by gamma radiation, copolymerizing vinyl acetate (VAc) with long alkyl ester monomers, blending with polyether or crystalline polyester-based polyurethane dispersions (semi interpenetrating polymer network, IPN) and modifying with silane or copolymerizing with cross-linkable monomers. However, the physical approaches, such as latex blending or particle size packing, and even copolymerization with high hydrophobic long-chain monomer only exhibit limited improvement in film water sensitivity. For instance, more than 20% water absorption was found for the VAc-VV 10 latex film after 8 hours of water immersion (see Appendix 1).

The functional monomer acetoacetoxy ether methacrylate (AAEM) will be introduced into the PVAc polymer backbone because the reactive methylene groups in AAEM can lead to many chemical crosslinking reactions. The water sensitivity of AAEM-containing latex is the key latex that was used throughout this entire research. The
synthesis of PVAc homopolymer and VAc-AAEM copolymer and their latex film characterization are discussed in this chapter.

As mentioned in Chapter 1, many functional monomers can be copolymerized into latex systems through emulsion polymerization. The type of functional groups incorporated in the latex particles determines the type of crosslinker that can be utilized for the corresponding crosslinking reactions. Some commercially available crosslinkers are shown in Table 2.1.

### Table 2.1: Commercially Available Crosslinkers for Water-Based Polymer

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of Crosslinker</th>
<th>Functional groups&lt;sup&gt;(1)&lt;/sup&gt;</th>
<th>Resources</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Addiox 1002 (ZnO)</td>
<td>Zinc oxide</td>
<td>American dispersion</td>
</tr>
<tr>
<td>2</td>
<td>Cabodolite V04 Zoldine LX-29SE Zoldine LX-29SE</td>
<td>Water based carbodimide Solvent based Carbodimide</td>
<td>Nisshinbo Industry Inc Japan Dow Chemical (Angus)</td>
</tr>
<tr>
<td>3</td>
<td>Epi-rez 3522W60 Epi-rez 5003W55 Araldite ENC</td>
<td>Epoxy (f=2) Epoxy (f=3) Epoxy (f=4)</td>
<td>Momentive Momentive Huntsman</td>
</tr>
<tr>
<td>4</td>
<td>ADH</td>
<td>Adipic acid dehydrate</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>5</td>
<td>CX-100</td>
<td>Aziridine</td>
<td>DSM NeoResins</td>
</tr>
<tr>
<td>6</td>
<td>PAE</td>
<td>Polyamine-epichlorohydrin adduct</td>
<td>Ashland</td>
</tr>
<tr>
<td>7</td>
<td>Phenolic resin (resole)</td>
<td>Phenol-formaldehyde adduct</td>
<td>Georgia Pacific</td>
</tr>
<tr>
<td>8</td>
<td>Glyoxal</td>
<td>Dialdehyde</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>9</td>
<td>Glutaric dialdehyde</td>
<td>Dialdehyde</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>10</td>
<td>Luprenate M20</td>
<td>Polymeric isocyanate</td>
<td>BASF</td>
</tr>
</tbody>
</table>

<sup>(1)</sup> f = functionality.
However, finding a safe and ambient-temperature-curing water-based crosslinkers are not easy. In this chapter, two water-soluble crosslinkers, glyoxal (GH) and glutaric dialdehyde (GTDA) are introduced, and their crosslinking kinetics and mechanism are fully studied in Chapters 4 and 5.

In general, the research aspects of latex film water sensitivity and mechanical performance are related to two approaches, physics and chemistry. This research project focuses on chemical crosslinking. The difference between this project and the reactive functional latex blend systems described in the literature is that the AAEM-containing functional latex reacts with small molecular crosslinkers (GH and GTDA). The details are given in Chapters 3 to 6.

2.1.1 Introduction to the Water Sensitivity of PVAc-Based Latexes

Better mechanical performance and lower water sensitivity of latex films can be achieved as described in Chapter 1. Latex film water sensitivity is directly related to the polymer backbone structure, polymer molecular weight, particle morphology, surface chemistry of the latex particle, latex film porosity or particle packing, and even the polymerization process variables such as the polymerization temperature profile, power feed or multi-step monomer feed techniques (e.g., a core-shell structure). The studies on latex film properties have always been of interest to researchers and scientists because the properties of latex films are directly related to end-use performance such as bond strength, adhesion, water sensitivity, and stain and weathering resistance in
coatings and adhesives. Some examples of reactive functional latex polymers included here are: (1) polymerizing conventional monomers with vinyl silane (vinyl triethoxysilane)\(^1\), with reactive hydrogen-containing monomers like hydroxy ethyl methacrylate (HEMA)\(^2\), with carboxylic acid-containing monomer like acrylic acid\(^3\); (2) using polymerizable surfactants as latex stabilizers\(^4\), (3) preparing a reactive core-shell structured latex\(^5\), (4) incorporating electrosteric stabilizers instead of conventional surfactants\(^6,7\), (5) and selecting initiator or redox system for emulsion polymerization\(^8\).

The types of stabilizer play a big role in latex film water sensitivity. The stabilizers can be surfactants or colloidal stabilizers including PVOHs or cellulosics.

Surfactant-containing acetoacetoxy-functional polymers (SAAP’s) were described by Jean and coworkers in their patent\(^9\). The acetoacetoxy-functional polymer is a surfactant-containing, polymeric (polyamino) enamine (PPAE). The polymers can be prepared as waterborne polymer for a variety of coating formulations, for example, paints, inks, sealants, and adhesives. When used in coatings formulations, the polymers of the invention provide adhesion and crosslinking in the final film. The film or coating can be cured at ambient temperatures or cured at elevated temperatures.

Preliminary study showed that functional colloidal stabilizers (Z-polymers and T330H) have a large impact on the water sensitivity of PVAc latex films. Figure 2.1 shows that the water sensitivity of latex films prepared using non-functional stabilizer (Mowiol 28-99) was higher than that obtained from functional stabilizer Z-polymers (acetoacetylated PVOH). However, the water sensitivity of latex film prepared from a
non-functional stabilizer (Mowiol 28-99) is much lower than the functional stabilizer T330H (carboxylated PVOH). The latex film derived from AAEM-VAc copolymer shows similar water sensitivity as uncrosslinked PVAc homopolymer. Latex films prepared from the acetoacetyl PVOH (Z-polymers) exhibited the lowest water sensitivity, while latex films prepared from the carboxylated PVOH (T330H) exhibited the highest water sensitivity. Additional details are discussed in section 2.3 and Chapter 3.3.

Roberson et al.\textsuperscript{10} reported that the water sensitivity of the PVAc films derived from an emulsion polymerization process is much higher than that from the corresponding solution polymerization. It is because the stabilizer-free film cast from solution polymer exhibits a denser film and higher molecular entanglement (no boundary) than that from an emulsion. The stabilizer on the emulsion particle surfaces has a negative impact in water resistance for the latex film (the water sensitive stabilizer is between the latex particles). Zhu et al.\textsuperscript{11} used maleic anhydride-modified surfmer for (vinyl acetate)-(butyl acrylate)-(VeolVa 10) emulsion polymerization and found that the latex prepared from the polymerizable surfactant had a much better water resistance than the latex prepared with conventional sodium dodecyl sulfate (SDS) surfactant.
Figure 2.1: Impact of various stabilizers on latex film water sensitivity (PVAc-based latexes, colloidal stabilizer / monomer ratio = 7.5%).

Functional polymers, such as acetoacetylated-containing copolymers, have been given great attention in that they can be crosslinked to form a thermosetting network structure\textsuperscript{12,13,14,15}. In practice, functional latex can be blended with other functional latexes or crosslinkers in a two-part system to achieve desired properties, such as using carbodiimide with carboxyl functional latex\textsuperscript{16}. Crosslinked functional latex films usually exhibited better mechanical performance and less water sensitivity compared to the non-crosslinked latex films. Modified anhydrides have been used in emulsion polymerization with VAc in the presence of anionic surfactant. Montes et al.\textsuperscript{17} reported
that butanol, dodecanol and hexadecanol were used for modification of maleic anhydride. The modified maleic anhydride monomers were polymerized with VAc monomer by batch and semi-batch polymerization processes. However, no physical or water resistance results were reported.

Todate, most of the research concerning the water sensitivity of latex films has been limited to vinyl-acrylic or vinyl-styrenic polymers where surfactants were used as stabilizers. However, the water sensitivity of PVOH-stabilized PVAc latex films has not been studied as much. It is known that surfactant or PVOH-stabilized PVAc films have higher hydrophilicity compared to most of the other acrylic systems. For example, a film prepared from PVAc latex will become hazy immediately upon immersion in water and the film will even lose its integrity if immersed in water over an extended period of time. This makes a quantitative study difficult because PVAc-based latex films are so water sensitive that physical approaches such as particle close-packing or even chemical approaches such as using traditional self-cross-linking co-monomers (e.g., N-methylol acrylamide) in the latex polymer backbone cannot satisfy the high demands needed for high water resistance of the latex film.

The high water sensitivity of the PVAc latex films results from the hydrophilicity of PVAc polymer structure in the latex particles and water-sensitive stabilizers on the latex surface. There have been several publications and dissertations by students from the Emulsion Polymer Institute (EPI) of Lehigh University on aspects of VAc emulsion polymerization in the presence of various types of PVOH, where
detailed kinetics and grafting mechanisms were explored\textsuperscript{18,19,20,21}. However, no water–
sensitivity studies of latex films were reported.

2.1.2 Techniques Used in Latex Film Characterization

Dense films prepared by close packed latex particles (large-small blend) can
improve the mechanical performance of a latex film and decrease film permeation.
Ellipsometry is a unique technique that has been used in latex film formation
studies\textsuperscript{22,23}. Dense film formation from a blend of bimodal particle size latexes is
gaining attention because they potentially enable the control of the dispersion rheology
and final film properties. Feng and Winnik studied a bimodal system with soft particles
[\text{Poly(BMA-BA), } D_w = 38 \text{ nm, } T_g = -35 ^\circ C \text{ to } 5.0 ^\circ C] \text{ and hard particles } \text{[PMMA, } D_w =110 \text{ nm, } T_g = 100\text{°C]}\textsuperscript{24}. They found that if the critical volume fraction of soft particles
was varied over a range of 0.38-0.50, a clear film could be obtained. The results imply
that proper particle packing will form a transparent film without any assistance of VOC
agents and make the product more environmentally friendly. Geurts \textit{et al.}\textsuperscript{22} studied soft
particle \text{poly(BA-MMA) (} D_w = 50 \text{ nm, } T_g = 20\text{°C}) \text{ and hard particle } \text{Poly(BA-MMA)}
(\text{D}_w= 286-297 \text{ nm, } T_g = 80\text{°C}) \text{ close packing by ellipsometry. When the large and small
soft particles were mixed together (diameter ratio of large:small particle is near 6:1),
the void fraction of the dried film reached a low value if the small particle size
concentration is close to 16.5\% by weight, which corresponds to a number ratio of
small:large particles of 43:1. The ellipsometry technique is useful for film formation
kinetic studies and also for refractive index measurements\textsuperscript{23}. Hence, the latex film density can be measured as well\textsuperscript{25}. When large hard particles are blended with small soft particles at a non-ideal ratio, film formation is hindered by the clustering of the large particles, and as a result more voids are created. Geruts \textit{et al.}\textsuperscript{22} also concluded that, in this case, no film is formed if the small particle size is less than 40\% by weight, which is referred to as sintering. In this case, the latex film exhibits high water sensitivity. Geruts’s finding is understandable since the number of small particles should be high enough to cover all of the large hard particles. Keddie \textit{et al.}\textsuperscript{23} also used ellipsometry to determine the kinetics of film formation in mixtures of film-forming and non-film forming acrylic latex. Their attention was focused on the changes in density and microstructure during the final stages of film formation. The sintering theory was used to describe the kinetics of film formation with and without added non-film-forming particles.

Atomic force microscopy (AFM) has been adopted for film formation studies, especially for film surface morphology and surface roughness characterization\textsuperscript{26,27}. Goudy \textit{et al.}\textsuperscript{26} studied the variation of polystyrene latex film properties with annealing conditions. They mentioned that a film prepared from monodisperse latex particles produced fewer surface defects, and the number of defects remained unaffected by aging or annealing. Annealing of the polystyrene latex film produced no change in the AFM peak-to-peak distances, but rather a dramatic decrease of the peak-to-trough heights when measured at a temperature above the $T_g$ of polystyrene (100 $^\circ$C). Budhlall
et al.\textsuperscript{27} studied PVOH-stabilized PVAc latex and found that a higher degree of polymerization (DP) of the PVOH resulted in a rougher latex film surface. In addition, PVOH with a higher degree of blockiness tended to have fewer free non-grafted PVOH chains on the latex film surface (i.e., free non-grafted PVOH chain: Poval 217E < Poval 217 < Poval 205; here Poval 217E has the highest blockiness and Poval 205 has the least blockiness).

SEM imaging of the cross-section fracture surface of a latex film can be used to see the packing and voids underneath the surfaces of the latex film\textsuperscript{22}. The SEM imaging on cross-section can give more information of latex particle inter-diffusion and interior particle packing. Figure 2.2 shows the cross section of VAc-VV10-MMA terpolymer latex film. This latex was made in two steps: 1) VAc-VV10 copolymerization, and 2) MMA as a second feed. Some latex sphere particles are shown in Figure 2.2, which implies a lack of coalescence during film formation. Figure 2.3 is a micrograph of the GH-crosslinked latex film after four hours at 80 °C annealing. The high roughness and porosity are seen in its cross-section. Detailed cross-section information of GH-crosslinked films is discussed in Appendix 2.
Figure 2.2: Cross-section of multi-feed latex film (VAc/ VV10/MMA, 25% MMA). Sphere particles can be seen in cross-section which means the inter diffusion is not sufficient. The polymerization was similar to AAEM-containing latex which is stabilized with fully-hydrolyzed PVOH (Table 2.4). Here, MMA is fed after VAc-VV10 and the PVOH/Monomer ratio is 7%).

Fluorescence decay measurements with the time-correlated single photon-counting technique have been used for film formation studies and especially for diffusion studies\textsuperscript{28}. 

lack of inter diffusion since sphere particles were present in the latex film
Figure 2.3: Cross-section of GH crosslinked film (GH/AAEM=3.0, cured room temperature and annealed at 80 °C for four hours; porosity formed in the latex film during annealing, see Appendix 2).

UV spectroscopy has also been used for large hard particle and small soft particle packing studies since a translucent film implies that enough soft small particles surround the large hard particles when a bimodal system is employed\textsuperscript{24}. The residual porosity in polymeric latex films can be characterized \textit{via} a permeation test. Balik \textit{et al.}\textsuperscript{29} studied a terpolymer latex film (vinyl chloride-vinyl acetate-butyl acrylate) using carbon dioxide (CO\textsubscript{2}) gas at 30°C under varying pressures. They found that CO\textsubscript{2} adsorption isotherm curves could be used to determine the diffusion coefficient under the test conditions. The low solubility of CO\textsubscript{2} in the polymer film is the key to the sensitivity of this technique. Film pore removal and gradual film coalescence were
accompanied by decreasing CO₂ solubility and decreasing diffusion coefficient. The pore removal kinetics can be followed by exposing the latex films to CO₂ at constant pressure and monitoring the weight loss as absorbed gas is “squeezed out” during film coalescence. They concluded that the estimated pore volume fraction from the condensed state of the terpolymer was less than 0.6%, which means that the polymer never became 100% void free.

A microbalance is very sensitive and can measure trace moisture absorption in given humidity or water immersion conditions to investigate the water sensitivities of latex films. A Quartz Crystal Microbalance (QCM) is a more sensitive instrument that can be used for weight change studies. The principle of QCM is to measure the frequency changes with trace weight changes.

The reported literature on latex film formation has been limited to non-PVAc latex systems where the latex was prepared with surfactants.

The water sensitivity and mechanical properties of PVOH-stabilized PVAc latex is interesting, not only because PVAc is the most inexpensive polymer in the world, but also because it has unique applications as mentioned in Chapter 1. Protective colloids play an important role in the emulsion polymerization of vinyl acetate (VAc) because of their impact on the viscosity, adhesion, latex stability and mechanical properties. PVOH has advantages over the other surfactants in that it is a synthetic polymer with a controllable degree of hydrolysis and chain length. The properties and
performance of the latexes can be very different if latexes are prepared with different
types of PVOH (see Figure 2.1).

2.1.3 Raw Materials

Vinyl acetate (Aldrich) was distilled at 40-50 °C under reduced pressure (27
(mmHg)) before use. Acetoacetyl ethyl methacrylate (AAEM, Eastman Chemical)
contained 100 ppm of butylated hydroxyl toluene stabilizer and was used as received.
VeoVa 10 (VV10) monomer was from Hexion and was used as received.

Sodium bicarbonate (NaHCO₃), sodium acetate, 35% hydrogen peroxide,
potassium persulfate and t-butyl peroxyde (t-BHP) were from Sigma-Aldrich and were
used as received. Sodium formaldehyde sulfoxylate (SFS) was from Eastman, Aerosol
MA-80I (Cytec) was used as received.

Fully-hydrolyzed PVOHs (see Table 2.2) were used for screening work and
Mowiol 28-99 was used to prepare a master batch latex for the crosslinking study. Fully hydrolyzed poly(vinyl acetate-co-ethylene) (PVEOH) and all of the PVOHs were
obtained from Kuraray as free samples or from Aldrich (made by Kuraray) and were
used as received.

Glyoxal (GH) and Glutaric dialdehyde (GTDA) were from Sigma-Aldrich and
were used as received. The GH is a 40% water solution and GTDA is 50% active in
water.
Functional PVOHs, Z-200 (99.1% hydrolysis, DP=1000) and Z-100 (99.0% hydrolysis, DP=500) were from Nippon Gohsei, Japan and T330H (99.0% hydrolysis) was from Marubeni Specialty Chemicals Inc, NY.

Table 2.2: Physical Properties of Fully-Hydrolyzed Poly (vinyl alcohols)\(^{(1)}\)

<table>
<thead>
<tr>
<th>PVOH Type</th>
<th>% Hydrolysis</th>
<th>Weight average molecular weight (M_w) (gmol(^{-1}))</th>
<th>Degree of polymerization (DP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mowiol 6-98</td>
<td>98%</td>
<td>47000</td>
<td>1000</td>
</tr>
<tr>
<td>Mowiol 10-98</td>
<td>98%</td>
<td>61000</td>
<td>1400</td>
</tr>
<tr>
<td>Mowiol 20-98</td>
<td>98%</td>
<td>125000</td>
<td>2800</td>
</tr>
<tr>
<td>Mowiol 28-99</td>
<td>&gt;99.3%</td>
<td>145000</td>
<td>3300</td>
</tr>
<tr>
<td>Mowiol 56-98</td>
<td>98%</td>
<td>195000</td>
<td>4300</td>
</tr>
<tr>
<td>Z-200</td>
<td>&gt;99.0%</td>
<td>N/A</td>
<td>DP=1000</td>
</tr>
<tr>
<td>Z-100</td>
<td>&gt;99.0%</td>
<td>N/A</td>
<td>DP=500</td>
</tr>
<tr>
<td>T300H</td>
<td>&gt;99.0%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

(1) The parameter DP was provided by supplier, poly(vinyl alcohol) = PVOH.

Hydrolysis indicates the degree of ester groups from PVAc that are replaced by hydroxyl functional groups. The PVAc polymer will become water soluble when the percent hydrolysis is greater than 80% (in this case the PVAc is called PVOH). Normally, only the water-soluble PVOH can be used as a colloidal stabilizer to make
emulsified monomer as the feed stream. The Z-polymer (Z200 and Z-100) are acetoacetoxylated functional PVOH and T-300H is carboxylated PVOH.

Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Transmission electron microscopy (TEM), Dynamic Light Scattering (DLS, Nicomp model C-370), Capillary Hydrodynamic Fractionation (CHDF), Direct and indirect Ultraviolet (UV, Shimadzu, UV210PC) (through color reaction), PerkinElmer Infrared (IR Spectrum 100), Nuclear Magnetic Resonance (NMR, Bruker DX-500, 500MHz), Energy Dispersive Spectroscopy (EDS), Instron (Model 5567) and other means were used for analyses of properties such as particle size, morphology, kinetics and to perform crosslinking mechanism studies.

2.2 Experimental Procedures

2.2.1 Homopolymerization of VAc with Fully-hydrolyzed PVOH

The batch homopolymerization of VAc was carried out in a 500 mL glass bottle containing 5.11 g fully-hydrolyzed (PVOH), 0.07 g sodium bicarbonate, 0.40 g potassium persulfate (KPS), 98.71 g VAc monomer and 310.99 g deionized water (DI water). The reaction was carried out in a 75 °C water bath for 10 hours.

The semi-batch polymerization was carried out in a 1000 mL or 2000 mL round glass kettle which was equipped with a condenser. Nitrogen was purged for 15 minutes before polymerization was started in order to remove oxygen. Continuous monomer
and redox initiator (t-BHP-SFS) feed were used and the polymerization was carried out at 75 °C in a constant water bath. The entire feed time was 2.5 hours. The PVAc homopolymerization semi-batch recipes are shown in Table 2.3.

**Table 2.3**: Semi-Batch Recipe Used to Prepare VAc Homopolymer Latex

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Semi-batch process (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>82.84</td>
</tr>
<tr>
<td>10% Poly(vinyl alcohols)(^{(1)})</td>
<td>120</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>0.07</td>
</tr>
<tr>
<td>Vinyl acetate as seed(^{(2)})</td>
<td>12.00</td>
</tr>
<tr>
<td>70% t-butyl peroxide (t-BHP)</td>
<td>0.10</td>
</tr>
<tr>
<td>1% Sodium formaldehyde sulfoxylate (SFS)</td>
<td>5.00</td>
</tr>
<tr>
<td>Vinyl acetate continuous feed</td>
<td>108</td>
</tr>
<tr>
<td>70% t-butyl peroxide (t-BHP)</td>
<td>0.40</td>
</tr>
<tr>
<td>1% Sodium formaldehyde sulfoxylate (SFS)</td>
<td>40.00</td>
</tr>
<tr>
<td><strong>Total (g)</strong></td>
<td><strong>368.41</strong></td>
</tr>
</tbody>
</table>

\(^{(1)}\) PVOH are presented on Table 2.2. The PVOH/Monomer= 10% by weight. 
\(^{(2)}\) VAc here was used as seed before continuous monomer and initiator feed.

### 2.2.2 Copolymerization of VAc and AAEM with Fully-hydrolyzed PVOH

In this work, the fully-hydrolyzed PVOH, Mowiol 28-99, was used as colloidal stabilizer to support the latex polymer particles during the master batch latex preparation; the functional monomer, acetoactoxy ether methacrylate (AAEM), was
copolymerized with VAc monomer and the AAEM-containing latex was used for the entire study. The master semi-batch recipe is shown in Table 2.4.

**Table 2.4: Master Batch Semi-batch Recipe of Copolymerization**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Master semi-batch process (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>164</td>
</tr>
<tr>
<td>10% Mowiol 28-99</td>
<td>225</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>0.175</td>
</tr>
<tr>
<td>Vinyl acetate as seed(2)</td>
<td>30</td>
</tr>
<tr>
<td>70% t-butyl peroxide (t-BHP)</td>
<td>0.25</td>
</tr>
<tr>
<td>1% Sodium formaldehyde sulfoxylate (SFS)</td>
<td>12.50</td>
</tr>
<tr>
<td>Vinyl acetate continuous feed</td>
<td>210</td>
</tr>
<tr>
<td>Acetoactoxy ether methacrylate (AAEM)</td>
<td>60</td>
</tr>
<tr>
<td>70% t-butyl peroxide (t-BHP)</td>
<td>1.00</td>
</tr>
<tr>
<td>DI water</td>
<td>99.00</td>
</tr>
<tr>
<td>1% Sodium formaldehyde sulfoxylate (SFS)</td>
<td>100</td>
</tr>
<tr>
<td><strong>Total (g)</strong></td>
<td><strong>900.43</strong></td>
</tr>
</tbody>
</table>

(1). PVOH/total monomer ratio = 7.5% by weight.
(2). VAc monomer here was used as seed. The rest of vinyl acetate and AAEM were blended together for continuous feed.
The master batch polymerization (semi-batch) process was carried out in a 2000 mL round glass kettle equipped with a condenser. Nitrogen purge was used before polymerization started. The polymerization was run at 75 °C for 8 hours with continuous monomer and redox initiator (t-BHP-SFS redox) feed. An anchor blade was used with agitation speed of 150 rpm. 20% AAEM based on total monomer was used in this recipe. The latex from this master recipe is the key latex which was used to study crosslinking kinetics and the determination of the crosslinking mechanism, water sensitivity studies and mechanical performance measurements.

The reason to choose fully-hydrolyzed PVOH, Mowiol 28-99, as stabilizer is that it exhibited the highest degree of hydrolysis compared to the other fully-hydrolyzed poly(vinyl alcohols) (PVOH) (see Table 2.2). It simplified the study of the grafting mechanism compared to partially-hydrolyzed PVOHs in VAc emulsion polymerization.

The partially-hydrolyzed PVOHs grafting mechanism during VAc polymerization was fully studied by Magallanes Gaudalupe and Bridgette Budhlall\textsuperscript{20,30}. Gonzalez reported that the vinyl acetate monomer will graft onto the PVOH stabilizer with or without chain transfer agents and the degree of grafting increases with monomer conversion. The rate of grafting reaction became lower after 37.5% conversion. Therefore, 37.5% conversion was taken as a base to draw a change in the slope of PVOH grafting. The grafting reaction happens on sites of methine group and methane group in PVOH.
Due to the absence of methane groups in fully-hydrolyzed PVOH (Mowiol 28-99), the grafting reaction should occur solely on the methine group in PVOH during polymerization. As mentioned above, Mowiol 28-99 and functional PVOH, Z-polymers and T330H, are all fully hydrolyzed PVOH.

Investigation of the grafting mechanism is not part of this thesis since the focus of this research is latex film water sensitivity, even though the degree of grafting may impact the film properties. Assuming that the fully-hydrolyzed PVOH (Mowiol 28-99) has a fixed degree of grafting during polymerization, then the trend of latex film water sensitivity of the crosslinked latex films shall not be affected.

The reason to choose AAEM functional monomer in polymerization is because the acetoacetyl functional groups present in AAEM is chemically reactive and AAEM-containing latex can be expected to be crosslinked by a variety of crosslinking agents. The molecular structure of AAEM is shown below:

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{CH}_2 = & \quad \text{C} - \text{O} - \text{C} \quad \text{H}_2 \cdot \text{CH}_2 \cdot \text{O} - \text{C} \cdot \text{H}_2 \cdot \text{C} \cdot \text{CH}_3
\end{align*}
\]

Boyars reported on the synthesis and characterization of two reactive functional latexes, AAEM-containing latex and amine-containing latex, which can be crosslinked at elevated temperature\textsuperscript{15}. The reactive methylene group (or acetoacetyl group) in the AAEM molecule is capable of many chemical reactions, such as reaction with isocyanate and melamine resin, Michael addition reaction\textsuperscript{31}, aldehyde reaction, enamine
reaction and chelating reaction\textsuperscript{32}. Hence, the latex film prepared from AAEM (minor monomer) is of great interest in this research.

Unlike other crosslinkers, the water-soluble crosslinkers, GH and GTDA, were chosen for crosslinking kinetics and mechanism studies. The water sensitivity of GH or GTDA crosslinked latex films is reported in Chapters 3 to 6.

The reasons to choose GH and GTDA as crosslinkers are because they are unique and different from polymeric crosslinkers. They are small molecules and water-soluble. Hence, they are easy to use and do not require high temperature for crosslinking reaction. The molecular structures of GH and GTDA are shown below:

\[
\begin{align*}
\text{CHO-CHO} & \quad \text{GH} \\
\text{CHO-CH}_2\text{CH}_2\text{CH}_2\text{-CHO} & \quad \text{GTDA}
\end{align*}
\]

The similarities between the two crosslinkers are that they are both difunctional and water-soluble. The difference between the two crosslinkers is different reactivity and different water affinity due to the presence of three methylene groups in GTDA. Their aqueous partitioning and reactivity are discussed in Chapters 4 and 5.

The PVOH solutions and corresponding latex surface tension are discussed in this chapter in section 2.3.1 and latex film water sensitivity of the non-crosslinked films is discussed in section 2.3.2.
2.3 Latex Properties and Latex Film Water Sensitivity

2.3.1 Latex Particle Size, Surface Tension and Viscosity

All PVOH solutions were prepared at 5% solid concentration for surface tension measurements and all of the homopolymers (Table 2.3) were diluted to 18% solids with DI water before measuring the surface tension. The surface tensions of latexes synthesized with different PVOHs were compared with values from their corresponding PVOH solution (5%). The latex particle sizes were measured by a dynamic light scattering instrument (Nicomp C370), Capillary Hydrodynamic Fractionation (CHDF) and Scanning Electron Microscope (SEM).

The batch and semi-batch polymerizations with Mowiol 28-99 as stabilizer and initiated with KPS resulted in significant coagulation. For example, the bottle polymerization reaction showed over 40% coagulum, and significant small grit was still present even after filtration through a 250 micron screen. This can be explained by the observation that fully-hydrolyzed PVOH cannot form a good pre-emulsion with vinyl acetate monomer. When the reaction starts, the large amount of monomer present leads to bulk polymerization and grafting onto PVOH in the aqueous phase because water-soluble initiator was used. A more oil-soluble initiator, such as t-butyl peroxide, is preferred in these reactions.

The semi-batch polymerization (Table 2.3) was carried out successfully under identical reaction conditions (75 °C for 2.5 hours) except that t-BHP-SFS was used as
initiator. Table 2.5 showed that the particle size and polydispersity of the latexes prepared from the five different PVOHs are fairly narrow with a range of 1.0-1.2. Latex viscosity (at 23 °C) was measured with a Brookfield Viscometer with spindle 4 at 20 RPM.

**Table 2.5:** Physical Properties of Latexes Prepared with Five PVOHs

<table>
<thead>
<tr>
<th>Latex</th>
<th>Conversion (%)</th>
<th>Viscosity (cps)</th>
<th>D_w (nm)</th>
<th>D_v (nm)</th>
<th>D_a (nm)</th>
<th>Polydispersity index(PDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mowiol 6-98</td>
<td>97.84%</td>
<td>75</td>
<td>386.2</td>
<td>411</td>
<td>336</td>
<td>1.15</td>
</tr>
<tr>
<td>Mowiol 10-98</td>
<td>98.89%</td>
<td>125</td>
<td>475</td>
<td>500</td>
<td>431</td>
<td>1.10</td>
</tr>
<tr>
<td>Mowiol 20-98</td>
<td>99.51%</td>
<td>500</td>
<td>408</td>
<td>412</td>
<td>399</td>
<td>1.03</td>
</tr>
<tr>
<td>Mowiol 28-99</td>
<td>100.00%</td>
<td>900</td>
<td>443</td>
<td>480</td>
<td>374</td>
<td>1.18</td>
</tr>
<tr>
<td>Mowiol 56-98</td>
<td>97.47%</td>
<td>1900</td>
<td>452</td>
<td>474</td>
<td>411</td>
<td>1.10</td>
</tr>
</tbody>
</table>

(1) All semi-batch runs were with the same recipe shown on Table 2.3.
(2) Particle size was measured by dynamic light scattering.

The t-BHP-SFS redox system worked well for fully-hydrolyzed PVOH stabilized emulsion polymerization. The latex films prepared from latexes synthesized with this redox system are smooth on glass surfaces with minimum aggregate formation. Latexes stabilized with PVOH usually have larger particle size than that from surfactant-stabilized latexes, which is caused by the absence of micelle formation with PVOH. The fully-hydrolyzed PVOH does not form a good pre-emulsion between water and monomer due to the absence of ester groups in PVOH. The viscosity of latex
increases with increasing molecular weight of PVOH. Latex viscosity can be easily adjusted by varying the molecular weight of the PVOH used (see Table 2.5). The master batch polymerization recipe is shown in Table 2.4. Polymerization kinetics are discussed in Chapter 3 (section 3.2.3).

Figure 2.4 shows a SEM micrograph of the master batch latex. The average particle size counted from multi SEM images is 313 nm ($D_w$) with a polydispersity index of 1.03. The smaller particle size obtained from the master latex batch compared to the results in Table 2.5 is due to a slower monomer feed rate and different measurements (the data in Table 2.5 are from dynamic light scattering). It can be seen the particle size polydispersities are all narrow in each case (see Table 2.5 and Figure 2.4).

Figure 2.1 shows that AAEM-containing latex film has similar water sensitivity to the PVAc homopolymer latex film. This can be explained by the fact that the AAEM molecule has three acetyl functional groups which makes the copolymer water sensitive, unless it is crosslinked.

The surface tensions of 5% PVOH solution and 18% solids latex were measured with a Fisher Autotensiomat surface tension meter (Model 215). The results are shown in Figure 2.5.
Figure 2.4: SEM Micrograph of AAEM-containing latex particles. Particle size by SEM (D_w=313 nm, D_n=303 nm, PDI =1.03).

Figure 2.5: Surface tension of aqueous solutions of 5% PVOH and 18% solids latex.
Except for Mowiol 10-98, the surface tension of the PVOH solutions slightly increase with increasing molecular weight (M6-98 < M20-98 < M56-98). Mowoil 28-99 exhibited a higher surface tension, but lower water absorption (see Figure 2.7), which may be attributed to its extremely low acetyl content (CH$_3$CO < 0.3% or hydrolysis > 99.7% hydrolysis) and high crystallites. The Mowiol 10-98 showed similar performance to Mowiol 28-99 which is not understandable. No detailed investigation on Mowiol 10-29 was carried out since this research program was mainly focused on Mowiol 28-99 in AAEM-containing latexes. Figure 2.7 shows the film water sensitivity of latexes prepared with different stabilizers (PVOH).

The structures of three fully-hydrolyzed PVOHs (Mowiol 28-99, Z-polymer and T330H) are shown below (Figure 2.6):
As mentioned previously (Section 2.1), films prepared from latexes synthesized with Z-polymers showed the lowest water sensitivities. However, latex film prepared from T-300H-containing latexes exhibited the highest water sensitivity (Figure 2.1). These results indicate that the surface chemistry on latex particles has a great impact on water sensitivity. Carboxylated PVOH on the latex surface made the film much more sensitive to water. The explanation for the effect of Z-polymer could be internal crosslinking and the high amount of grafting that occurred during the emulsion synthesis.

**Figure 2.6**: Structure of fully-hydrolyzed poly(vinyl alcohols).
polymerization process. The carboxyl functional groups –COO– on the latex particle surface can form a salt with metal ions. Such a salt is more soluble in the aqueous phase, hence, the latex film made from T330H is more water sensitive than the latex made from non-functional PVOH (Mowiol 28-99). The detailed mechanism of Z-polymer polymerization is not clear, and it is not part of the scope of this research.

Table 2.6 shows that carboxyl-functional PVOH (Nippon T330H) is quite different in surface tension than the other PVOHs (Table 2.6). The aqueous solution of T300H exhibits a much lower surface tension than that of Mowiol 28-99 due to the –COONa functional groups present in T330H. However, the surface tension of latex prepared with T330H is the same as that of Mowiol 28-99. Figure 2.5 and Table 2.6 both show that all of the latexes have similar surface tensions despite differences in their PVOH solution surface tensions. When most of the PVOH was grafted with PVAc during the polymerization, there is very little free PVOH left in the aqueous phase after the polymerization, so the surface tensions show little variation.

<table>
<thead>
<tr>
<th>Table 2.6: Surface Tension of PVOH Solution (5% in DI water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Hydrolysis</td>
</tr>
<tr>
<td>Surface tension of 5% PVOH aqueous solution (dynes/cm)</td>
</tr>
<tr>
<td>Latex surface tension (18% solids) (dynes/cm)</td>
</tr>
</tbody>
</table>
2.3.2 Latex Film Water Absorption

Latex films prepared from the formula in Table 2.3 (homopolymer) and Table 2.4 (master batch, AAEM-containing copolymer) were used for water sensitivity studies. Three grams of latex was placed in a custom-made round silicon mold (diameter 38 mm). The latexes were dried at 23 °C for 2 weeks at ambient atmosphere and then the dried haze-free films were placed in a desiccator for two more weeks before testing. This drying procedure was applied to crosslinker-containing latexes as well.

The 8 hr water absorption of the corresponding latexes prepared using PVOH as stabilizers (i.e., different degrees of polymerization) is shown in Figure 2.7. The film derived from latex containing Mowiol 10-98 shows a relatively low water uptake compared to Mowiol 6-98, Mowiol 20-98 and Mowiol 56-98. The reasons for the high surface tension in Mowiol 10-98 solution and the low water absorption of its corresponding latex film are not clear. It is believed that high surface tension materials usually have better hydrophobic behavior. Among the non-functional colloidal stabilizers, latex prepared with Mowiol 28-99 exhibited the lowest water absorption (21.6%) in the 8 hr water immersion test. In the remaining chapters, fully-hydrolyzed PVOH, Mowiol 28-99 only are studied in detail.
2.3.3 Latex Film Permeability

Latex film gas permeability was examined in order to determine the impact of the PVOH on dried film permeability. Latex film samples for the oxygen permeability test were prepared with an adhesive applicator and 50 mL wet thickness of latex was prepared from the desired side of applicator (note: the square adhesive applicator has different thickness on each side for desired wet thickness). The latex was drawn down on a clean Mylar film which was on top of a glass plate. The latex film can be made in even thickness with the adhesive applicator. The same drying process is as described in section 2.3.2.

The dried films (about 0.2 mm thickness) were then tested using oxygen gas to characterize their permeabilities. The supply oxygen pressure during each test was 200
KPa or 340 KPa and the test was carried out at room temperature (23 °C). The surface area of the testing cell (chamber) is 2.82 cm² with a depth of 1 cm. The principle of the test is to monitor the pressure differences (ΔP) in both sides of cell and then the ΔP was converted to a standard volume (ΔV) of gas in the lower pressure side based on the calibration. A detailed discussion can be found in Appendix 2. The oxygen permeation results are shown in Figure 2.8.

It is seen that Mowiol 10-98 is different from Mowiol 6-98, Mowiol 20-98 and Mowiol 56-98 in that: 1) The surface tension of the Mowiol 10-98 solution is higher than that of all three PVOHs (Figure 2.5); 2) water absorption of the latex film made from Mowiol 10-98 is lower than that of all the three PVOHs (Figure 2.7); 3) the oxygen permeability of the latex film made from Mowiol 10-98 is lower than all three PVOHs (Figure 2.8). It can be assumed that the lower water absorption and low permeability of the dried film can be attributed to the film morphology. However, the differences in absolute permeability values among all the latexes are small and their magnitude is in the same order of 3-5x10⁻⁶ [cm³(STP)/(cm².sec.atm)].
Figure 2.8: Latex film O₂ permeability as a function of PVOH type (200KPa at 23 °C).

It was reported that the PVAc polymer has a free volume of 85-90 (Å²)³³. The free volume in polyvinyl acetate film is much greater than the size of the oxygen gas molecule (only 1.2 Å in bond length). Figure 2.9 shows that the free volume of PVAc changes with temperature. For a fixed latex composition and for constant test conditions (200 KPa oxygen pressure, 23 °C), the oxygen solubility and diffusion coefficient is assumed to be the same for the dry films; hence, the permeability is constant (defined as Permeability = Solubility x Oxygen Diffusion Coefficient.)
Figure 2.9: Ortho-positronium life time and calculated hole size vs. temperature\textsuperscript{33}.

Oxygen permeability of the latex film obtained from the master latex batch, with and without GH and GTDA, were studied and the details can be found in Appendix 2.

2.4 Summary

The water sensitivity of PVAc-based latex films is controlled by the latex backbone polymer composition and the type of stabilizer. It was found that physical and copolymerization approaches to enhance water resistance for PVAc-based film were limited because of the extreme water sensitivity of PVAc and the hydrophilic nature of the latex particle surface. For example, the VAc-VV10 copolymer exhibited
20% water absorption after 8 hours water immersion. Higher VV10 didn’t show any positive impact (see Appendix 1); the 20% AAEM-containing VAc-AAEM copolymer latex showed 21.6% water absorption after 8 hr water immersion which is close to VAc-VV10 copolymer (see Figure 2.1), unless the VAc-AAEM latex is chemically crosslinked.

The use of t-BHP/SFS redox as initiator has been successfully used for VAc-AAEM emulsion polymerization where fully-hydrolyzed PVOH serves as stabilizer. The latex surface tension is almost the same even if the surface tension of the corresponding PVOH solution is different. The homopolymerization and AAEM-containing PVAc-based latexes exhibited very narrow particle size distributions in semi-batch and master latex batch processes. The latex film from the master latex batch (20% AAEM) shows not much difference in water sensitivity as compared to PVAc homopolymer which implies that AAEM does not sufficiently contribute to latex film water sensitivity unless a crosslinking reaction takes place.

2.5 References


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18. Kim, N. *Ph.D. Dissertation*, Lehigh University, **2003**.


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32. Eastman publication N-319C, Dec. **1999**.

Chapter 3

Crosslinked AAEM-Containing PVAc-Based Latex Film
Water Sensitivity

3.1 Introduction

Although poly(vinyl acetate) (PVAc) latex films display good aging characteristics and resistance to UV and oxidation, vinyl acetate polymers are water sensitive and brittle below ambient temperature ($T_g = 35^\circ$C). PVAc latexes are usually formulated with a coalescing aid or plasticizer to achieve proper flexibility. The PVAc homopolymer is the lowest cost polymer and exhibits good adhesion to many porous substrates such as wood and paper, as mentioned in Chapter 1. PVAc has been widely used in interior or exterior coatings and furniture and packaging applications. However, PVAc is very sensitive to water, even after the film has coalesced. Dried latex films can re-emulsify when exposed to water and this results in loss of adhesion to bonded substrates. PVAc polymer experiences significant hydrolysis which converts the PVAc into water-soluble poly(vinyl alcohol) (PVOH), especially under alkaline conditions (Chapter 1, Scheme 1). Although the nature of PVAc can’t be changed, its polymer structure can be modified chemically and physically in order to meet different
application demands in terms of water resistance as well as mechanical properties, such as modulus, water resistance, abrasion resistance, and surface gloss.

Reactive surfactant has been used in vinyl acetate copolymerization, and some modified colloidal stabilizers (i.e., functional PVOHs) have been mentioned for improving film water resistance. However, the effect of reactive surfactant on latex film water sensitivity has not been fully studied even their polymerization kinetics were explored by a variety of researchers. There is no reported fundamental research on the impact of the polymer structure and latex particle surface chemistry on the water sensitivity of PVAc-based films. Compared to the polymerization mechanism and film characteristics of other latexes such as polystyrene and poly(methyl methacrylate), the mechanism of PVAc polymerization is very different due to highly grafting reactions during polymerization. The mechanism of vinyl acetate polymerization actually falls between emulsion and suspension polymerization because PVOH is not a good emulsifier for forming micelles for vinyl acetate (VAc) monomer. This is especially true for fully-hydrolyzed PVOH due to the absence of acetate ester groups. PVAc latex and latex film characterization are distinguished from other polymers due to differences in its polymerization mechanism, its high degree of grafting during polymerization, its relationship of latex surface chemistry and polymer structure to film water sensitivity, and its latex hydrolysis and chemical crosslinking mechanism.

Chapter 2.1.1 introduced PVOH stabilizers, which have a large impact on latex film water sensitivity. Figure 3.1 shows the PVAc latex stabilized with Aerosol MA80-
I surfactant (sodium dihexyl sulfosuccinate with isopropanol) during polymerization. The latex exhibits different hydrolysis behavior as the level of stabilizer used in the recipe is changed. The higher the level of MA80-I, the higher the hydrolysis rate ("D" > "C" > "B"). “A” is fresh made latex with a 4.1% surfactant/monomer ratio and is an emulsion in appearance.

**Figure 3.1:** PVAc latex hydrolysis at 23 °C (bottle reactions at 60 °C for 12 hours, 20% solid). A: fresh latex prepared with 4.1% MA80-I; B: 6 month old latex with 4.1% MA80-I; C: 5 month old latex with 5.5% MA-80I and D: 3 month old latex with 6.8% MA80-MA.

Latex A, after 6 months of aging at 23 °C, has become water clear (see B). It is known that when over 80% of the latex is hydrolyzed, the PVAc starts to become water-soluble; hence, the latex loses resistance to water entirely.
Latexes prepared from fully-hydrolyzed PVOH (see Tables 2.1 and 2.2) showed that the type of colloidal stabilizer has a huge impact on latex film water sensitivity. Figure 3.2 (the same as Figure 2.1) shows the water sensitivity of latex films after immersion in water. Acetoacetylated PVOH (Z-polymers: Z-200 and Z-100) stabilized PVAc exhibited much lower water sensitivity in cast films while carboxylated PVOH (T330H) exhibited the highest water sensitivity in this group.

The results of water up-take and film volume expansion as a function of water immersion time are shown in Tables 3.1 and 3.2.

**Figure 3.2:** The impact of stabilizer on latex film water sensitivity as a function on immersion time in water (colloidal stabilizer/monomer ratio = 7.5%).
### Table 3.1: The Impact of Colloidal Stabilizers on Latex Film Water Absorption

<table>
<thead>
<tr>
<th>PVOHs</th>
<th>Z200/Z100</th>
<th>Z100</th>
<th>Mowiol-28-99</th>
<th>Mowiol-28-99&lt;sup&gt;(1)&lt;/sup&gt;</th>
<th>T330H</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 min weight increase (%)</td>
<td>5.00%</td>
<td>12.00%</td>
<td>21.00%</td>
<td>18.00%</td>
<td>70.00%</td>
</tr>
<tr>
<td>8 hrs weight increase (%)</td>
<td>7.00%</td>
<td>14.00%</td>
<td>24.00%</td>
<td>23.00%</td>
<td>63.00%</td>
</tr>
<tr>
<td>7 days weight increase (%)</td>
<td>8.00%</td>
<td>16.00%</td>
<td>28.00%</td>
<td>27.00%</td>
<td>62.00%</td>
</tr>
</tbody>
</table>

<sup>(1)</sup> 20% AAEM was used in the latex polymer and the others are VAc homopolymer.

### Table 3.2: Latex Film Volume Increase versus Water Immersion Time

<table>
<thead>
<tr>
<th>PVOH Type</th>
<th>Film wt. loss (%) in 7 days</th>
<th>Film volume increase (%) in 7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z200/Z100</td>
<td>0.40%</td>
<td>2.62%</td>
</tr>
<tr>
<td>Z100</td>
<td>0.40%</td>
<td>4.11%</td>
</tr>
<tr>
<td>Mowiol 28-99</td>
<td>0.90%</td>
<td>13.27%</td>
</tr>
<tr>
<td>Mowiol 28-99, 20% AAEM</td>
<td>1.20%</td>
<td>7.57%</td>
</tr>
<tr>
<td>T330H</td>
<td>7.60%</td>
<td>57.46%</td>
</tr>
</tbody>
</table>

### Table 3.3: Physical Properties of Fully-Hydrolyzed PVOHs

<table>
<thead>
<tr>
<th>PVOH</th>
<th>T300H</th>
<th>Mowiol 28-99</th>
<th>Z100</th>
<th>Z200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>Carboxyl</td>
<td>None</td>
<td>Acetoacetyl</td>
<td>Acetoacetyl</td>
</tr>
<tr>
<td>Hydrolysis (%)</td>
<td>&gt; 99%</td>
<td>99.3%</td>
<td>99.1%</td>
<td>99.1%</td>
</tr>
<tr>
<td>Degree of polymerization</td>
<td>2000</td>
<td>3300</td>
<td>500</td>
<td>1100</td>
</tr>
</tbody>
</table>
Films prepared from the Z100 and Z200 stabilizers exhibited the lowest weight loss and lowest film volume expansion compared to the other PVOHs (Table 3.2). This can be attributed to a high degree of grafting that occurred during polymerization. Latex films prepared with Mowiol 28-99, with or without AAEM present, exhibited similar water absorption and weight loss values after 7 days of water immersion. However, the film with AAEM present in the latex polymer backbone displayed lower swollen values than the film prepared from AAEM-free latex. This implies that the longer chain monomer (AAEM) present in the polymer backbone lowered the bulk $T_g$ of the latex films and therefore more molecules diffused between particles during the drying process, i.e., reaching a higher level of molecular entanglement. The sample with the worst water resistance was the latex prepared with carboxyl-functional PVOH (T330H); this film had the highest weight loss and highest swollen values. This can be attributed to the high water affinity behavior of carbonyl groups present in the latex film surface as discussed in Chapter 2. When a carboxyl-functional PVOH such as T330H was used as a stabilizer, more water-soluble polymer could be formed due to the high water sensitivity of the carboxyl functional groups. The swollen film may exhibit further hydrolysis during water immersion due to a higher surface area of water contact compared to the other latex films. The colloidal stabilizers (PVOH) used for latex preparation in Figure 3.2 are shown in Table 3.3.

Prescreening studies showed that the 20% AAEM-containing latex (master batch) and homopolymer latex, both stabilized with Mowiol 28-99, showed similar
water absorption (Figure 3.2). Water sensitivity was reduced when AAEM-containing latex was crosslinked with glyoxal (GH) and glutaric dialdehyde (GTDA) (Figures 3.16 and 3.18. Further details can be found in section 3.3.3 and in Chapters 4 and 5.

One of the objectives of this Chapter is to determine the amount of acteoactyl functional groups in Z-polymer. This finding is considered to be the AAEM composition to be incorporated into the latex for further crosslinking reactions. Another major objective of this Chapter is to study the water sensitivities of crosslinked and non-crosslinked latex films.

3.2: Review of Emulsion Polymerization and Master Batch Kinetics

3.2.1 Acetoacetyl Functional Group Determination in Z-Polymers (Z200 and Z-100)

The original plan was to study the impact of reactive colloidal stabilizers (Z-polymers) on water sensitivity in the presence of crosslinkers. However, it was surprising to find that latex prepared with Z-polymers as stabilizers exhibited very high water resistance without the use of external crosslinkers. The performance of Z-200 latex is similar to that of the neat PVAc film which was produced by solution polymerization (Figure 3.2). This finding shifted the focus of further crosslinking studies to only polymers containing the acetoacetyl functional monomer. (AAEM-containing polymer). Acetoacetyl functional groups reside on the latex particle surface when the latexes were prepared using Z-polymer as stabilizer, and the acetoacetyl
functional groups is present within the latex particle when the latex was prepared by copolymerizing AAEM and VAc monomers, if stabilized with nonfunctional Mowiol 28-99. Results from Figure 3.2, Tables 3.1 and 3.2 imply that the location of functional groups or the surface chemistry of latex particle have a large impact on the water resistance of PVAc-based films.

In order to determine the optimum level of functional monomer (AAEM) in the latex for crosslinking studies, it is important to know the concentration of acetoacetyl functional groups in the Z-polymers since these values are not reported by either the material suppliers nor reported in the literature. It was found that the 20% AAEM-containing latex exhibited much higher water sensitivity than that of the latex synthesized with Z-polymer as stabilizer even though the amount of acetoacetyl functional groups were the same (see Table 3.5).

Infrared (IR) analysis was used to characterize the functional groups present in the PVOH stabilizers. It was found that the T330H, Mowiol 28-99 and Z-polymer PVOHs exhibited very different IR absorption peaks between 1500-1850cm$^{-1}$ (Figures 3.3 and 3.4).
**Figure 3.3:** A full scan FTIR spectra of three different types of poly(vinyl alcohols).

**Figure 3.4:** FTIR spectra of three different types of poly(vinyl alcohols) between the wavelengths from 1500-1850 cm\(^{-1}\).
Since the IR spectra showed significant differences among the three types of PVOHs, the acetoacetyl functional groups could be quantitatively determined by the characteristic peak (near 1725 cm\(^{-1}\)) of the Z-polymer sample. Acetoacetyl functional groups in Z-polymer were determined through an infrared spectrum calibration curve generated from homopolymerization of AAEM with various PVOH/AAEM weight ratios.

A bottle emulsion polymerization method was used to prepare latexes using fully-hydrolyzed PVOH, Mowiol 28-99, as a stabilizer. Acetoacetylether methacrylate (AAEM) was used as the sole monomer during the emulsion polymerization (AAEM homopolymer) in order to create the calibration curve. The bottle polymerization recipes are shown in Table 3.4.
**Table 3.4: Batch Polymerization Design with Varied AAEM/PVOH Ratios**

<table>
<thead>
<tr>
<th>AAEM% (based PVOH)</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
<th>40%</th>
<th>45%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Mowiol 28-99 (g)</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>DI water (g)</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
<td>49.1</td>
</tr>
<tr>
<td>AAEM monomer (g)</td>
<td>0.25</td>
<td>0.50</td>
<td>0.75</td>
<td>1.00</td>
<td>1.25</td>
<td>1.50</td>
<td>1.75</td>
<td>2.00</td>
<td>2.25</td>
<td>2.50</td>
</tr>
<tr>
<td>DI water (g)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>KPS (g)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Calc. solid content (%)</td>
<td>5.3</td>
<td>5.6</td>
<td>5.8</td>
<td>6.0</td>
<td>6.3</td>
<td>6.5</td>
<td>6.7</td>
<td>6.9</td>
<td>7.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Conversion (%wt)</td>
<td>75.3</td>
<td>67.4</td>
<td>10.0</td>
<td>94.3</td>
<td>96.1</td>
<td>96.2</td>
<td>94.1</td>
<td>96.9</td>
<td>96.9</td>
<td>97.9</td>
</tr>
</tbody>
</table>

*The reactions were carried out in 200 mL round bottles for 12 hours in a tumbler in a constant temperature water bath at 60 °C (AAEM% = AAEM/PVOH by weight).

The FTIR absorption intensity was plotted against the concentration of AAEM to generate the calibration curve as shown in Figures 3.5 and 3.6.
Figure 3.5: FTIR spectra of the characteristic peaks obtained from latexes containing AAEM (the latex films were dried at 23 °C for one week before measurement).

Figure 3.6: Calibration curve of AAEM concentration in latex films.
The calibration curve was successfully used to determine the unknown concentration of acetoacetyl ester functional groups in the Z-polymers (Z-200 or Z-100). The calibration curve exhibited a linear relationship between the absorption intensity and the concentration of AAEM between 5-45% by weight ratio (based on stabilizer Mowiol 28-99). Based on the IR absorption and AAEM concentration calibration curve, the functional group concentration in Z-polymers was calculated with Eqs. 3.1 and 3.2 and the results are shown in Table 3.5.

Due to slight side chain structural differences between the Z-polymers and AAEM, the FTIR spectra obtained from Z-polymers showed two peaks at a wavelength near 1725 cm\(^{-1}\). The average of these two peak values were used in the calculations. The ratio of carbonyl ester groups in AAEM to the carbonyl groups in Z100 or Z200 is 3:2, as expected from their chemical structures (see structure in Chapter 2 section 2.2.2 for AAEM and Chapter 2 Figure 2.6 for Z-polymer, three ester groups in AAEM homopolymer per side chain *versus* two ester groups present in Z-polymer).

**Table 3.5: Functional Group in Z-polymers Based on IR Calibration Curve\(^{(1)}\)**

<table>
<thead>
<tr>
<th></th>
<th>FT-IR Peak 1</th>
<th>FT-IR peak 2</th>
<th>Average absorption</th>
<th>Calculated (%wt.) based on AAEM</th>
<th>% wt. based on actual functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z200</td>
<td>1.30</td>
<td>1.60</td>
<td>1.45</td>
<td>21.06%</td>
<td>14.91%</td>
</tr>
<tr>
<td>Z100</td>
<td>1.14</td>
<td>1.40</td>
<td>1.27</td>
<td>18.08%</td>
<td>12.71%</td>
</tr>
</tbody>
</table>

(1)AAEM mole mass is 214 g/mole and acetoacetyl functional group in Z100 and Z200 mole mass is 101 g/mole.
\[
\frac{\% \text{ wt. of AAEM in latex}}{\text{Molecular weight of AAEM}^3} = \frac{\% \text{ wt. of functional groups in latex}}{\text{Molecular weight of functional groups in PVOH}^2} \tag{3.1}
\]

Percentage of functional group in Z200 (Z100)

\[
= \frac{\% \text{ wt. of AAEM in latex} \times 3}{\text{Molecular weight of AAEM} \times 101} \times 101 \tag{3.2}
\]

Table 3.5 shows that the acetoacetylated PVOH (Z-100 and Z-200) contains 18-21\% AAEM equivalent monomer based on the calculation curve in Figure 3.6. That is, it contains between 12-15\% acetoacetyl functional group by weight. Z-200 shows a functional group content similar to Z-100 (Z-200 may be slightly higher), but Z-200 and Z-100 have different molecular weights (DP of Z-100 and Z-200 are 500 and 1100, respectively).

### 3.2.2 Emulsion Polymerization with Varied AAEM Level

It is believed that higher concentrations of AAEM in the latex particles could incorporate more crosslinker, and raise the crosslinking density. A series of semi-batch emulsion polymerizations with varied AAEM percentages in the latex were ran under conditions of continuous monomer and initiator feed (t-BHP-SFS redox) at 75 °C. The entire feed time was 2.5 hours. The polymerization process is described in Chapter 2.2.1, but with different monomer compositions. A master batch of 20\% AAEM-containing latex (900 grams) was carefully prepared for water absorption and
crosslinking studies. The monomer and redox initiator pair were fed at the same time at constant rates. The master batch polymerization was also carried out in a 75 °C water bath with precise temperature control with 0.1 °C deviation during an 8 hour reaction time instead of 2.5 hour reaction time. All latexes had a solids content of 36%. The AAEM-containing polymer structure is shown below and the latex properties are shown in Table 3.6.

Table 3.6: Latex Properties of Semi-Batch and a Master Batch Run*

<table>
<thead>
<tr>
<th></th>
<th>5% AAEM</th>
<th>10% AAEM</th>
<th>15% AAEM</th>
<th>20% AAEM</th>
<th>25% AAEM</th>
<th>30% AAEM</th>
<th>Master batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#51709</td>
<td>#52009</td>
<td>#52109</td>
<td>#52209</td>
<td>#52309</td>
<td>#52309B</td>
<td>#71009</td>
</tr>
<tr>
<td>pH</td>
<td>3.32</td>
<td>3.40</td>
<td>3.49</td>
<td>3.51</td>
<td>3.38</td>
<td>3.61</td>
<td>3.48</td>
</tr>
<tr>
<td>% Conversion</td>
<td>98.04</td>
<td>98.43</td>
<td>98.34</td>
<td>95.80</td>
<td>96.13</td>
<td>96.36</td>
<td>99.04</td>
</tr>
<tr>
<td>Latex surface</td>
<td>50.0</td>
<td>49.8</td>
<td>49.8</td>
<td>49.8</td>
<td>50.0</td>
<td>50.0</td>
<td>N/A</td>
</tr>
<tr>
<td>tension (dyne/cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D_w (nm)</td>
<td>428.4</td>
<td>444.3</td>
<td>463.4</td>
<td>460.6</td>
<td>512.0</td>
<td>576.3</td>
<td>309.8</td>
</tr>
<tr>
<td>D_n (nm)</td>
<td>276.0</td>
<td>278.3</td>
<td>297.5</td>
<td>274.3</td>
<td>265.3</td>
<td>264.2</td>
<td>279.9</td>
</tr>
<tr>
<td>PDI (D_w/D_n)</td>
<td>1.55</td>
<td>1.60</td>
<td>1.56</td>
<td>1.68</td>
<td>1.93</td>
<td>2.18</td>
<td>1.11</td>
</tr>
</tbody>
</table>

*Particle size was measured by CHDF and PDI stands for polydispersity index (D_w/D_n).
In the semi-batch process, latex particle size and polydispersity index (PDI) both increased with increasing AAEM dosage. This may relate to different reactivity ratios between AAEM and VAc. Latexes with and without AAEM functional monomer in the polymer backbone did not show much difference in water sensitivity (Figure 3.2). This implies that AAEM itself does not have much impact on water sensitivity unless the latex is crosslinked properly. In general, the polymerizations were successful with the selected initiator system. Particle size and particle size distribution of the master batch were much smaller than that of the small batch runs, which could be attributed to a slower monomer feed rate (8 hours versus 2.5 hours) and higher instant monomer conversion which overcame the reactivity difference between the two monomers. The slower feed rate allowed monomer polymerization on existing particles. This resulted in narrower particle size distributions and even distribution of functional groups inside of the latex particles. This is one of the important assumptions used for the derivation of the Shrinking-Core Model equation (Chapter 6). The reactivity of AAEM and Styrene or Methyl Methacrylate is reported in Table 3.7. However the reactivity ratio of AAEM-VAc was not reported.
Table 3.7: Reactivity of AAEM to Monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Reactivity ratio $r_1 = k_{11}/k_{12}$</th>
<th>Reactivity ratio $r_2 = k_{22}/k_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Methacrylate (MMA)</td>
<td>0.95</td>
<td>0.90</td>
</tr>
<tr>
<td>Styrene (St.)</td>
<td>0.60</td>
<td>0.70</td>
</tr>
</tbody>
</table>

It was observed that the AAEM can easily polymerize with methyl methacrylate to form random copolymers. However in this case of AAEM-Styrene copolymerization, the alternating monomer unit in the polymer structure is preferred because their reactivity ratios are much smaller than 1.0, being closer to 0.5.

While there may be interest in exploring the reactivity ratios between AAEM and VAc, it is less important in this work. In fact, the VAc-AAEM can be any ratio with no polymerization issues (see Table 3.6)

### 3.2.3 Kinetics of VAc-AAEM Master Batch Polymerization

A master batch kinetics study was then carried out. The scaled-up run profile and particle size changes with feeding time are shown in Figures 3.7 and 3.8. Overall conversion of the scaled-up run was higher than 99% and the weight average particle size ($D_w$) increased with feeding time. It was observed that lower conversion rates (93-96%) and broader particle size polydispersity (PDI) occurred in the first 1 to 4 hours of
polymerization. However, the conversion rate increased to 98-99% and the PDI became much narrower with further monomer feeding (Figures 3.7 and 3.8). The broader PDI and lower conversion rates of the first four hours of polymerization may be caused by the different reactivity of AAEM being introduced into the reactor after the VAc seed. The slower reaction rate resulted in a lower conversion which affected particle nucleation, and thus resulted in a higher level of free monomer in the reactor and a higher PDI. As the reaction time and volume in the reactor increased, the phenomena of broad PDI and high free monomer concentration disappeared. The final latex particle size measured by Capillary Hydrodynamic Fractionation (CHDF) closely matched the SEM particle size values (Chapter 2.3, Figure 2.4).

Figure 3.7: Conversion, solids content, and monomer consumption versus feeding time of master batch polymerization.
Section 3.2.1 revealed that there was about 20% acetoacetyl functional group in Z-polymer. This was why 20% AAEM monomer was used with vinyl acetate monomer in the master batch for further studies, such as film water sensitivity, crosslinking and oxygen permeation. The 20% AAEM-containing emulsion polymerization recipe and conditions were discussed in Chapter 2 (Table 2.3).

**Figure 3.8:** Weight-average particle size and particle size polydispersity index (PDI) versus feeding time of master batch polymerization. Particle size was run by CHDF.
3.3 Latex Film Water Sensitivity

3.3.1 Latex Film Preparations

The GH and GDTA crosslinkers were used with master latex and the crosslinker/AAEM mole ratio or weight percent based total solid content of latex were used for crosslinking studies. Water uptake samples were prepared with 3 grams of crosslinker-containing latexes in a silicon round mold (diameter = 38 mm). Tensile strength samples were prepared with 7-8 grams of latexes, with and without crosslinkers, in a larger silicon mold (diameter = 60 mm). Latex film samples for oxygen permeability and optical analysis were prepared with an adhesive applicator on the side of 50 mil thickness. Details of crosslinking film preparation and drying conditions were the same as described in Chapter 2 section 2.3.2.

20% and 30% AAEM-containing latexes were mixed with 10% ferrous sulfate and 28% aluminum chloride solutions with the desired mole ratios (e.g. [Fe$^{2+}$]/[AAEM] = 0.5 or 1.0, that is 50% or 100% based on the moles of AAEM in the latex). 25 grams of each latex were mixed with the iron solutions for 5 minutes with a stir bar before casting. The stable (aggregated free) mixtures then were cast as described in Chapter 2 section 2.3.2.

The latex film prepared from the master batch was used as a control to compare the crosslinked latex films for comprehensive studies, such as crosslinking density, water sensitivity, gas permeability, diffusion coefficient and mechanical performance.
3.3.2 Crosslinking Studies with Metal Ions

This section will give a brief exploration of using metal ions as crosslinkers in AAEM-containing latex. It was discovered that AAEM-containing latexes could be crosslinked with ferrous ion (Fe$^{2+}$) and the resulting crosslinked latex was pink in color due to its specific light absorption wavelength.

20% AAEM-containing latex was used for this ionic crosslinking study. Figure 3.9 shows that ferrous ion-crosslinked films exhibited lower water absorption than a control in early stage of immersion; the higher the mole ratio, the lower the water absorption that was observed. However, the lower mole ratio film (Fe$^{2+}$/AAEM = 0.5) demonstrated lower water absorption than the higher mole ratio film (Fe$^{2+}$/AAEM = 1.0) at extended water immersion times. This was caused by excess free ions present in the sample since only a portion of the AAEM functional groups were on the latex particle surface for the crosslinking reaction.
Figure 3.9: Effect of Fe$^{2+}$ ionic crosslinked film on water up-take. 25g 20% AAEM-containing latex was mixed with 0.50 grams FeSO$_4$.7H$_2$O (Fe$^{2+}$/AAEM = 0.5); 25g 20% AAEM containing latex mixed with 1.0 gram FeSO$_4$.7H$_2$O(Fe$^{2+}$/AAEM = 1.0).

30% AAEM-containing latex was also used for ionic crosslinking studies and the results are shown in Figure 3.10. Films with a higher crosslinker mole ratio (Fe$^{2+}$/AAEM = 0.5) displayed less water absorption than a lower mole ratio (Fe$^{2+}$/AAEM = 0.25) films. This implies that the 0.25 mole ionic latex film did not form enough or as many crosslinking sites as did the 0.50 mole ionic latex.
Figure 3.10: Effect of iron crosslinked film on water uptake. 25 g 30% AAEM containing latex mixed with 8 g 10% FeSO₄•7H₂O solution (50% mole ratio of Fe⁺²/AAEM=0.5); 25 g 30% AAEM containing latex mixed with 4 g 10% FeSO₄•7H₂O solution (25% mole ratio of Fe⁺²/AAEM=0.25).

Figures 3.9 and 3.10 demonstrated the lowered water sensitivity of crosslinked PVAc-based films when the mole ratio is at 0.5. This ratio is close to the theoretical Fe⁺²/AAEM value (1:2) since 1 mole ferrous ion will need 2 moles AAEM for crosslinking. When 30% AAEM-containing latex was used, the extended water absorption time of iron crosslinked films were still lower than the control film, which differed from the 20% AAEM-containing latex results. It can be explained that the key for better water resistance is sufficient ion-AAEM crosslinking in this system.
In order to prove the chemical reaction between the ion and acetoacetyl-containing latex, a model reaction of straight AAEM monomer and ferrous ion (Fe^{2+}) was prepared. The equivalent number of moles of AAEM and Fe^{2+} were mixed together and agitated for 3 days, and a deep pink color developed. The gelled material was rinsed 5 times with DI water in order to remove any unreacted ions. The sample was centrifuged to remove the water, and then the remaining pink material was washed with water two times, and then further washed with 0.2 HCl solutions 3 times (20 mL/each time). The final product was a pink solid, insoluble in acetone, THF and DMSO solvents. This confirmed that the crosslinking reaction had taken place. Unlike the small molecular complex (ferrous acetylacetonate), the insoluble pink solid (Fe^{2+}/AAEM-containing latex) complex did not show a crystal structure from x-ray diffraction experiments. This is because the AAEM-iron complex could not form symmetric structures like the small molecular complexes present in ferrous acetylacetonate (Figure 3.15).

A mixture of iron (Fe^{2+}) and AAEM-containing latex (mole ratio 0.50) was stirred at 50 °C for one hour and a pink color was observed. The crosslinked latex was then isolated from the liquid phase and washed with water a few times in order to remove entrapped latex particles (the coagulum was kept for further study). The precipitated coagulum then was cleaned with 20 mL acetone two times, and the residue was soaked in 20 mL 0.02 N HCl solution to remove any inorganic iron (e.g. Fe(OH)_3, or FeSO_4). The HCl wash was repeated one more time and then the residue was washed
with DI water again. The insoluble pink particles were then dried for Energy Dispersive Spectroscopy (EDS) elemental analysis. Figures 3.11 and 3.12 give the EDS spectra and Figure 3.13 is the TEM image of the coagulum.

**Figure 3.11:** EDS spectrum of latex-ferrous ion complex after cleaning with acetone (ferrous ion detected).
Figure 3.12: EDS spectrum of latex-ferrous ion complex after cleaning with acetone and then with HCl solution (ferrous ion detected).
Figures 3.11 and 3.12 both show significant ferrous ion peaks which indicate a complex was formed between AAEM-containing latex and ferrous ion. There is very little chance that the EDS spike represents free ions in the sample since extensive acetone and HCl solution extraction was performed prior to the EDS experiment.

The water sensitivity of aluminum ion (Al$^{3+}$ from aluminum chloride) crosslinked latex film was also studied. However, crosslinked structures between the AAEM-containing latex and aluminum ions could not be proved from the test. Unlike the ferrous ion crosslinked film, the aluminum-cured film exhibited 3 times more water
absorption than the latex control, as seen in Figure 3.14 (20% AAEM-containing latex was used, $\text{Al}^{3+/\text{AAEM}} = 0.50$).

![Figure 3.14](image_url)  

**Figure 3.14**: Effect of $\text{Al}^{3+}$ ionic crosslinked film in water up-take (top curve: $\text{Al}^{3+/\text{AAEM}}=0.50$ with 20% AAEM-containing latex; bottom curve: 20% AAEM containing latex as control).

One possible explanation for this observation is that the aluminum ion (from $\text{AlCl}_3$ solution) cannot form strong chemical bonds with AAEM-containing latex, even though the aluminum acteylacetonate molecular complex does exist (Figure 3.15) $^4$. The increase in water absorption discovered when using aluminum ions as the crosslinker with AAEM-containing latex suggests a weak bond strength between the acetoacetyl functional groups and aluminum ions, as well as the bulky size of
aluminum ions. The complex decomposed when the cured film was placed in water; the aluminum ions leached into the water phase and left ‘holes’ which provided a pathway for water penetration into the film. Thus, a much a high degree of water absorption occurred.

Using metal ions as crosslinkers was only considered as a screening test and the crosslinking mechanisms are beyond the scope of this research.

Figure 3.15: Metal complexes with the small molecule acetylacetonate. Right: Aluminum acetylacetonate; Left: Ferrous acetylacetonate.

3.3.3 Crosslinking with Glyoxal (GH) and Glutaric Dialdehyde (GTDA) Crosslinkers.

As mentioned in Chapter 2.2.2, the reactive methylene group in AAEM monomer can be subjected to many chemical reactions\(^3,5,6,7,8\). Screening studies found that the master batch latex (20% AAEM functional monomer) exhibited similar water sensitivity as AAEM-free latex from water absorption experiments (Figure 2.2).
However, after proper crosslinking, the water sensitivity of AAEM-containing latex film improved. The AAEM-containing latex can react with a variety of crosslinkers such as ferrous ion or with primary amine\(^9\), which can be used for crosslinking with an amine functional polymer.

Aldehydes and dialdehydes, such as glyoxal (GH) and glutaric dialdehyde (GTDA), have been used as crosslinkers in latex applications to improve water resistance for hydroxypropyl cellulose\(^{10,11}\). The mechanism of this crosslinking is the reaction of reactive hydroxyl functional groups in cellulose with aldehyde from GH and GTDA.

As mentioned above, fundamental crosslinking reactions between AAEM-containing PVAc based latex and GH or GTDA have not been found in the literature. According to AAEM-containing latex and dialdehyde reactions, the theoretical crosslinker level, by weight percent or by mole ratio, can be calculated based on Eqs. 3.3a, 3.3b and 3.4.

\[
A \text{ (mole ratio)} = \frac{\text{Mole of crosslinker}}{\text{Mole of AAEM}}
\]

\[
= \frac{\% \text{ Conc. of crosslinker} \times \text{wt of crosslinker (g)}}{M_w \text{ of crosslinker (g/mole)}}
= \frac{\% \text{ AAEM in latex} \times \text{wt of latex (g)}}{M_w \text{ of AAEM (g/mole)}} \tag{3.3a}
\]
or \[ A(\text{mole ratio}) = \frac{\% \text{Conc of crosslinker} \times \text{wt of crosslinker (g)}}{\frac{M_M \text{of crosslinker (g/mole)}}{\% \text{AAEM in latex} \times \text{wt of latex (g)}}} \] (3.3b)

\[
\% \text{wt. of crosslinker} = 100A \frac{M_M \text{of crosslinker}}{M_M \text{of AAEM}} \times \frac{\% \text{ of AAEM in latex by wt}}{\% \text{ solid content of latex}} \] (3.4)

It is known that the molecular weight of AAEM is 214.12 g/mole; the master batch latex solids content is 36.0%; the AAEM concentration by weight is 6.67%; the molecular weight of GH and GTDA are 58 and 100 g mol\(^{-1}\), respectively and the concentrations of GH and GTDA are 40% and 50% by weight respectively. Thus, the relationship between weight percentage and crosslinker/AAEM mole ratio (A) can be represented by Eqs.3.5 and 3.6.

For glyoxal (GH):

\[
\text{Wt\% of crosslinker} = 100A \frac{58}{214.12} \times \frac{6.67\%}{36\%} = 5A \] (3.5)

For glutaric dialdehyde (GTDA):

\[
\text{Wt\% of crosslinker} = 100A \frac{100}{214.12} \times \frac{6.67\%}{36\%} = 8.65A \] (3.6)
The dry latex films were placed into 23 °C DI water and the weight changes of the films were measured over time. Three films at each condition were used in order to determine standard deviation of each measurement.

### 3.3.3.1 Latex Crosslinked with Glyoxal (GH)

GH was one of the primary crosslinkers used in these studies. The procedures of crosslinked film preparation were as described in 3.3.1. 40% GH solution reagent was mixed with master batch latex with mole ratios designated at 0.5, 1.0, 2.0, 3.0 and 4.0. The water absorption versus immersion time is shown in Figure 3.16. The GH/AAEM mole ratio or weight percentages (based on total solids) are calculated in Table 3.8.

**Figure 3.16:** Water uptake for GH-crosslinked films (GH/AAEM mole ratio: A=0.5, B=1.0, C=2.0, D=3.0 and E=4.0). Water absorption of the control latex after 8 hours was 23.09%.
When the mole ratio of GH/AAEM was 0.5, the crosslinked films exhibited the lowest water absorption after 8 hours of immersion (Figures 3.16 and 3.17). The water absorption of crosslinked latex films increased with increases of the GH/AAEM mole ratio from 0.5 to 2.0. However, when the GH/AAEM mole ratio is higher than 2 (e.g., $D = 3.0$ mole and $E = 4.0$ mole), the apparent water absorption dramatically decreased. The extended water immersion results exhibited the same trend (Figure 3.17 and Table 3.9). The mole ratio of GH/AAEM = 0.5 latex showed the best water resistance performance for the extended water immersion test. The mole ratio of 0.5 is equal to the GH to AAEM theoretical stoichiometric reaction. It must be noted that the decrease in water absorption with increasing GH level in the latex films is unexpected. This behavior is different from GTDA-crosslinked films shown in Figure 3.19. The

<table>
<thead>
<tr>
<th>Latex (#71009)</th>
<th>Wt. of GH (g)</th>
<th>Mole of AAEM in latex</th>
<th>Mole of GH used</th>
<th>Mole ratio of GH/AAEM</th>
<th>GH to latex solids (%wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5g latex</td>
<td></td>
<td>1.56 x 10^{-2}</td>
<td>0.78 x 10^{-2}</td>
<td>0.5</td>
<td>2.50%</td>
</tr>
<tr>
<td>1.13</td>
<td>2.25</td>
<td>1.56 x 10^{-2}</td>
<td>1.0</td>
<td>5.00%</td>
<td></td>
</tr>
<tr>
<td>4.50</td>
<td>3.10 x 10^{-2}</td>
<td>2.0</td>
<td>10.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.75</td>
<td>4.66 x 10^{-2}</td>
<td>3.0</td>
<td>15.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.00</td>
<td>6.21 x 10^{-2}</td>
<td>4.0</td>
<td>20.00%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
unexpected observation from GH-crosslinked film in water absorption is discussed in Chapters 4 and 5.

Table 3.9: GH-Crosslinked Latex Film Water Absorption and Net Weight Change versus Immersion Time

<table>
<thead>
<tr>
<th>GH/AAEM Mole Ratio</th>
<th>8 hrs wt. Change (%)</th>
<th>32 hrs wt. Change (%)</th>
<th>12 Days wt. Change (%)</th>
<th>Volume Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.000</td>
<td>23.09%</td>
<td>26.60%</td>
<td>48.40%</td>
</tr>
<tr>
<td>A (0.50)</td>
<td>0.500</td>
<td>13.29%</td>
<td>14.81%</td>
<td>15.58%</td>
</tr>
<tr>
<td>B (1.00)</td>
<td>1.000</td>
<td>15.00%</td>
<td>18.38%</td>
<td>19.17%</td>
</tr>
<tr>
<td>C (2.00)</td>
<td>2.000</td>
<td>16.50%</td>
<td>17.94%</td>
<td>14.49%</td>
</tr>
<tr>
<td>D (3.00)</td>
<td>3.000</td>
<td>11.04%</td>
<td>15.14%</td>
<td>13.12%</td>
</tr>
<tr>
<td>E (4.00)</td>
<td>4.000</td>
<td>9.77%</td>
<td>15.43%</td>
<td>9.17%</td>
</tr>
</tbody>
</table>

(1) Data of volume changes was over 12 day immersing test. 20% AAEM containing latex was used for studies and crosslinker-free latex was used as control.
Figures 3.16 and 3.17 and Table 3.9 show that due to chemical crosslinking, the presence of GH at any level decreased the water absorption compared to the PVAc-based control film. GH-crosslinked films also underwent less volume change than did the control film after 12 days of water immersion (Figure 3.21). It must be noted that the volume decrease with increasing GH level in latex after 12 days immersion is also unexpected. Studies and explanation for their phenomena are given in Chapters 4 and 5.
3.3.3.2 Latex Crosslinked with Glutaric Dialdehyde (GTDA)

As with GH, GTDA was also investigated as another primary crosslinker. A 50% GTDA solution was mixed with latex from the master batch and the mole ratios of GTDA/AAEM were 0.125, 0.25, 0.50, 1.0, 2.0 and 3.0. The water absorption versus immersion time is shown in Figure 3.18. The GTDA/AAEM mole ratio and weight percentage based on total solids are calculated in Table 3.10.

![Figure 3.18: Water uptake of GTDA-crosslinked films (GTDA/AAEM mole ratio varied F=0.125, G=0.25, H=0.50, I=0.75 and Q=3.00). Curves (J=1.0, K=1.25, L=1.50, M=1.75, N=2.0 and P=2.5) are not displayed. These curves lay between curves I and Q. Water absorption of the control latex after 8 hours was 23.09%.](image-url)
Table 3.10: Mole Ratio of GTDA/AAEM and Weight Percent in Latex

<table>
<thead>
<tr>
<th>Latex (71009)</th>
<th>GTDA (g)</th>
<th>Mole of AAEM in latex</th>
<th>Mole of GTDA</th>
<th>Mole ratio of GTDA/AAEM</th>
<th>GTDA to latex solids (%wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g latex</td>
<td>0.39</td>
<td>1.56 x 10^{-2}</td>
<td>1.95 x 10^{-3}</td>
<td>0.125</td>
<td>1.08%</td>
</tr>
<tr>
<td></td>
<td>0.78</td>
<td></td>
<td>3.80 x 10^{-3}</td>
<td>0.250</td>
<td>2.16%</td>
</tr>
<tr>
<td></td>
<td>1.80</td>
<td></td>
<td>8.98 x 10^{-3}</td>
<td>0.58</td>
<td>5.00%</td>
</tr>
<tr>
<td></td>
<td>3.60</td>
<td></td>
<td>1.80 x 10^{-2}</td>
<td>1.15</td>
<td>10.00%</td>
</tr>
<tr>
<td></td>
<td>5.40</td>
<td></td>
<td>2.70 x 10^{-2}</td>
<td>1.73</td>
<td>15.00%</td>
</tr>
<tr>
<td></td>
<td>7.81</td>
<td></td>
<td>3.90 x 10^{-2}</td>
<td>2.50</td>
<td>21.69%</td>
</tr>
<tr>
<td></td>
<td>9.37</td>
<td></td>
<td>4.68 x 10^{-2}</td>
<td>3.00</td>
<td>26.03%</td>
</tr>
</tbody>
</table>

As seen in Figure 3.18, water absorption of the film decreased during the 8 hour test when the GTDA/AAEM mole ratio was increased from 0.125 to 0.75 moles. However, further increases of GTDA in the latex did not follow the same absorption trend. For instance, the film with a GTDA/AAEM mole ratio of 3.0 (Q) exhibited higher water absorption value than did films prepared with mole ratios of 0.75, 1.0, 1.5, 2.0 and 2.5 (the shaded area in Figure 3.18). This will be discussed in section 3.3.3.3. The overall trend of increased water absorption with immersion time is reasonable, since PVAc-based polymer water uptake increases over time. No matter what crosslinking density, latex films will absorb more moisture over time (Figure 3.18). The lowest amount of water sensitivity is achieved when the GTDA/AAEM mole ratio is between 0.25-0.50; ideally at 0.25 (see Figure 3.19). In the range of GTDA/AAEM 0.125 and 0.25, water uptake is independent of extended immersion time which is very
useful information for potential industrial applications. This implies that there is an optimized mole ratio level for crosslinking reactions. The mole ratio of 0.25 is close to the GTDA to hydroxyl functional group ratio in latex, not in the theoretical GTDA to AAEM stoichiometric reaction ratio. The extended time water absorption and latex film volume expansion data are shown in Figure 3.19 and Table 3.11.

**Figure 3.19:** Extended time for water uptake for GTDA-crosslinked films (GTDA/AAEM mole ratio varied from 0.125 to 3.0).
Table 3.11: GTDA-Crosslinked Latex Films Water Absorption and Net Weight Change versus Immersion Time(1)

<table>
<thead>
<tr>
<th>GTDA to AAEM Mole Ratio</th>
<th>GTDA to AAEM Mole Ratio</th>
<th>8 hrs wt. Change (%)</th>
<th>32 hrs wt. change (%)</th>
<th>12 days wt. change (%)</th>
<th>Volume Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.000</td>
<td>23.09%</td>
<td>26.60%</td>
<td>48.40%</td>
<td>25.35%</td>
</tr>
<tr>
<td>F(0.125)</td>
<td>0.125</td>
<td>12.30%</td>
<td>12.74%</td>
<td>13.40%</td>
<td>5.51%</td>
</tr>
<tr>
<td>G(0.250)</td>
<td>0.250</td>
<td>9.36%</td>
<td>11.26%</td>
<td>11.30%</td>
<td>5.10%</td>
</tr>
<tr>
<td>H(0.500)</td>
<td>0.500</td>
<td>7.03%</td>
<td>10.01%</td>
<td>12.31%</td>
<td>7.14%</td>
</tr>
<tr>
<td>I(0.750)</td>
<td>0.750</td>
<td>4.95%</td>
<td>9.41%</td>
<td>13.00%</td>
<td>7.78%</td>
</tr>
<tr>
<td>J(1.000)</td>
<td>1.000</td>
<td>4.42%</td>
<td>8.48%</td>
<td>14.48%</td>
<td>8.46%</td>
</tr>
<tr>
<td>K(1.250)</td>
<td>1.250</td>
<td>4.22%</td>
<td>7.90%</td>
<td>15.24%</td>
<td>8.26%</td>
</tr>
<tr>
<td>L(1.500)</td>
<td>1.500</td>
<td>4.38%</td>
<td>7.82%</td>
<td>15.30%</td>
<td>9.83%</td>
</tr>
<tr>
<td>M(1.750)</td>
<td>1.750</td>
<td>4.97%</td>
<td>9.27%</td>
<td>20.11%</td>
<td>13.73%</td>
</tr>
<tr>
<td>N(2.000)</td>
<td>2.000</td>
<td>5.00%</td>
<td>9.18%</td>
<td>22.23%</td>
<td>14.61%</td>
</tr>
<tr>
<td>P(2.500)</td>
<td>2.500</td>
<td>5.48%</td>
<td>10.17%</td>
<td>26.21%</td>
<td>18.53%</td>
</tr>
<tr>
<td>Q(3.000)</td>
<td>3.000</td>
<td>6.01%</td>
<td>11.19%</td>
<td>32.80%</td>
<td>20.95%</td>
</tr>
</tbody>
</table>

(1) Data of volume changes (increasing) was 12 days after immersion. 20% AAEM containing latex (crosslinker-free) was used as control.

Figures 3.18 and 3.19 and Table 3.11 show that all GTDA-crosslinked films provided lower water absorption and volume gain compared to the control film, but that films prepared with GTDA/AAEM mole ratios between 0.125 and 0.50 exhibited the lowest increase in water absorption and swollen size. This confirms the effectiveness of
the GTDA crosslinking reactions in this latex. As expected, the crosslinked films showed significant expansion over an extended immersion time. However, as mentioned before, this behavior does not match the results of GH-crosslinked films (Figures 3.17 and 3.19, Tables 3.9 and 3.11). Further discussion and explanation are presented in the next section.

3.3.3.3 Comparison of GH-and GTDA-Crosslinked Films

Figure 3.20 shows the performance of both GH and GTDA crosslinkers with the AAEM-containing latex prepared from fully-hydrolyzed PVOH (Mowiol 28-99). While the presence of either crosslinker decreased water absorption, the inclusion of GTDA resulted in lower water sensitivity compared to the use of GH. This data points to GTDA as a more effective crosslinker for this latex system than GH. The kinetic and mechanism studies and discussion follow in Chapters 4 and 5.
Figure 3.20: Comparison of the impact crosslinker on latex film water sensitivity (top curve is 20% AAEM latex film as control; A: GH-crosslinked; B: GTDA- crosslinked film and bottom curve is neat poly(vinyl acetate) (PVAc) prepared from solution polymerization with molecular average weight 220,000 gmol⁻¹.

Theoretically, the effective crosslinking reaction will occur if both sides of the aldehyde molecules reacted with methylene groups from the AAEM units and only in this case could network structures form. Thus, significant improvements of the water resistance or mechanical performance of latex films are expected. The theoretical mole ratio of crosslinker to AAEM is 0.5 since one molecule of crosslinker can react with two methylene groups. This ratio is fairly true for GH-crosslinked systems, and generally supported by experimental data (see 3.3.3.1). This result may imply that GH
diffused into the latex particles during mixing and the crosslinking loci were located inside of the particles. If GH does not diffuse into the particles, then the crosslinked film should not reach its minimum water sensitivity with a 0.5 mole ratio. For GTDA/AAEM latex films, lowered water sensitivity can be obtained with a mole ratio less than the theoretical 0.50 (between 0.125 and 0.25). The reaction kinetic and mechanism are fully studied in Chapter 5. GTDA-crosslinked films exhibited an increase in water absorption with increasing of the mole ratio under extended water immersion conditions when the mole ratio is greater than 0.25 (Figure 3.19). The extra crosslinker remaining in the latex can actually contribute to water sensitivity because it is water-soluble, which explains any performance decreases as the mole ratio increases (if present in excess). This implies that some GTDA may not have fully reacted or fully crosslinked. Although partially-bonded GTDA presented in the latex matrix may allow moisture to penetrate the film, the fully-reacted GTDA portion within the latex imparts a tight network structure, and thus the crosslinked films can swell over immersion time without loss to the film integrity.

Figure 3.21 gives a comparison between the volume expansion of GH and GTDA-crosslinked latex under the same conditions. When the GH/AAEM mole ratio is increased over 0.5, the latex volume change is generally decreased. This phenomenon is the opposite trend compared to the GTDA-crosslinked films. While the crosslinker mole ratios for both GH and GTDA were increased in the same increments (from 0.5 to 3.0), the water swelling results of both films were very different.
Figure 3.21: Latex volume expansion versus crosslinker/AAEM mole ratio (calculated after 12 days of water immersion).

GH-crosslinked films exhibited a significant weight loss during water immersion experiments when compared to the control, while GTDA-crosslinked latex films only had a minimal weight loss, even at a high mole ratio of GTDA/AAEM (see Figure 4.3). Referencing Chapter 4.4, it may be suggested that GH did not produce as tight a crosslinking structure as GTDA. The explanation for this behavior can be attributed to the reversible crosslinking reaction. Additional discussing can be found in Chapters 4 and 5.
3.4 Summary

Screening studies showed that latex film water sensitivity can be greatly affected by the type of colloidal stabilizer used. Latex prepared with Z-polymer (PVOH) as colloidal stabilizer demonstrated great water resistance even without any crosslinker present. This better performance in water sensitivity may be attributed to grafting and the surface chemistry of the latex particles.

Water sensitivity of latex containing AAEM can be greatly improved through proper chemical crosslinking using ferrous ion or organic water-soluble crosslinkers, such as glyoxal (GH) and glutaric dialdehyde (GTDA). Water absorption of GH and GTDA-crosslinked films were studied in more detail, and the behavior of the two water-soluble crosslinkers were found to be very different. GH is a less effective crosslinker than GTDA for AAEM-containing latex films (Figure 3.20).

For extended water immersion tests, the lowest water sensitivity of GH-crosslinked latex film fell short of the theoretical stiochiometric reaction (GH/AAEM = 0.50); the lowest water sensitivity of GTDA-crosslinked latex film was with molar ratio of GTDA/AAEM between 0.125-0.50. It matched the stoichiometric reaction between GTDA and –OH functional groups in latex (GTDA/OH ≈ 0.25).

Water absorption after extended immersion does not increase with an increase of GH/AAEM molar ratio (i.e., > 0.5 in Figure 3.17), which is an abnormal situation. Unlike GH-crosslinked films, the GTDA-crosslinked films exhibited higher water
absorption after extended immersion time, when the GTDA/AAEM molar ratio is greater than 0.25 (Figures 3.19). It was found that the more GH was present in the film, the less volume changes were found for extended immersion times (Figure 3.21). However, the GTDA-crosslinked films didn’t demonstrate the same results. Conversely, the higher the level of GTDA in latex film, the higher was the observed volume expansion. The GH-latex crosslinking reaction was suggested as a reversible crosslinking reaction while the GTDA-latex crosslinking reaction is considered an irreversible crosslinking reaction (see Chapters 4 and 5).

3.5 References

4. Aluminum acetylacetonate CAS number is 13963-57-0 and ferrous acetylacetonate CAS number is 14024-17-0.


Chapter 4

Diffusion Coefficients and Crosslinker Partitioning Studies

4.1 Introduction

It was reported that amide groups in latexes can act as functional sites because they are readily capable of reacting with glyoxal (GH) or other dialdehydes to form methylol compounds. Under acidic conditions, the dialdehydes react further with methylol compounds to form crosslinking sites. The reaction of GH with polyacrylamide polymer was reported by Coscia et al.\textsuperscript{1}. The reaction of GH with polyamide polymer is used as a wet strength agent for paper manufacturing. Although GH is excellent for paper, the GH-crosslinked products do not meet many of the water resistance requirements in applications because paper is an extremely water-sensitive material and treatment with GH will only impart limited water resistance\textsuperscript{2}. In the process of wood hardening, the crosslinking of cellulose with GH is essential for improving wood characteristics. The chemical intermediate glyoxal, which strengthens the treated wood and protects it from moisture, is an efficient starch and cellulose crosslinker. Glutaric dialdehyde (GTDA) has been reported as a crosslinker for protein-related latex\textsuperscript{3}. GTDA reacts with amino-functional groups present in proteins very effectively and forms permanent bonds. It is also reported that GTDA has been used
with fully-hydrolyzed PVOH in permanent hydrophilic column coatings for capillary electrophoresis\(^4\). However, no report was found for PVAc polymer as crosslinker.

The overall goal of this research project is to gain a more fundamental understanding of PVAc-based latex film water sensitivity. The scope of the entire research, as mentioned in Chapter 1, includes the behavior of the water-soluble crosslinker, crosslinker partitioning in an AAEM-containing latex, crosslinking reaction kinetics and mechanism, properties of crosslinked latex films such as water sensitivity and mechanical performance, kinetic models, and Shrinking-Core Model (SCM) and scaling theory application. In this Chapter, crosslinked latex films, via GH and GTDA, were further studied in regards to the water sensitivity of the film, swelling of the film, partitioning upon mixing in latex, and its behavior in leaching experiments. The water diffusion coefficient and GH diffusion coefficient are determined from experiments.

Water molecules are relative small and in the liquid and solid states are strongly associated through hydrogen bond formation. This combination of features distinguishes it from the majority of organic penetrants. Whereas the diffusion coefficient generally increases with concentration for an organic vapor, marked decreases have been observed with water in several polymers\(^5\). Values for the enthalpy of formation of hydrogen bonds in the range 3.4 to 6.6 kcal mole\(^{-1}\) have been obtained\(^6\). As a result, strong localized interactions may develop between the water molecule and
suitable polar groups in polymers. On the other hand, in relatively non-polar polymer materials, clustering or association of the absorbed water occurs\textsuperscript{5}.

Kishimoto \textit{et al.}\textsuperscript{7} reported that the water diffusion coefficient in PVAc polymer was constant under isotherm condition (2.60 x 10\textsuperscript{-8} cm\textsuperscript{2}s\textsuperscript{-1} at 23\textdegree{}C). This value agreed with the value determined from sorption (desorption) rate curves both above and close to the glass transition temperature of the PVAc. The diffusion coefficient value changes with temperature (Figure 4.1)\textsuperscript{8}. At higher temperatures, higher diffusion coefficients were observed. For instance, the water diffusion coefficient, D\textsubscript{e}, is 1.20 x 10\textsuperscript{-7} cm\textsuperscript{2}s\textsuperscript{-1} at 40 \degree{}C, which was reported by Long and Thomas\textsuperscript{9}. This value agreed with findings by Kishimoto.

Assuming that Fick’s second law of diffusion is applicable, the relationship of the diffusion coefficient, D\textsubscript{AB}, concentration of water in a film, C\textsubscript{A}, at a given point of interest Z and time t are given in Eq 4.1. The Z is the distance to the center of film. Theoretically, D\textsubscript{AB} can be obtained since C\textsubscript{A}, C\textsubscript{A0} and Z can be measured.

\[
\frac{C\textsubscript{A} - C\textsubscript{A0}}{C\textsubscript{A0}} = 1 - \text{erf}(\frac{Z}{\sqrt{2D\textsubscript{AB} t}})
\]

(4.1)
Figure 4.1: Reprint from book “Diffusion in Polymers”. Concentration dependence of the diffusion coefficient for water-PVAc. ○ = diffusion from sorption (desorption) experiments; ● = diffusion from steady-state permeation experiment.

However, it is very difficult to find a solution for Eq 4.1 due to its complexity. For the initial linear water absorption versus immersion time, Gurney-Lurie charts for Unsteady-State transport in a large flat slab is an alternative way to determine the diffusion coefficient $D_{AB}$ (see Figure 4.2). Four dimensionless parameters are shown in Equations 4.2 to 4.5:
Concentration change $Y$:

$$Y = \frac{C_A - C_{A,0}}{C_{A,s} - C_{A,0}} \quad (4.2)$$

Relative time $X_D$:

$$X_D = \frac{D_{AB} \ t}{x_1^2} \quad (4.3)$$

Relative position $n$:

$$n = \frac{x}{x_1} \quad (4.4)$$

Relative resistance $m$:

$$m = \frac{K_c}{h x_1} \quad (4.5)$$

where $C_A$ is the concentration of water in the film at a given time; $C_{A,0}$ is the concentration of water in the film at time zero, $C_{A,s}$ is the equilibrium concentration of water in the film, $D_{AB}$ is the water diffusion coefficient, $x_1$ is a characteristic length which is half the thickness of the latex film if the midpoint of film is the point of interest; $m$ is the ratio of the convective mass transfer resistance to internal molecular resistance; $K_c$ is convective mass transfer resistance, and $h$ is internal molecular resistance.

For water absorption studies, $m$ is zero since the internal molecular resistance is extremely high, hence, $m = 0$. If only the center concentration of the film is of interest, then $n = 0$. Instead of solving Eq 4.1 in terms of the four dimensionless parameters
above, the Gurney-Lurie charts (Figure 4.2) were used for water diffusion coefficient and GH diffusion coefficient determinations.

![Figure 4.2: Gurney-Lurie charts for diffusion coefficient measurement](image)

4.2. **GH and GTDA UV Absorption-Concentration Calibration Curves**

Latexes used in the crosslinking study were from the master latex batch as described in Chapter 2.2. Latex film preparations were described in Chapter 2 and
Chapter 3. All crosslinked films were cured at ambient temperature for two weeks and then the cured films were put in desiccators for two more weeks to remove any adsorbed moisture (to make sure the films were dry) before experiments, such as the water uptake test, leaching test etc were carried out.

GH and GTDA showed different efficiencies in reducing the water sensitivity for PVAc-based latex films, which can be seen in Figure 3.20. After extended immersion time, the latex films were dried at 60 °C for 3 days and then conditioned in a dessicator for 14 days. It was surprising that GH-crosslinked films showed significant weight loss as shown in Table 4.1 and Figure 4.3. The higher the amount of GH in the film, the higher was the observed weight loss. Conversely, the GTDA-crosslinked films after extended water immersion times exhibited a minimal weight loss which is close to the control latex (Tables 4.1 and Figure 4.3).
Table 4.1: Weight Loss of GH- and GTDA-Crosslinked Latex Films

<table>
<thead>
<tr>
<th>GH/AAEM mole ratio</th>
<th>12 Days wet wt. loss (%wt)</th>
<th>GTDA/AAEM mole ratio</th>
<th>12 Days wet wt. loss (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.19%</td>
<td>0.00</td>
<td>1.19%</td>
</tr>
<tr>
<td>0.50</td>
<td>2.26%</td>
<td>0.125</td>
<td>1.01%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
<td>1.17%</td>
</tr>
<tr>
<td>1.00</td>
<td>4.48%</td>
<td>0.50</td>
<td>1.09%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75</td>
<td>0.64%</td>
</tr>
<tr>
<td>2.00</td>
<td>13.99%</td>
<td>1.00</td>
<td>0.64%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.25</td>
<td>0.39%</td>
</tr>
<tr>
<td>3.00</td>
<td>16.18%</td>
<td>1.50</td>
<td>0.39%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.75</td>
<td>1.01%</td>
</tr>
<tr>
<td>4.00</td>
<td>20.28%</td>
<td>2.00</td>
<td>0.95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.50</td>
<td>1.35%</td>
</tr>
</tbody>
</table>
Figure 4.3: Weight loss of GH and GTDA cured films (after 12 days immersion).

In order to address what occurs during the immersion of these films, a UV technique was used to determine if there was partitioning to the aqueous phase during water immersion experiments.

The characteristic UV absorption peak of GH is at 191 nm and GTDA UV absorption is at 235 nm. To generate UV absorption-concentration calibration curves, a series of GH and GTDA samples at different concentrations were prepared with DI water, and the data are shown in Figures 4.4 to 4.7.
Figure 4.4: UV absorption intensity versus wavelength (nm). GH concentration in DI water: (a) 83 ppm, (b) 167 ppm, (c) 500 ppm, (d) 833 ppm, (e) 1167 ppm, (f) 1500 ppm, (g) 1833 ppm, (h) 2167 ppm and (i) 2500 ppm.
Figure 4.5: Calibration curve of UV absorption intensity versus GH concentration in DI water (83-2500 ppm).

It is seen that a linear relationship of GH concentration VS. UV adsorption in the range between 100 and 2500 ppm was established. This calibration curve was used to interpret the GH leaching experiment in section 4.4.
Figure 4.6: UV absorption intensity *versus* wavelength (nm). GTDA concentration from bottom to top: 25-800 ppm.
**Figure 4.7:** Calibration curves of UV absorption intensity versus GTDA concentration in DI water (top curve: 25-1400 ppm, bottom curve: 50-800 ppm).

- **GTDA in AAEM containing latex**

**Upper Graph:**

- Equation: \( y = -2E-10x^3 - 9E-07x^2 + 0.0036x + 1.2061 \)
- \( R^2 = 0.999 \)

**Lower Graph:**

- Equation: \( y = 0.0026x + 1.32 \)
- \( R^2 = 0.988 \)
The GTDA concentrations were prepared between 25 and 1400 ppm for the preparation of the calibration curve. Figure 4.7 shows two calibration curves which can be used for GTDA partitioning studies (see section 4.4). In Figure 4.7 (top) the polynomial curve is valid for concentrations between 25 and 1400 ppm. It was found that the UV absorption-GTDA concentration plot was linear only in the range of 50 to 800 ppm, which is shown in Figure 4.7 (bottom). Both calibration curves in Figures 4.7 (1) and 4.7 (2) were used for calculations in section 4.5 and Chapter 5.2. However, the linear curve is more reliable in normal practice.

4.3. GH and GTDA Crosslinked Film Water Diffusion Coefficients

Chapter 3 (Figures 3.16 and 3.18) showed plots of water absorption versus immersion time for the GH- and GTDA-crosslinked films. It was seen that the extent of water absorption in a film increased with immersion time. The saturated water absorptions were attained at close to 500 minutes immersion (this assumption was used for the diffusion coefficient calculation). The plot of initial water absorption versus immersion times was linear as shown in Figure 4.8.
Figure 4.8: Initial water absorption curve (water absorption versus immersion time).

In terms of the Gurney-Laurie Charts described previously in section 4.1, the diffusion coefficient ($D_e$) can be calculated. The calculated water diffusion coefficients are listed in Table 4.2. Here $D_e = X_D \chi_1^2 / t$, $\chi_1 = 0.45$ mm, $X_D$ is from the Gurney-Laurie Chart which is depending on the base $Y$ value calculated from Eq 4.2 and $t$ is immersion time (s).

It was found that the water diffusion coefficients in crosslinked polymer films were independent of the crosslinkers that were used and were also independent of the crosslinker concentrations in the films. This phenomenon can be explained from the observation that the water absorption coefficient is controlled by both crosslinking
density (or driving force) and absorption rate. For low crosslinked films, the water absorption rate is high (higher slope), but the driving force is low (less resistance to diffusion through the film). On the other hand, the highly crosslinked films have low water absorption rates, but high driving force (higher resistance for mass transport). Hence, the values of water absorption coefficient are similar for all of the crosslinked films. The experimental data (3.08-3.53 x 10⁻⁷ cm²/s) are about 12-14 times higher than the results reported by Kishimoto et al.⁷ with a value of 2.60 x10⁻⁸ cm²/sec⁻¹ (calculated from Figure 4.1).

**Table 4.2: Diffusion Coefficient (Dₑ) of Water through Crosslinked Films**

<table>
<thead>
<tr>
<th>Crosslinked films</th>
<th>GH/AAEM</th>
<th>Water diffusion coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (no crosslinker)</td>
<td>0.0</td>
<td>3.97 x 10⁻⁷</td>
</tr>
<tr>
<td>GH/AAEM</td>
<td>2.0</td>
<td>3.08 x 10⁻⁷</td>
</tr>
<tr>
<td>GH/AAEM</td>
<td>4.0</td>
<td>3.30 x 10⁻⁷</td>
</tr>
<tr>
<td>GTDA/AAEM</td>
<td>1.0</td>
<td>3.53 x 10⁻⁷</td>
</tr>
<tr>
<td>GTDA/AAEM</td>
<td>2.0</td>
<td>3.24 x 10⁻⁷</td>
</tr>
</tbody>
</table>

It needs to be noted that Kishimoto’s result was obtained from neat PVAc film which is different from the latex films used in this study. As discussed in Chapter 3 (Figure 3.2), neat polymer showed much lower water sensitivity than any latex films since there is no water sensitive stabilizer present in the films. The neat PVAc film cast from solution has higher molecular entanglements than polymers in latex films.
Therefore, the higher water diffusion coefficient from the crosslinked latex films compared to neat polymer films is understandable. Actually, these values are only 12-14 times different. The results may imply that the surface chemistry in latex particles plays an even larger role to latex film water resistance.

Without crosslinker, the films prepared from the master latex batch showed only slightly higher diffusion coefficientse than crosslinked films (Table 4.2 and Figure 4.9). The diffusion coefficient of GTDA-crosslinked films slightly decreased with the amount of GTDA present in the film, but the value leveled out after the mole ratio exceeds 0.5. This can imply that the GTDA/AAEM mole ratio 0.25 gives the densest film or the lowest water sensitivity in film, which is in agreement from the water absorption experiment described in Figure 3.19.
Figure 4.9: GTDA-crosslinked film water diffusion coefficient (run at 23 °C).

It has to be noted that the diffusion coefficient is affected by temperature. At 40 °C, the neat $D_e$ for PVAc was $1.20 \times 10^{-7}$ cm$^2$/s, which is about 5 times higher than the $D_e$ value of $2.60 \times 10^{-8}$ cm$^2$/s at 23 °C (calculated from Figure 4.1). The differences of diffusion coefficients from experiments are small, in the range of $3-4 \times 10^{-8}$ cm$^2$/s.
4.4. GH Leaching Test and Diffusion Coefficients

Figure 4.3 showed that the GH-crosslinked film had a large weight loss after extended water immersion times which raises the question if GH reacts with AAEM-containing latexes. The answer is positive since Figures 3.16 and 3.20 exhibited lower water absorption effects compared to a control. Another question is what component was lost during the water immersion experiments: was it part of the polymer lost due to hydrolysis or due to GH leaching out of the crosslinked films?

There are two extreme conditions which could occur: (1) all of the GH was bonded to functional groups presented in latex. For an excess of GH, it is assumed that at least one end of the molecule was bound to the latex or trapped well inside the latex film, or (2) all GH didn’t crosslink with the functional polymer at all. Hence, the GH molecule remained free and was leached out of the film when the film was immersed in water. Figure 4.10 shows the two weight-loss curves which present the two extreme conditions. It must be noted that none of these extreme conditions will exist since (i) the fact that the data (Figures 3.16 and 3.20) indicated that the crosslinking reaction between GH and latex existed and the crosslinking reaction was also confirmed from the higher lap shear strength of the films with varying GH/AAEM ratios (Chapter 6, Table 6.1), and (ii) UV detection showed significant free GH in DI water during the leaching test (see this section below).
Figure 4.10: Latex film weight loss vs. the GH/AAEM in the latex (top curve is from experiments which represents the maximum weight loss, and bottom curve is the calculated weight loss by assuming that all GH was leached out of the film in the extended water immersion experiments.

The “Minimum Weight Loss” (dotted line in Figure 4.10) represents calculated data which are based on the assumption that all GH molecules are leached out of the film during the immersion test. The “Maximum Weight Loss” data was from direct experiment assuming that all GH had bonded with the latex functional groups. The actual weight loss of the crosslinked films was definitely higher than the minimum weight loss value and lower than the maximum weight loss value (shadow area).
In order to prove what was leaching out of the GH-crosslinked films during water immersion, dry films (about 1.0-2.0 g each), which were prepared as described in Chapter 3.3, were placed in 100 grams of DI water and a small magnetic stir bar was used for agitation during the leaching test (not in contact with the film). Samples from the water phase were taken periodically for UV analysis. Table 4.3 showed that 81.96% GH was leached out from GH/AAEM = 2.0 crosslinked film and 66.31% GH from GH/AAEM = 4.0 crosslinked film in 4 hours of water immersion.

**Table 4.3:** GH Concentration versus Leaching Time in Water

<table>
<thead>
<tr>
<th>Crosslinked films</th>
<th>GH/AAEM mole ratio 2.0</th>
<th>GH/AAEM mole ratio 4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original sample weight (g)</td>
<td>1.7336</td>
<td>1.3350</td>
</tr>
<tr>
<td>Weight of GH in crosslinked films (g)</td>
<td>0.1378</td>
<td>0.2661</td>
</tr>
<tr>
<td>GH conc. in films (%wt.)</td>
<td>9.96</td>
<td>19.93</td>
</tr>
<tr>
<td>Amount of GH diffused into water after 4 hours</td>
<td><strong>81.96%</strong></td>
<td><strong>66.31%</strong>(1)</td>
</tr>
</tbody>
</table>

(1) This value is not comparable since the GH concentration in water was too high which is out of the calibration range (actual value should be larger).

Leaching experiments proved that the GH diffused from the films into water during the immersion test. The minimum weight loss values calculated from GH-crosslinked films were slightly higher than the values obtained from latex control (crosslinker-free films, see Figure 4.10). This occurred because of higher porosity in these films after GH was leached out. The higher the porosity in the latex films, the higher surface area for water attack. Therefore, higher weight loss was observed.
The true polymer weight loss after 12 days of the water immersion test was the shadowed area between the two curves in Figure 4.10. GH diffused into water due to the weak chemical bond or free GH molecule in the film and entropy is the driving force. Due to the high weight loss value of the GH-containing latex films, the effectiveness of GH as a crosslinker in this system is questionable.

In terms of the calibration curve showed in Figure 4.5, the leaching experimental data were calculated, and are shown in Figure 4.11. The linear relationship of concentration (ppm) versus leaching time between UV absorptions of 0.2 and 0.5 can be used for determination of the GH diffusion coefficient. The GH diffusion coefficients for the crosslinked films are given in Table 4.4.
Figure 4.11: GH cured film leaching experiments. (top): UV absorption versus leaching time; (bottom): GH concentration (ppm) versus leaching time.
The top curve in Figure 4.11 represents UV absorption versus leaching time, and the bottom curve shows the GH concentration in DI water versus leaching time, which was calculated from the calibration equation in Figure 4.5. The negative data in Figure 4.11 (bottom curve) occurred because the calculated range fell outside of calibration curve and hence are not reliable (i.e., concentration is less than 83 ppm). Like the water diffusion coefficient calculation, the GH diffusion coefficient can also be determined by Gurney-Laurie Charts. The calculated GH diffusion coefficient data are listed in Table 4.4.

**Table 4.4: GH Diffusion Coefficient of Crosslinked Films**

<table>
<thead>
<tr>
<th>Crosslinked films</th>
<th>Mole ratio</th>
<th>Water diffusion coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GH/AAEM</td>
<td>2.0</td>
<td>8.78 x 10⁻⁸</td>
</tr>
<tr>
<td>GH/AAEM</td>
<td>4.0</td>
<td>7.22 x 10⁻⁸</td>
</tr>
</tbody>
</table>

The GH diffusion (leaching) coefficient is about 4-5 times smaller than the water diffusion coefficient (Tables 4.2 and 4.4). The smaller leaching coefficients are caused by low concentrations of GH in films and high resistance for GH to diffuse out to the aqueous phase compare to water diffusing into the films.

Finally, it needs to be noted that the two types of diffusion coefficients are different. Determination of water diffusion is done by measuring how quickly water
can diffuse into the crosslinked film, while GH diffusion represents the GH molecule diffusing from the crosslinked film to the water phase. Actually, mass transport takes place at the same time. However, in the initial water immersion, the rate of GH migration to water is slower than water diffusion to the film since the GH was bound to the latex functional groups (at least a large portion was chemically bound). This assumption is reasonable since Figure 4.11 showed no significant concentration of GH in water after 50 minutes of immersion (too low and beyond the calibration range). However, in this time window, the water diffusion coefficient tests were already finished (Figure 4.8). This significant GH concentration in water after the crosslinked films become re-wet suggested that the GH crosslinking reaction is a reversible chemical crosslinking reaction. The reversible crosslinking reaction may be caused by the weak bonding between GH and the functional group in the latex due to internal bonding stress between rigid aldehyde (CHO-CHO) and latex. The higher modulus of the GH-crosslinked film explains the rigidity of GH in latex films (see Chapter 6, Table 6.1). However, the linkage is weak and reversible when the crosslinked films were immersed in water due to the internal stress. This is an entropy controlled process. The reversible crosslinking kinetics can be found in Chapter 5.

4.5 Crosslinker Partitioning Studies

As discussed in section 4.2, the concentration of GTDA and GH in the aqueous phase of the latex can be determined with an UV/visible spectrophotometer. The
GTDA has a characteristic absorption at wavelength 235 nm, and GH has a strong absorption at wavelength 191 nm, respectively. Hence the calibration curves from section 4.2 were used here for partitioning studies. This is a meaningful study since the results will help to understand where the crosslinkers go after they are mixed with latex. In other words, it is necessary to determine if the chemical crosslinking reaction occurs on the particle surface or inside of the particles.

4.5.1 GTDA Aqueous Phase Partitioning Studies-Direct UV Technique

25 g of 20% AAEM-containing PVAc latex from the master batch was mixed with various GTDA/AAEM mole ratios and each time 1 gram of the mixture was taken and diluted with DI water (1 gram mixture with 19 grams or 39 grams of DI water depending on the GH concentration) and then immediately centrifuged at 12,000 rpm for 10 minutes. This experiment was to determine the equilibrium time and concentration of GTDA in the two phases after mixing. The top clear aqueous solution obtained from centrifugation was collected for determination of GTDA present in the aqueous phase.

Using the equation from Figure 4.7 (UV calibration curves), the GTDA partitioning was calculated and the results are shown in Figure 4.12.
**Figure 4.12**: GTDA distribution/partition after mixing with latex. (top) GTDA partitioning in water phase; (bottom) GTDA partition in latex particles.
It is clear that 40% GTDA remains in the water phase (with 60% adsorbed onto the particle surface), and is independent of the GTDA/AAEM mole ratio. In the case of GTDA/AAEM = 0.5, the UV absorption was beyond the calibration range (too low), hence, water phase partitioning data are not reliable. The adsorption rate of GTDA was fast and the time to achieve equilibrium concentration in the aqueous phase was less than 5 minutes. GTDA partitioning in the two phases remains the same for up to 4 hour of mixing. The results imply that GTDA is primarily absorbed on the latex particle surface. Otherwise, the concentration of GTDA should decrease with mixing time if GTDA was absorbed into latex particles and if the reaction takes place inside of the latex particles.

The partitioning of GTDA in the aqueous phase is independent of the GTDA/AAEM mole ratio (Figure 4.12). Chapter 2, Figure 2.4 showed the particle size of the master batch latex ($D_w \approx D_n = 313$ nm, PDI =1.02) and this value can be used to calculate the surface coverage of GTDA. Assuming that each GTDA molecule has an area of 20 square angstroms, in the case of GTDA/AAEM = 1.0, the coverage of GTDA on the particle surface is saturated, with a calculated value of 110% coverage (see Table 4.5).
Table 4.5: Theoretical GTDA Coverage on Latex Particle Surface (GTDA/AAEM mole ratio =1:1)

| Total number of (25 g) latex particles (36% solid) | 6.37E+14 |
| Total area of (25 g) latex surfaces (cm²) | 2.37E+06 |
| Per GTDA molecule _surface area (cm²) | 2.00E-15 |
| GTDA/AAEM mole ratio | 0.50 | 1.00 | 2.00 |
| Weight of 50% GTDA | 0.78 | 1.56 | 3.11 |
| Total number of GTDA molecules | 1.10E+21 | 2.19E+21 | 4.37E+21 |
| Total GTDA area (cm²) | 2.19E+06 | 4.39E+06 | 8.74E+06 |
| Number of molecules of GTDA per latex particle | 1.72E+06 | 3.44E+06 | 6.86E+06 |
| Actual number molecules of GTDA per latex particle (60%) | 1.03E+06 | 2.07E+06 | 4.12E+06 |
| Actual coverage by GTDA per latex particle | 56% | 110 % | 220% |

Assuming density of latex particle is 1.0 g/cm³; all GTDA was absorbed on particle surface and 20 Å² surface areas per GTDA molecule.

4.5.2 GH Aqueous Phase Partitioning Studies –Direct UV Technique

A valuable tool for the detection of parts-per-trillion mixing concentration of glyoxal has been developed by the Keutsch group at the University of Wisconsin-Madison¹¹. GH is the smallest α-dicarbonyl which has a relatively low atmospheric lifetime of around 1.3 hours (not stable in its pure form)¹². Hence, commercial GH is always prepared as an aqueous solution, typically 40% in water. Due to the relatively dynamic nature of GH in air, measurements of aerosol GH are taken using the Madison Laser-Induced Phosphorescence (LIP) instrument. A more detailed explanation of the
LIP instrument was provided by Huisman, et al. The LIP technique was developed to determine the aerosol GH concentration among a deciduous forest canopy and its accuracy is up to 6 ppb. Several factors shape the creation and destruction of GH in the atmosphere. Some of the parameters that are recognized to have the greatest influence on the production of GH include OH radical and ozone concentration. The principal of using LIP for GH detection is based on an excitation pathway that allows the molecule to absorb energy, enter an excited singlet state, by colliding with other molecules and entering a unique triplet state, and finally releasing a photon to reassume its ground state. The Madison LIP instrument utilizes a very specific range of wavelengths surrounding 400.25 nm, which provides an energetic pathway for GH molecules to enter that excited singlet state. Following excitation, a partial relaxation allows GH to cross the threshold to a di-radical triplet state with a lifetime of approximately 10 microseconds at 100 Torr. At this point, around a third of the originally excited molecules will remain in the triplet state, while the others will settle to lower energetic levels.

It is also reported that the GH concentration can also be determined by a UV/visible technique at a wavelength of 405 nm in terms of 3-methyl-2-benzoethiazolinone hydrazone hydrochloride (MBTH); this procedure was designed for free GH detection in modified cellulose. There are several situational dependent methods which can be used to determine GH concentrations. The main instrument used
in this study was a conventional UV/visible spectrophotometer due to its accessibility and suitability to testing conditions.

For the GH sample preparation, 25 grams 36% solids latex (20% AAEM) was mixed with 40% GH with varying GH/AAEM mole ratios. The mixture was stirred with a magnetic stir bar in a covered beaker at room temperature. For the partitioning study, the mixtures were agitated for a period of time (15 minutes up to 4-5 hours). 1 gram sample of the mixture was removed periodically and diluted with 19 g or 39 g DI water and the diluted suspension was placed in a centrifuge tube and centrifuged for 10 minutes at 12,000 rpm. The top clear liquid serum was taken for direct UV test to determine crosslinker partitioning in the aqueous phase.

The calibration curve in section 4.2 in Figure 4.5 was used for the GH partitioning calculation. The data from direct UV technique were shown in Figures 4.13 and 4.14.
**Figure 4.13:** Glyoxal concentration changes (distribution or partitioning) after mixing with latex (GH/AAEM mole ratio: 0.5, 1.0 and 2.0).

**Figure 4.14:** Glyoxal (GH) concentration changes after mixing with latex (GH/AAEM = 2.0 mole). Upper line is GH-free latex as control.
It was found that the GH concentration in the aqueous phase is not constant since its UV absorption intensity changes with mixing time. There was no equilibrium concentration between the water phase and latex particles. Figure 4.13 or Figure 4.14 show the concentration of GH decreasing with mixing time, which is very different from GTDA in latex. This implies that the GH was consumed over time by a chemical reaction with the AAEM-containing polymers. The reaction may occur in the latex particles, on the particle surface, or in the aqueous phase if any reactive materials are present. It was surprising that the clear aqueous solution (in latex serum) from GH-free latex control, exhibited high UV absorption values with an average UV absorption value of 0.99 (straight line in Figure 4.14, bottom). The high UV absorption value from the control latex implies that water-soluble material that was present in the clear serum separated by centrifugation. When this serum was used as the UV reference in GH partitioning studies, a serious error occurred since negative UV absorption value present. Theoretically, all of the GH absorption curves were supposed to be above the straight line (control) and also to be positive values because of the presence of GH in the aqueous phase. In other words, the GH present in the aqueous phase should exhibit higher absorption values compared to the control latex.

The GH present in the water phase was consumed quickly due to chemical reactions with AAEM-containing latex (AAEM or OH functional groups). However, it is difficult to explain the negative absorption data shown in Figures 4.13 and 4.14, even through a linear relationship between absorption and mixing time was observed (except
for the curve of GH/AAEM = 0.5, these data from the lower ratio of GH/AAEM = 0.5 was less reliable because the concentration of GH in the aqueous phase falls in the lower limits of the calibration range in Figure 4.5). It needs to be noted that the absolute absorption curves in Figure 4.14 can not be compared since they are obtained from different dilutions during the test. However, the trend of direct UV absorption data *versus* mixing time is correct individually.

Table 4.6 lists the components which were used during the master latex batch preparation. It is seen that a very low concentration of poly(vinyl alcohol) (0.1% in aqueous phase), sodium acetate (0.01%) and tert-butyl peroxide (0.006%) all had high UV absorption at wavelength of 191 nm. Hence, all of these materials if located in the aqueous phase will interfere with the actual GH determination. Their UV absorption curves are shown in Figure 4.15.

**Table 4.6: Water Soluble Material Used in Latex Preparation**

<table>
<thead>
<tr>
<th>Water-soluble material in formula</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol) (PVOH)</td>
<td>2.5000%</td>
</tr>
<tr>
<td>Sodium acetate (NaAc)</td>
<td>0.0194%</td>
</tr>
<tr>
<td>Tert-butyl peroxide (t-BHP)</td>
<td>0.139%</td>
</tr>
<tr>
<td>Sodium formaldehyde sulfoxylate(SFS)</td>
<td>0.125%</td>
</tr>
</tbody>
</table>
Figure 4.15: UV absorption of water-soluble materials (Mowiol 28-99, poly(vinyl alcohol)), sodium formaldehyde sulfoxylate-SFS, tert-butyl peroxide-t-BHP and sodium acetate-NaAc).

All three materials PVOH, t-BHP and NaAc have absorptions at 191 nm. Therefore, a direct UV technique cannot be used since GH UV absorption was in the same absorption wavelength. It can be assumed that free PVOH has the most effect since there is always some free PVOH present in the aqueous phase. According to Noma Kim’s findings\textsuperscript{16}, when the PVOH/monomer ratio was between 5-10%, the water-soluble grafted PVOH present in the serum will remain at about 38% for the conventional and miniemulsion polymerization system (PVOH-nBA-MMA). In the case of VAc polymerization, if the water-soluble PVOH is only 10% of the starting
concentration in the aqueous phase, then the 0.25% (2.5% x 10% = 0.25%, >> 0.10% PVOH, see Table 2.4 in Chapter 2) PVOH present in the aqueous phase will make the GH detection invalid with the direct UV absorption technique.

4.5.3 GH-MBTH Reagent Color Reaction-New Calibration Curve

The serum (extract) was prepared in the same way as the procedure described in 4.5.2, and the MBTH reagent was prepared as shown in Table 4.7.

Table 4.7: MBTH (1, 3-methyl-2-benzothiazolinone Hydrazone Hydrochloride hydrate) Reagent

<table>
<thead>
<tr>
<th>Ingredients of MBTH reagents</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glacial acetic acid</td>
<td>80</td>
</tr>
<tr>
<td>MBTH</td>
<td>0.4</td>
</tr>
<tr>
<td>DI water</td>
<td>20</td>
</tr>
</tbody>
</table>

The reagent, 1, 3-methyl-2-benzothiazolinone hydrazone hydrochloride hydrate (MBTH), reacts with GH easily at room temperature and forms a golden color, even at very low GH concentrations such as a few ppm (0.7-5.0 ppm). Figure 4.16 is the UV absorption of MBTH reagent (top curve: DI water as reference) and Extract-MBTH absorption (bottom curve: MBTH reagent solution as reference).
Figure 4.16: UV absorption of MBTH reagent solution with DI water as reference (top curve) and an extract-MBTH mixture using MBTH reagent as reference (bottom curve).

Figure 4.16 shows that MBTH has a strong UV absorption between 190-350 nm, but no peaks were seen beyond 350 nm when DI water was used as reference. The extract or serum from the master batch latex (GH free) had no reaction with MBTH since no UV peaks appeared in Figure 4.16 (bottom curve). Here MBTH reagent was used as reference.

Figure 4.17 is the UV absorption after the MBTH-GH reaction. It is seen that a new strong peak formed at a wavelength of 405 nm.
It is obvious that the new peak absorption at 405 nm is far from the 191 nm wavelength where all of the interference absorption occurs. Hence, this indirect UV approach, “Color Reaction”, can be used for the GH partitioning study.

The prepared reaction mixtures showed color developing with GH concentration changes (Figure 4.18). Due to the high mole ratio of MBTH to GH (during color reaction, the MBTH/GH mole ratio a few hundred), the color develops in just a few minutes and the actual UV test was performed after two hour reaction period.
Figure 4.18: Color reaction of MBTH with GH (5 mL MBTH reagent solution with 1.8 mL DI water and 0.2 mL standard GH solution).

Figure 4.19: UV absorption at 405 nm obtained through color reaction (5 mL MBTH reagent solution + 1.8 mL DI water and 0.2 mL standard GH solution). a: 0.071 ppm, b: 0.143 ppm, c: 0.179 ppm, d: 0.357 ppm, e: 0.536 ppm, f: 0.714 ppm, g: 1.071 ppm, and h: 1.429 ppm.
in order to ensure that all GH was converted. The higher the concentration of GH, the deeper was the color observed. The corresponding UV absorption values changes with GH concentration as shown in Figure 4.19.

Based on the UV color reaction data, a new calibration curve was developed, and is shown in Figure 4.20. This indirect UV color reaction calibration curve can be used for the determination of extremely low GH concentrations (between 0.10-1.40 ppm) with less error. The curve between 0.10-0.75 ppm is nearly a linear line.

![Graph showing UV absorption vs. GH concentration](image)

**Figure 4.20:** Calibration curve generated from color reaction (5 mL MBTH reagent solution+ 1.8 mL DI water and 0.2 mL standard GH solution).
4.5.4 GH Aqueous Phase Partitioning Studies –Indirect UV Technique

Now, GH partitioning can be calculated in terms of the new calibration from section 4.5.3. The calculated GH concentration in the aqueous phase is shown in Figure 4.21 (compared with Figure 4.13).

![Figure 4.21: Glyoxal partitioning in the aqueous phase (indirect UV technique through color reaction) with mixing times (GH/AAEM mole ratio: 0.5, 1.0 and 2.0)](image)

Direct and indirect UV techniques showed that the GH concentration in the aqueous phase decreases with mixing time (the two methods showed same trends). The new UV technique through the color reaction gave a reliable analysis of GH partitioning due to the sensitivity and accuracy of calibration. It is seen in Figure 4.21
that the initial GH concentration in the aqueous phase is about 60%, disregarding the initial GH/AAEM mole ratio. After 5 hours of mixing, the GH concentration drops to near 40% (GH/AAEM = 0.5 and 1.0 mole). It must be noted that the “UV Color Reaction” approach worked very well for low GH/AAEM mole ratios since it is a more sensitive technique than the direct UV approach.

4.5 Summary

Water absorption coefficients are independent of GH or GTDA concentration in films even when the water absorption rates are different. The water diffusion coefficient data of crosslinked films showed that the diffusion coefficient was 12-14 times higher than the neat, PVAc polymer film because of the existence of water-sensitive stabilizer on the latex surface and less molecule entanglement than the films cast from solution polymer. A calibration curve (Figure 4.7) generated from a direct UV technique was used for GH diffusion coefficient measurements. GH diffusion coefficients are 4-5 times smaller than water diffusion coefficients due to more restriction for GH to be leached out in a short time. All of the diffusion processes were entropy controlled.

GTDA calibration curves were prepared with direct UV techniques for the partitioning study; indirect UV calibration curves were built and were successfully used for the GH partitioning study. 40% GTDA was found in the aqueous phase and its
concentration didn’t change during a few hour of mixing. This implies that GTDA was adsorbed on the latex particle surface. Theoretical calculations indicate that there is about 110% surface coverage of the GTDA on latex particles when the GTDA/AAEM mole ratio is 1.0. 60% GH was in the aqueous phase initially, but its concentration decreased with mixing time. This result implies that GH tends to be absorbed into the latex particles and suggests that the crosslinking reaction also occurs inside of the latex particles; otherwise its concentration should reach an equilibrium state with mixing time.

Latex crosslinked with GH demonstrated large weight loss in the cast film during water immersion test. The main reason for this large weight loss may be that the GH-latex reaction is a reversible crosslinking reaction, which can be explained by the lack of flexibility in the GH molecule (no -CH₂- between CHO-CHO), weak bonding and its higher water sensitivity than GTDA. The reversible crosslinking reaction was proved by the UV technique during the leaching test. More study on the reversible reaction kinetics can be found in Chapter 5. It needs to be noted that the hydrolysis of PVAc-based polymer could also take place during the extended immersion test which will cause more weight loss.

Crosslinker/AAEM mole ratio also impacts the weight loss since all crosslinkers are water-soluble. This makes sense especially when the ratio is greater than 0.50, which implies that excess crosslinker was used. The higher the level of GH in the film, the greater the weight loss occurred. However, the GTDA crosslinked film
does not show the same trend. This suggests that the two crosslinkers have different crosslinking mechanisms in latex. Detailed studies can be found in Chapter 5.

All of the differences were linked to the chemical structures of the GH and GTDA. The difference between GH and GTDA is the extra three methylene groups which made GTDA very different in reactivity, flexibility, partitioning and water sensitivity compared to GH crosslinker.

4.5 References


16. . Kim, N. Ph.D. Dissertation, Lehigh University, **2003**.
Chapter 5

Crosslinking Kinetics and Mechanism Studies

5.1 Introduction

Chapter 2 (section 2.2) and Chapter 3 (section 3.3) mentioned that the AAEM monomer and AAEM-containing latex are subject to many crosslinking reactions. For example dialdehydes, such as GH and GTDA, can react with active hydrogen groups from polymer backbone or from groups present on latex particle surfaces. GH as crosslinker has been reported for PVAc-based latex to strengthen latex water resistance. Zhang reported that GH was used as a crosslinker to improve moisture-resistance for films derived from latex\textsuperscript{1}. Takahashi reported using GH as crosslinker with acetoacetylated PVOH-based adhesive\textsuperscript{2}. Columbus reported using GH for PVAc latex as a high strength adhesive in the presence of propylene glycol\textsuperscript{3}. Columbus also reported GH as crosslinker for PVAc latex to improve water resistance in the derived film\textsuperscript{4}. Browning reported using dialdehydes for protein-stabilized PVAc for adhesive applications\textsuperscript{5}. GTDA has been reported as a crosslinker for protein-related latex\textsuperscript{6}. GTDA reacts very effectively with amino-functional groups present in proteins and forms permanent bonds. It is also reported that GTDA has been used with fully-hydrolyzed PVOH in permanent hydrophilic column coatings for capillary
electrophoresis. The adjacent –OH groups in the fully-hydrolyzed PVOH provides an acetal structure when cured with GTDA in aqueous solution (scheme I).

Scheme I: Crosslinking reaction of fully-hydrolyzed PVOH with GTDA

Most GH related literatures are patent-related and so does not reveal fundamental information. However, a discussion of GTDA as crosslinker in poly(vinyl alcohol) stabilized latex has not been found in the literature. Scheme I, Figures 5.1 and 5.2 show that AAEM monomer and neat fully-hydrolyzed PVOH both can react with GTDA to form an insoluble hard resin. The mole ratio of GTDA/PVOH in Figure 5.1(A) and GTDA/AAEM in Figure 5.1(B) were 10:1. The GTDA crosslinked PVOH in sample “A” was a clear hard resin, and all water from PVOH solution was squeezed out during the crosslinking reaction; the GTDA-AAEM mixture in sample “B” after crosslinking was an insoluble hard resin which does not dissolve in any solvent such as
Figure 5.1: Room temperature-cured samples: (A) 5 g, 10% Mowiol 28-99 (PVOH) mixed with 0.25 g GTDA, and (B) 5 g AAEM monomer mixed with 0.50 g GTDA. The mixture was gelled at ambient temperature for four weeks. Mixture B was turbid in beginning resulting from small amount of water from GTDA solution. The vial was rotated for the two weeks and then was kept at ambient temperature until is gelled.

THF or toluene, which means that the polymerization of AAEM monomer and crosslinking reaction between acetoacetyl functional group in AAEM and GTDA took place at the same time. The fact that the films were not soluble in solvents proved that the AAEM-GTDA crosslinking reaction does occur, otherwise the homopolymer of AAEM would, at least partially, be soluble in solvent.
Figure 5.2 also shows that the reaction occurred between the crosslinkers, GH and GTDA, and the fully-hydrolyzed PVOH. The 10% fully-hydrolyzed PVOH solution (Mowiol 28-99) was mixed with GH and GTDA at a designated mole ratio. For quick screening study, the GH-PVOH reactions were carried out at constant temperature, but with varied mole ratios; the GTDA-PVOH reaction was carried out at varied temperatures, but with fixed mole ratio. Viscosity changes with reaction time were monitored using a Brookfield viscometer DV-II Plus. The increase in viscosity with increase in reaction time indicated that the crosslinking reaction took place, as shown in Figure 5.2. The use of a higher mole ratio of GH/PVOH resulted in a shorter gel time, and the use of higher reaction temperature resulted in early gelation for the fixed GTDA/PVOH mole ratio mixture. The gelation occurred as early as 20% crosslinker conversion, which was determined by statistical equation, Eq 5.1\(^8\), and average functionality \(f_{av}\) is determined by Eq 5.2\(^9\). Where \(\rho = 1/2\), A represents the difunctional crosslinker (GDTA) and B represents PVOH; \(f_A\) and \(f_B\) are functionality of reactants A and B respectively. The low critical conversion for gelation is due to the very high functionality of Mowiol 28-99 (\(f_B = 3295\)).

\[
P_c = \frac{1}{[r + r\rho(f_{av} - 2)]^{1/2}} \quad (5.1)
\]

Where:

\[
f_{av} = \frac{2rf_Af_B}{f_A + r\rho f_B + r(1 - \rho)f_B} \quad (5.2)
\]
Figure 5.2: Model reaction of GH and GTDA with Mowiol 28-99. Top: GH/PVOH reaction with varied molar ratios at 23°C; bottom: fixed GH/PVOH mole ratio, but reacted at varied temperatures.
The model reactions of GH-PVOH and GTDA-PVOH described above implied that GH and TDA will react with colloidal PVOH stabilizer (Mowiol 28-99) in the latex system.

Figure 3.20 in Chapter 3 and Figure 5.3 show that GTDA-crosslinked films prepared from AAEM-containing latex had much lower water absorption values compared to control latex. The 8 hour water absorption value for the GTDA-crosslinked film without AAEM present was 22.0%, while the water absorption for GTDA-crosslinked film derived from AAEM-containing latex was only 6.0% (GTDA/AAEM = 3.0). The water absorption for film prepared without crosslinker (control) was 25.9%. Hence, the presence of AAEM and crosslinker in latex play a big role in determining the water sensitivity for the crosslinked films. When small amounts of GTDA were present in the latex, the water uptake decreased dramatically. The use of a molar ratio of GTDA/AAEM around 0.50 (weight percentage of GTDA based onlatex is 4.3%, see Eq. 3.6) gives the lowest water sensitivity (or the crosslinked films exhibit maximized water resistance) in 8 hours water immersion. This mole ratio was similar to the theoretical reaction ratio since 1 mole GTDA could react with 2 moles of AAEM molecule due to the difunctional nature of the GTDA molecule. However, not all of the AAEM functional groups were available for crosslinking reaction. Hence, chemical crosslinking can occur on any reactive hydrogen atom. This molar ratio of GTDA/AAEM (0.50) corresponds to molar ratio of GTDA/OH (0.25), which is expectedly halved since the stoichiometric reaction of GTDA with –OH is one molar
GTDA will react with 4 molar –OH functional groups from the latex particles (see Scheme I).

Figure 5.3: Water absorption vs GTDA concentration. Upper curve: 8 hours water sensitivity of GTDA-crosslinked films without AAEM functional monomer present in the latex; lower curve: water sensitivity of GTDA crosslinked films with AAEM-containing latex.

Figure 3.20 in Chapter 3 shows that GH-crosslinked films have lower water uptake values compared with control latex, which implies that GH does crosslink with AAEM-containing latex. However, in terms of water resistance, its effectiveness seems less than that of GTDA-crosslinked films since the water absorption curve of GTDA-crosslinked films is lower than that of GH-crosslinked films.
As introduced in the beginning of this chapter, GH has been reported as crosslinker in PVAc-based latex, but almost all related documents are given in the patent literature and no academic literature was found in terms of the kinetics and curing mechanism. The use of GH and GTDA as crosslinkers in acetoacetoxyether methacrylate (AAEM)-containing PVAc latex was not found, and their behavior during mixing, after crosslinking, and their mechanical performances need to be explored for better fundamental understanding.

The fact that GH and GTDA crosslinkers both react with the latex either through the AAEM functional groups present in latex particles or react with PVOH on the surface of the latex particles where PVOH is present. Hence, there are four competitive crosslinking reactions for the two crosslinking systems. The detailed studies are described in sections 5.2, 5.3 and 5.4.

5.2 Model Reactions

As mentioned above, in the real crosslinking system, the crosslinker, GH or GTDA, can react with either hydrogen-containing functional groups, or hydroxyl and acetoacetyl functional groups. In order to simplify the system and understand what crosslinking reaction is dominant for a given condition, four model reactions were used to mimic the real crosslinking reaction. The two small model molecules are shown in Figure 5.4 and the four model reaction pairs are presented in Table 5.1.
Ethyl acetoacetate (EAA), CH₃CH₂OCOCH₂COCH₃

2, 4-Pentanediol (PD), CH₃CH(OH)CH₂CH(OH)CH₃

Figure 5.4: Structure of molecular model for Kinetics and mechanism studies. Top: ethyl acetoacetate (EAA), bottom: 2, 4-pentanediol (PD).

Table 5.1: Model Reactions for Kinetics Studies and Analysis Approaches

<table>
<thead>
<tr>
<th>Crosslinkers</th>
<th>Model molecule Ethyl acetoacetate (EAA)</th>
<th>Model molecule Pentanediol (PD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyoxal (GH)</td>
<td>UV detection through color reaction at wavelength 405 nm</td>
<td>UV detection through color reaction at wavelength 405 nm (Reversible reaction)</td>
</tr>
<tr>
<td>Glutaric dialdehyde (GTDA)</td>
<td>NMR [detect -(COCH₂CO-) from EAA]</td>
<td>IR detection (Wavelength 1374 and 827 cm⁻¹)</td>
</tr>
</tbody>
</table>

Table 5.2 lists all model reaction conditions, parameters and techniques used to carry out the fundamental analysis.
Table 5.2: Model Reaction Conditions for the Kinetics Studies

<table>
<thead>
<tr>
<th></th>
<th>GTDA-EAA</th>
<th>GTDA-PD</th>
<th>GH-EAA</th>
<th>GH-PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactants (g)</td>
<td>50% GTDA 21.02g</td>
<td>50% GTDA 8.03g</td>
<td>40% GH 2.04g</td>
<td>40% GH 1.50g</td>
</tr>
<tr>
<td></td>
<td>EAA 27.51g</td>
<td>EAA 4.21g</td>
<td>EAA 48.00g</td>
<td>Pentanediol 36.02g</td>
</tr>
<tr>
<td>Crosslinker/model molecular mole ratio</td>
<td>1:2.0</td>
<td>1:1.00</td>
<td>1:26.74</td>
<td>1:33.44</td>
</tr>
<tr>
<td>Initial crosslinker concentration $C_0$ (wt %)</td>
<td>21.78%</td>
<td>32.77%</td>
<td>1.60%</td>
<td>1.60%</td>
</tr>
<tr>
<td>Initial crosslinker concentration $C_0$ (mole/L)</td>
<td>2.1657</td>
<td>3.2802</td>
<td>0.2759</td>
<td>0.2759</td>
</tr>
<tr>
<td>Reaction temp.($^\circ$C)</td>
<td>23, 50, 70 $^\circ$C</td>
<td>23, 50, 80 $^\circ$C</td>
<td>23, 35, 45 $^\circ$C</td>
<td>23, 35, 45 $^\circ$C</td>
</tr>
<tr>
<td>Analytical approaches</td>
<td>Proton NMR</td>
<td>IR</td>
<td>UV color reaction</td>
<td>UV color reaction</td>
</tr>
</tbody>
</table>

The reacting mixtures in sealed vials were placed in a constant temperature water bath set at the specified temperatures and samples were taken periodically from the vials for conversion analysis. Necessary dilutions were used for proper analysis, such as using color reaction calibration curve for GH determination (see Chapter 4, section 4.5).
5.2.1 NMR for GTDA-Ethyl Acetoacetate (EAA) Model Reactions

In the case of GTDA-EAA, mg samples were taken periodically and NMR analysis was carried out with DMSO-D6 as solvent. The methylene groups from EAA were monitored because it has a stronger signal than the aldehyde functional group in GTDA. Because the –CHO/-CH₂- reaction is a one-to-one reaction, the GTDA consumption can be calculated (see Figure 5.5).

**Figure 5.5:** NMR spectrum of GTDA/EAA = 0.50. The –COCH₂CO- was monitored and –CHO conversion was calculated without calibration.

Figure 5.6 shows the remaining concentration (%wt.) versus reaction time. The natural logarithm plot showed a linear relationship with reaction time, which implies that the reaction is a pseudo-first-order chemical reaction. Here the concentration of
EAA is much higher than the concentration of GTDA (GTDA/EAA mole ratio = 1:2). Hence, this pseudo-first-order reaction assumption is reasonable.
Figure 5.6. GTDA concentration changes vs reaction time for the GTDA-EAA model reaction. Top: $C_t/C_0$ vs reaction time, and bottom: $\ln(C_t/C_0)$ vs reaction time.

At all reaction temperatures used in the experiments, the Arrhenius plot exhibited a near linear relationship between reaction constant $k$ (or initial reaction rate) and reaction temperature ($1/T$) (see Figure 5.7).
5.2.2 IR for GTDA-Pentanediol (PD) Model Reactions

In the case of GTDA-PD model reaction, samples were taken periodically out of the vial for IR spectrum analysis. A calibration curve Figure 5.8 was generated from immediate mixing of a series GTDA and PD at varies ratios. The response characteristic peak, such as carbonyl or other peaks on the spectrum can be used for quantitative kinetics analysis.
Figure 5.8: IR calibration curve from absorption peaks 827 and 1374 cm\(^{-1}\).

The model reactions were carried at 23 °C, 35 °C, 50 °C and 80 °C. Figure 5.9 shows the concentration changes with reaction time and the linear natural logarithm versus reaction time relationship proves that this model reaction is also a pseudo-first-order chemical reaction. At low conversion, the assumption is reasonable.
Figure 5.9: GTDA concentration change vs reaction time for the GTDA-PD model reaction. Top: $C_t/C_0$ vs reaction time and bottom: $\ln(C_t/C_0)$ verse reaction time.
The relationship of the initial reaction constant to the reaction temperature is shown in Figure 5.10. The relationship of $k-1/T$ follows the Arrhenius Eq 5.4.

$$k = Ae^{-\frac{E}{RT}} = 4.64 \times 10^7 e^{-\frac{53151}{83.14T}} = 4.64 \times 10^7 e^{-\frac{6396.03}{T}} \quad (5.4)$$

It is seen that temperature has very big impact on the reaction rate, which implies that the crosslinking reaction is a temperature controlled reaction. At lower reaction temperature, the Arrhenus plots show a near linear relationship. The difference between the initial reaction constant and initial reaction rate is only a factor of initial concentration since, $-(\Delta C/\Delta t) = kC_o$, where $C_o$ is the initial GTDA concentration, 32.77% by weight (see Table 5.2).

![Arrhenius plot of GTDA-Pentanediol reaction](image)

**Figure 5.10:** Initial reaction constant $k$ (1/hr) vs reaction temperature $1/T$, (1/K). This curve follows Arrhenius Eq 5.4.
5.2.3 UV for GH-Ethyl Acetoacetate (EAA) Model Reactions

GH-EAA and GH-PD model reactions were carried out at three different temperatures, 23 °C, 35 °C and 45 °C which all are below the boiling point of GH(50 °C). During mixing, 1 g samples were drawn from of the vials at various times and the sample was then mixed with 399 g DI water. Then 0.2 mL of the diluted sample was mixed with 1.8 mL DI water plus 5 mL MBTH reagent. The mixtures were then placed in sealed vials for 2 hours to develop the color reaction before carrying out UV analysis. The GH-EAA kinetics data are shown in Figure 5.11.
Figure 5.11: GH concentration change with reaction time for the GH-EAA model reaction. Top: $\frac{C_t}{C_o}$ vs reaction time and bottom: $\ln(\frac{C_t}{C_o})$ vs reaction time.
Figure 5.11 shows that the concentration changes with reaction time gives a linear relationship with reaction time, which implies that the reaction is another pseudo-first-order reaction. Here the concentration of EAA is much higher than the concentration of GH (Table 5.2, GH/EAA mole ratio = 1:26.74). This assumption is reasonable at low conversion, especially when the concentration of EAA is in excess.

5.2.4 Indirect UV Measurement for GH-Pentanediol (PD) Model Reactions

Finally, the reaction kinetics of GH-PD was investigated. Figure 5.12 shows that the reaction is similar to the reactions discussed earlier.
Figure 5.12: GH concentration change with reaction time for the GH-PD model reaction. Top: $C_t/C_0$ vs reaction time and bottom: $\ln(C_t/C_0)$ vs reaction time.
At all reaction temperatures, the Arrhenius plot (Figure 5.13) showed a linear relationship between the reaction constant, $k$, and the reaction temperature ($1/T$). The only difference between the initial reaction constant, $k$, and the initial reaction rate from experiment data is the initial concentration $C_o$ like GH-EAA reaction (in Table 5.2, $C_o = 1.60\%$, GH to PD ratio = 1:33.44). Like the other three model reactions, the initial reaction of GH-PD is also a pseudo-first-order reaction. More details on the GH-PD kinetics model reaction is in section 5.3.

**Figure 5.13:** Initial reaction constant $k$ (1/hr) and initial reaction rate (%/hr) at lower reaction temperature vs reaction temperature ($1/T$).
5.3 Reversible GH-PD Reaction Kinetics

Chapter 3 (section 3.3) and Chapter 4 (section 4.4) discussed a significant weight loss of the GH-crosslinked films after water immersion experiments and stated that such weight loss was due to the weak crosslinking bond between GH and latex. Chapter 4 (section 4.4) assumed that the crosslinking reaction between latex particles and GH was a reversible reaction due to the discovery of a significant amount of GH that was present in water from the leaching test. Figure 5.14 shows the equilibrium concentration of GH after extended reaction time for the GH-PD reaction. The equilibrium time for all three reaction temperatures is about 18.5 hours. Hence, the real kinetics of the GH-PD model reaction in the entire reaction time span is complex and is different from the other three model reactions (GH-EAA, GTDA-EAA and GTGA-PD).
Figure 5.14: Remaining concentration of GH as a function of reaction time (hours). An equilibrium concentration was observed at a reaction time 18.5 hours at varied reaction temperatures (°C).

The reversible chemical reaction kinetics are expressed in detail below:

\[
\begin{align*}
&\text{CHO-CHO} + \text{HO-R-OH} \quad \underset{K_1}{\overset{K_2}{\rightleftharpoons}} \quad \text{CHO-CH-OR-OH} \\
&\text{OH} \\
&\text{CHO-CH-OR-OH} + \text{HO-R-OH} \quad \underset{K_3}{\overset{K_4}{\rightleftharpoons}} \quad \text{HO-R-OCH - CH-OR-OH} \\
&\text{OH} \quad \text{OH} \\
&\text{HO-R-OCH - CH-OR-OH} + \text{CHO-CHO} \quad \underset{K_5}{\overset{K_6}{\rightleftharpoons}} \quad \text{HO-R-OCH - CH-OR-OCH-CHO} \\
\end{align*}
\]
Assume $k_1 = k_3 = k_5$ and $k_2 = k_4 = k_6$ and assume that the reversible reaction is a first order reaction. The consumption of functional groups $–$CHO to $–$OH mole ratio during the reaction is 1:1. So, the kinetics can be derived in detail as below.

In this work, we assume concentration $C_{B0} \geq C_{A0}$.

$$\frac{-dC_A}{dt} = k_1 C_A C_B - k_2 C_C$$

(5.5)

$$C_B - C_{B0} \text{ and } C_C = C_{A0} - C_A$$

(5.6)

$$C_B = C_A - C_{A0} + C_{B0}$$

$$\frac{-dC_A}{dt} = k_1 C_A [C_A - C_{A0} + C_{B0}] - k_2 (C_{A0} - C_A)$$

(5.7)

At equilibrium state,

$$\frac{-dC_A}{dt} = 0, \text{ so}$$

$$k_1 C_{A(E)} [C_{A(E)} - C_{A0} + C_{B0}] = k_2 (C_{A0} - C_{A(E)})$$

(5.8)

$$k_2 = \frac{k_1 C_{A(E)} [C_{A(E)} - C_{A0} + C_{B0}]}{(C_{A0} - C_{A(E)})}$$

(5.9)

$$\frac{C_{A(E)} [C_{A(E)} - C_{A0} + C_{B0}]}{(C_{A0} - C_{A(E)})} = N \text{ (constant)}$$

(5.10)

$N > 0 \text{ since } C_{B0} > C_{A0} \text{ and } C_{A0} > C_{A(E)} > 0$
Here, \( C_A(E), C_{A0} \) and \( C_{B0} \) are equilibrium concentration of A, initial concentration of A and initial concentration of B respectively.

\[
k_2 = k_1 N \tag{5.11}
\]

\[
- \frac{dC_A}{dt} = k_1 C_A [C_A - C_{A0} + C_{B0}] - k_1 N (C_{A0} - C_A)
\]

\[
= k_1 C_A^2 - k_1 C_A C_{A0} + k_1 C_A C_{B0} - k_1 N C_{A0} + k_1 N C_A
\]

\[
= k_1 C_A^2 + (-k_1 C_{A0} + k_1 C_{B0} + k_1 N) C_A - k_1 N C_{A0}
\]

\[
= k_1 C_A^2 + (k_1 C_{B0} - k_1 C_{A0} + k_1 N) C_A - k_1 N C_{A0}
\]

\[
= X C_A^2 + Y C_A + Z \tag{5.12}
\]

\[
X = k_1 \tag{5.13}
\]

\[
Y = k_1 (C_{B0} - C_{A0} + N) \tag{5.14}
\]

\[
Z = -k_1 N C_{A0} \tag{5.15}
\]

\[
- \frac{dC_A}{dt} = X C_A^2 + Y C_A + Z = X (C_A + \frac{Y}{2X})^2 - \frac{Y^2 - 4XZ}{4X} \tag{5.16}
\]

\[
- \int_{C_{A0}}^{C_A} \frac{dC_A}{X (C_A + \frac{Y}{2X})^2 - \frac{Y^2 - 4XZ}{4X}} = \int_{t=0}^{t=t} dt = t \tag{5.17}
\]
\[- \int_{C_{A0}}^{C_A} \frac{dC_A}{X(C_A + \frac{Y}{2X})^2 - \frac{Y^2 - 4XZ}{4X}} = - \int_{C_{A0} + \frac{Y}{2X}}^{C_A + \frac{Y}{2X}} \frac{du}{Xu^2 + (- \frac{Y^2 - 4XZ}{4X})} \]

(5.18)

Here, \(X = k_1 > 0; - \frac{Y^2 - 4XZ}{4X} = - \frac{[k_1(C_{B0} - k_{A0} + N)]^2 + 4k_1^2NC_{A0}}{4k_1} \)

\([k_1(C_{B0} - k_{A0} + N)]^2 + 4k_1^2NC_{A0} > 0 \) since \(N > 0 \) and \(C_{A0} > 0 \)

so, \(- \frac{Y^2 - 4XZ}{4X} = - \frac{[k_1(C_{B0} - k_{A0} + N)]^2 + 4k_1^2NC_{A0}}{4k_1} < 0 \)

Hence, \(\int \frac{du}{Xu^2 - \frac{Y^2 - 4XZ}{4X}} = \frac{1}{2 \sqrt{X}} \log \frac{\sqrt{X}u - \sqrt{\frac{Y^2 - 4XZ}{4X}}}{\sqrt{X}u + \sqrt{\frac{Y^2 - 4XZ}{4X}}} \)

\(= \frac{1}{2 \sqrt{\frac{Y^2 - 4XZ}{4}} \sqrt{X}u + \sqrt{\frac{Y^2 - 4XZ}{4}}} \log \frac{\sqrt{X}u - \sqrt{\frac{Y^2 - 4XZ}{4X}}}{\sqrt{X}u + \sqrt{\frac{Y^2 - 4XZ}{4X}}} \)

(5.19)

Here, \(X = k_1 > 0 \) and \(- (Y^2-4XZ)/4X < 0 \).
\[
\frac{1}{2\sqrt{\frac{Y^2 - 4XZ}{4}}} \left[ \log \frac{\sqrt{X} \left( C_A + \frac{Y}{2X} \right) - \sqrt{\frac{Y^2 - 4XZ}{4X}}}{\sqrt{X} \left( C_A + \frac{Y}{2X} \right) + \sqrt{\frac{Y^2 - 4XZ}{4X}}} \right] - \sqrt{\frac{Y^2 - 4XZ}{4X}} \right]
\]

So, the kinetics can be presented as:
\[
\frac{1}{2\sqrt[\frac{Y^2 - 4XZ}{4}} \left[ \log \frac{\sqrt{X} (C_{A0} + \frac{Y}{2X}) - \sqrt{\frac{Y^2 - 4XZ}{4X}}}{\sqrt{X} (C_{A0} + \frac{Y}{2X}) + \sqrt{\frac{Y^2 - 4XZ}{4X}}} \right] - \log \frac{\sqrt{X} (C_A + \frac{Y}{2X}) - \sqrt{\frac{Y^2 - 4XZ}{4X}}}{\sqrt{X} (C_A + \frac{Y}{2X}) + \sqrt{\frac{Y^2 - 4XZ}{4X}}} = t \quad (5.22)
\]

Here:

\[X = k_1 \quad (5.23)\]

\[Y = k_1 (C_{B0} - C_{A0} + N) \quad (5.24)\]

\[Z = -k_1 NC_{A0} \quad (5.25)\]

\[N = \frac{C_{A(E)}[C_{A(E)} - C_{A0} + C_{B0}]}{(C_{A0} - C_{A(E)})} \quad (5.26)\]

\[C_{A0} = C_{(GH)0} = 1.6\% \quad \text{or} \]

\[C_{A0} = C_{(GH)0} = \frac{[(0.5 \times 0.4)/12.5]/(1000/58)}{mole/L} = 1.6\%/1000/58 \text{ mole/L} = 0.2759 \text{ mole/L} ; \]

\[C_{(PD)0} = C_{B0} = 9.2160 \text{ mole/L} ; \]

\[C_{A(E)} = 66.37\% \times 0.2759 = 1.8311 \times 10^{-1} \text{ mole/L} \]

At 35 °C:
So, 35 °C the kinetics model can be presented as:

\[
t = 31356 \left( -2.4703 + \log \frac{\sqrt{k_1} (C_A + 13.4730) - 1.4756 \times 10^{-2}}{\sqrt{k_1} (C_A + 13.4730) + 1.4756 \times 10^{-2}} \right)
\]  

(5.29)

Here, \( t \) is reaction time (s), \( k_1 \) is the forward reaction constant (L/s.mole) which is related to the initial pseudo-first-order reaction constant from section 5.2.4 and \( C_A \) is the GH concentration (mole/L) at time \( t \).

The initial pseudo-first-order reaction constant \( k \) from experiments in section 5.2.4 is actually \( k_1 C_{B0} \) (\( k = k_1 C_{B0} \)). \( C_{B0} \) was considered to be a constant during the model reaction since \( C_{B0} >> C_{A0} \), \( C_{B0}/C_{A0} = 33.44 \) (see Table 5.2). At low conversion for the initial reaction, the second order reaction constant \( k_1 = (k/3600)/C_{B0} \) (Ls\(^{-1}\)mol\(^{-1}\)).
Eq 5.22 is the kinetics model for the real reversible reaction and Eq 5.29 is the kinetics model for the given reaction condition at 35 °C. Similar reversible reaction models for varied reaction conditions can be derived in the same manner since the kinetics of the reaction is temperature dependent. The calculated $C_{GH}$ versus reaction time $t$ at 35 °C from the established kinetics model Eq. (5.29) and experimental data are shown in Figure 5.15.

Figure 5.15 shows that the value from the 35 °C kinetics model are very close to the experimental values, which implies that the kinetics model is correct, and the GH-PD reaction is confirmed again as being a reversible reaction. When the reaction temperature increases, the equilibrium concentration of $C_{GH(E)}$ increases (see Figure 5.14), which implies that the reversible reaction is temperature-favorable reaction.
5.4 Model Reaction Comparison

The activation energy $E$ and the Arhrenius constant $A$ for all 4 model reactions are listed in Table 5.3. It should be noted that the GH-PD model reaction exhibited very low activation energy compared with the other three reactions; which means the GH-PD reaction occurs easily. However, their collision constant $A$ is very small (or the effective collision is very low). GH is a short molecule. It has higher internal stress on bonded linkage and it is more polar than GTDA. When one side of GH reacts with AAEM or forms hydrogen bonds with active hydrogen, the other end of the GH
molecule loses its mobility due to internal molecular stress. Hence, the chemical reaction may be incomplete. It can be expected that in a real reaction with latex, GH would react with AAEM quickly but the incompletely reacted reaction would reduce the crosslinking efficiency. Even though the full reaction occurred, the internal molecular stress from GH makes this reaction reversible (rigid molecule without flexible “spacer” between two CHO functional groups).

Table 5.3. Kinetics Summary of Model Reactions

<table>
<thead>
<tr>
<th></th>
<th>Ethyl acetoacetate (EAA)</th>
<th>Pentanediol (PD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (Joule/mole)</td>
<td>A (1/hr)</td>
</tr>
<tr>
<td>Glyoxal (GH)</td>
<td>46178</td>
<td>1.47E07</td>
</tr>
<tr>
<td>Glutaric dialdehyde (GTDA)</td>
<td>31806</td>
<td>1.25E03</td>
</tr>
</tbody>
</table>

When GH or GTDA is present in the AAEM-containing latex, there are two existing competitive reactions: (1) reaction between crosslinker and surface hydroxyl functional groups from the PVOH colloidal stabilizer and; (2) the reaction between crosslinker and AAEM which is assumed to be evenly distributed throughout the latex particles. Hence, it is necessary to understand which crosslinking reaction dominates the reaction for given conditions.
5.4.1 Competition Reaction of GH with EAA or PD

According to the above model reaction, the Arrhenius plots showed that the initial reaction constant \( k \) (1/hr), at relative low reaction temperature, exhibits a linear relationship with reaction temperature (1/T). So, the competitive reactions can be compared in terms of Arrhenius equations for a given activation energy, \( E \), and collision constant, \( A \). Table 5.4 lists the experimental reaction constant \( k \) and initial reaction rate for given reaction temperatures. Table 5.5 gives the initial reaction rate constant ratio (or initial reaction rate ratio) \( (k_{EAA}/k_{PD})_{GH} \) or \( [(-\Delta C/\Delta t)_{EAA}/(-\Delta C/\Delta t)_{PD}]_{GH} \).

Table 5.4. Comparison of Kinetics of GH with EAA or PD

<table>
<thead>
<tr>
<th>Temp</th>
<th>( k_{GH-EAA} )</th>
<th>Initial ( (-\Delta C/\Delta t)_{EAA} )</th>
<th>( k_{GH-PD} )</th>
<th>Initial ( (-\Delta C/\Delta t)_{PD} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>1.05E-01</td>
<td>2.23E-03</td>
<td>3.15E-02</td>
<td>5.86E-04</td>
</tr>
<tr>
<td>35°C</td>
<td>2.33E-01</td>
<td>3.72E-03</td>
<td>3.87E-02</td>
<td>7.20E-04</td>
</tr>
<tr>
<td>45°C</td>
<td>3.83E-01</td>
<td>5.56E-03</td>
<td>5.01E-02</td>
<td>8.78E-04</td>
</tr>
</tbody>
</table>

Table 5.5. Reaction Rate Constant Ratio \( (k_{EAA}/k_{PD})_{GH} \) or Reaction Rate Ratio \( [(-\Delta C/\Delta t)_{EAA}/(-\Delta C/\Delta t)_{PD}]_{GH} \)

<table>
<thead>
<tr>
<th>Temp</th>
<th>Experimental ( (k_{EAA}/k_{PD})_{GH} )</th>
<th>Experimental ( [(-\Delta C/\Delta t)<em>{EAA}/(-\Delta C/\Delta t)</em>{PD}]_{GH} )</th>
<th>Calc ( (k_{EAA}/k_{PD})_{GH} )</th>
<th>Calc ( [(-\Delta C/\Delta t)<em>{EAA}/(-\Delta C/\Delta t)</em>{PD}]_{GH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>3.33</td>
<td>3.80</td>
<td>3.32</td>
<td>3.32</td>
</tr>
<tr>
<td>35°C</td>
<td>6.00</td>
<td>5.17</td>
<td>5.60</td>
<td>5.60</td>
</tr>
<tr>
<td>45°C</td>
<td>7.66</td>
<td>6.33</td>
<td>8.40</td>
<td>8.40</td>
</tr>
</tbody>
</table>

\( (C_{GH})_{EAA} = (C_{GH})_{PD} = 1.60\% \) (0.27 mole/L).
Table 5.5 shows that the GH-EAA reaction is 3.3 times faster than the GH-PD reaction at 23 °C, with the reaction occurring at a faster rate with increased reaction temperature (e.g. 7.7 times at 45 °C). This implies that the crosslinking reaction is preferred between GH and functional groups from AAEM molecules in the latex particles in the actual crosslinking reactions. Figure 5.16 shows the Arrhenius plots of two reactions and Figure 5.17 gives the reaction constant ratio of the reactions.

![Arrhenius plot of GH-EAA and PD Reaction](image)

**Figure 5.16.** Arrhenius plot of GH-EAA and GH-PD reaction: $k_{GH-EAA} > k_{PD-GH}$. 

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Figure 5.17. Ratio of reaction constants of \((k_{EAA}/k_{PD})_{GH}\) vs reaction temperature (1/T).

The trends in Figure 5.17 are given by Eqs 5.30 to 5.32. The trends of the experimental reaction constant ratio \((k_{EAA}/k_{PD})_{GH}\) is equal to trends in the initial reaction rate ratio \(\left\{\frac{(-\Delta C/\Delta t)_{EAA}}{(-\Delta C/\Delta t)_{PD}}\right\}_{GH}\) since the initial GH concentration in the two separated reactions were the same \([C_{GH}]_{EAA} = [C_{GH}]_{PD} = 1.60\%\) or 2.76 mole/L.

\[
\frac{k_{EAA}}{k_{PD}}_{GH} = \frac{A_{EAA}}{A_{PD}} \exp\left(\frac{E_{PD} - E_{EAA}}{RT}\right)
\]

\[
= \frac{1.4763 \times 10^7}{6.5878} \exp\left(\frac{13145 - 46178}{8.314T}\right)
\]  

(5.30)
\[
\left( \frac{k_{EAA}}{k_{PD}} \right)_{GH} = 2.2410 \times 10^6 \exp \left( -\frac{33033}{8.314T} \right)
\]

\[= 2.2410 \times 10^6 \exp \left( -\frac{3973.18}{T} \right) \quad (5.31)\]

\[
\left( \frac{\Delta C}{\Delta t} \right)_{EAA} = \left( \frac{kC_{GH}}{kC_{GH}} \right)_{EAA} \left( \frac{k_{EAA}}{k_{PD}} \right)_{GH}
\]

Even though temperature favors the reversible GH-PD reactions (see Figure 5.14), the temperature is more preferred for reaction of GH-EAA since the \( k_{GH-EAA} \) is higher than \( k_{GH-PD} \) and their ratio increases with temperature (Table 5.5 and Figure 5.17). The model reaction implies that the reaction mechanism of GH in latex is preferred between GH-AAEM and the crosslinking reaction is also influenced by temperature. The crosslinking reaction loci is in latex particle since AAEM is evenly distributed in latex particle. Section 5.3 proved that the GH-PD crosslink reaction is reversible; hence, in the case of GH present in latex, the GH-EAA reaction is a dominant crosslinking reaction. The GH-AAEM-containing latex reaction is a fast chemical reaction or it is a diffusion-controlled reaction according to deGenne’s film formation theory. The details about deGenne’s theory can be found in Chapter 6 (section 6.2).
5.4.2 Competition Reaction of GTDA with EAA or PD

The competitive reaction of GTDA to EAA or PD can also be compared in terms of the Arrhenius equation for a given activation energy, $E$ and collision constant, $A$ as described previously. Table 5.6 lists the experimental reaction constant $k$ and initial reaction rate for given reaction temperatures. Table 5.7 gives the reaction rate constant ratio (or initial reaction rate ratio) $(k_{EAA}/k_{PD})_{GTDA}$ or initial reaction rate ratio $(\frac{(-\Delta C/\Delta t)_{EAA}}{(-\Delta C/\Delta t)_{PD}})_{GTDA}$.

**Table 5.6.** Comparison of Kinetics of GTDA with EAA or PD

<table>
<thead>
<tr>
<th>Temp</th>
<th>$k_{GTDA-EAA}$</th>
<th>Initial $(-\Delta C/\Delta t)_{EAA}$</th>
<th>$k_{GTDA-PD}$</th>
<th>Initial $(-\Delta C/\Delta t)_{PD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>1.24E-03</td>
<td>3.82E-04</td>
<td>2.24E-02</td>
<td>7.33E-03</td>
</tr>
<tr>
<td>35°C</td>
<td>5.04E-03</td>
<td>1.10E-03</td>
<td>4.49E-02</td>
<td>1.47E-02</td>
</tr>
<tr>
<td>45°C</td>
<td>7.45E-03</td>
<td>1.62E-03</td>
<td>8.62E-02</td>
<td>2.83E-02</td>
</tr>
</tbody>
</table>

**Table 5.7.** Reaction Rate Constant Ratio $(k_{EAA}/k_{PD})_{GTDA}$ or Reaction Rate Ratio $\left(\frac{(-\Delta C/\Delta t)_{EAA}}{(-\Delta C/\Delta t)_{PD}}\right)_{GTDA}$

<table>
<thead>
<tr>
<th>Temp</th>
<th>$(k_{EAA/PD})_{GTDA}$</th>
<th>$(k_{PD/EAA})_{GTDA}$</th>
<th>$\left(\frac{(-\Delta C/\Delta t)<em>{PD}}{(-\Delta C/\Delta t)</em>{EAA}}\right)_{GTDA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>0.0547</td>
<td>18.27</td>
<td>27.49</td>
</tr>
<tr>
<td>35°C</td>
<td>0.05927</td>
<td>16.87</td>
<td>25.38</td>
</tr>
<tr>
<td>45°C</td>
<td>0.06309</td>
<td>15.85</td>
<td>23.85</td>
</tr>
</tbody>
</table>
Unlike the reaction of GH with EAA or PD (Table 5.5 and Figure 5.17), Table 5.7 shows that the GTDA reacts with PD much faster than with EAA. Table 5.7 shows that the GTDA-PD reaction rate is 18.3 times faster than GTDA-EAA at room temperature. This implies that the crosslinking reaction is preferred between GTDA and the hydroxyl functional groups present on the latex particle surface (from absorbed PVOH) rather than with AAEM inside the latex during the real crosslinking reactions. Higher temperature would be more favorable for the reaction between GTDA and AAEM functional groups in the latex since the \((k_{PD/EAA})_{GTDA}\) ratio is slightly lower at higher reaction temperature. However, the GTDA-PVOH reaction is still the dominant reaction at 45 °C (e.g. 15.85 times at 45 °C). Figure 5.18 shows the Arrhenius plots for both reactions and Figure 5.19 is the reaction constant ratio and initial reaction rate ratio of the reactions.

**Figure 5.18.** Arrhenius plot of GTDA-PD and GTDA-EAA reaction: \(k_{GTDA-PD} \gg k_{GTDA-EAA}\).
Figure 5.19. Ratios of reaction constants \( \frac{k_{PD}}{k_{EAA}} \)\(_{\text{GTDA}} \) and initial reaction rate \( \left[ \frac{(-\Delta C/\Delta t)_{PD}}{(-\Delta C/\Delta t)_{EAA}} \right]_{\text{GTDA}} \) vs reaction temperature (1/T).

In the model reaction of GTDA-PD, \((C_{\text{GTDA}})_{PD} = 32.77\% \text{ (3.28 mole/L)} \) and \((C_{\text{GTDA}})_{EAA} = 21.78\% \text{ (2.16 mole/L)} \) (Table 4.2). The difference of \( \frac{k_{PD}}{k_{EAA}} \)\(_{\text{GTDA}} \) and \( \left[ \frac{(-\Delta C/\Delta t)_{PD}}{(-\Delta C/\Delta t)_{EAA}} \right]_{\text{GTDA}} \) are 1.5 times in value (Eqs. 5-25 and 5-26).

\[
\left( \frac{k_{PD}}{k_{EAA}} \right)_{\text{GTDA}} = \frac{A_{PD}}{A_{EAA}} \exp \left( \frac{E_{EAA} - E_{PD}}{RT} \right) = \frac{4.6365 	imes 10^7}{1.9700 \times 10^7} \exp \left( \frac{58194 - 53151}{8.314T} \right)
\]

or,

\[
\left( \frac{k_{PD}}{k_{EAA}} \right)_{\text{GTDA}} = 2.3536 \exp \left( \frac{5043}{8.314T} \right) = 2.3536 \exp \left( \frac{606.57}{T} \right) \quad (5.33)
\]
\[
\frac{-[\frac{\Delta C}{\Delta t}]_{PD}}{-[\frac{\Delta C}{\Delta t}]_{EAA}}_{GTDA} = \frac{(k_{GTDA})_{PD}}{(k_{GTDA})_{EAA}}_{0} = \frac{(C_{GTDA})_{PD}}{(C_{GTDA})_{EAA}}_{0} \frac{k_{PD}}{k_{EAA}}_{GTDA}
\]

or,

\[
\frac{-[\frac{\Delta C}{\Delta t}]_{PD}}{-[\frac{\Delta C}{\Delta t}]_{EAA}}_{GTDA} = 32.77\% \frac{k_{PD}}{k_{EAA}}_{GTDA} = 1.5046\frac{k_{PD}}{k_{EAA}}_{GTDA} \quad (5.35)
\]

### 5.4.3 Cross Comparison of Crosslinker Reactivity

Table 5.8 lists all four competitive model reaction rate constants. It is useful to have a cross comparison for these reaction constants in order to give a meaningful ranking of crosslinking reactions for given conditions.

<table>
<thead>
<tr>
<th>Table 5.8. Cross Comparison of Crosslinking Reaction (crosslinker to EAA and PD)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp.</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>23 °C</td>
</tr>
<tr>
<td>35 °C</td>
</tr>
<tr>
<td>45 °C</td>
</tr>
</tbody>
</table>

All the comparisons were made with initial reaction constant.

For given conditions, such as fixed concentration of EAA or PD (actually \(k\) is independent of concentration), the ratio of \([(k_{GH}/k_{GTDA})_{PD}]_0\) is close to 1, which means
GTDA and GH both have similar reactivity to PD. It can be expected that GTDA and GH will have similar reactions with hydroxyl functional groups in latex. The latter is a reversible reaction. However, the ratio of \([\frac{(k_{\text{GH}}/k_{\text{GTDA}})_{\text{EAA}}}{0}}\) is very large, or \([\frac{(k_{\text{GH}})_{\text{EAA}}}{0} \gg \frac{(k_{\text{GTDA}})_{\text{EAA}}}{0}}\) (84 times at 23 °C), which means the GH has a much faster reaction rate with EAA than the rate of GTDA to EAA. We can expect the GH-AAEM reaction will be the selective reaction upon mixing with latex. The crosslinker reactivity (reaction constant) for given condition (23 - 45 °C) is ranked as:

\[
K_{\text{GH-EAA}} \gg k_{\text{GH-PD}} \approx k_{\text{GTDA-PD}} \gg k_{\text{GTDA-EAA}}
\]

or extended as

\[
K_{\text{GH-AEEM}} \gg k_{\text{GH-PVOH}} \approx k_{\text{GTDA-PVOH}} \gg k_{\text{GTDA-AEEM}} \quad (5.36)
\]

The relative low reactivity of GTDA to PD (or GTDA to PVOH) and high temperature response (Figures 5.18) are very suitable for real world applications for the GTDA-PVOH system. That is, the components can be mixed at lower temperature with a long shelf-life, and the film can be quickly cured at elevated temperature.

5.5 Summary

Kinetics of four competitive model reactions were studied in detail and a complex GH-PD reversible reaction model was derived which fits the experimental
data very well. The reaction constants were compared and cross comparisons were made for all model reactions.

It was found that GH will prefer to react with AAEM than to PD, which implies that it will prefer to react inside of particles. This finding is agreed with GH partitioning studies in Chapter 4 where the GH concentration decreased with time in the aqueous phase since it was absorbed into the latex particles during mixing. It can be concluded that the GH-AAEM reaction in latex is the dominant reaction, not only because of its higher reaction constant, but also due to its competitive reaction, i.e. the GH-PVOH reaction is a reversible reaction.

GTDA will prefer to react with PD rather than EAA, which implies that GTDA will mainly react with PVOH present on the latex surface during crosslinking reaction. This finding also agrees with GTDA partitioning studies which has been discussed in Chapter 4 where the GTDA concentration in the aqueous phase reached an equilibrium state and remained there for a few hours during mixing since it was adsorbed on the latex particles. The hydroxyl functional group from PVOH was assumed to be present on the latex particle surface which made the surface reaction even easier. The latex particle surface reaction is assumed to occur in the outer 3 nm layer of the particles.

Chapters 3 and 4 concluded that GTDA crosslinked films have much lower water sensitivity compared to GH crosslinked films. GTDA-latex reaction is GTDA-PVOH reaction which happens on latex surface. Thus, it can be concluded that the
latex particle surface has a larger impact on the water sensitivity of PVAc film than the internal latex structure.

5.6 References


Chapter 6

Shrinking-Core Model and Scaling Theory Applications

6.1 Introduction

Lu et al. reported that diamine crosslinked AAEM-containing PVAc-based adhesives improves water resistance and lap-shear mechanical performance.\(^1\) Dialdehydes have been also reported as crosslinkers for adhesives or natural polymers such as soy protein, and chitosan for mechanical performances\(^2-4\). Hansen reported that the dialdehyde can be used as a crosslinker with fully-hydrolyzed PVOH to form a polymer gel\(^5\). Such polymer gel can be used to improve the oil recovery from an oil reservoir\(^6\). The GTDA crosslinked polymer gel has an advantage over the chromium iron (Cr\(^{3+}\)) crosslinked polymer gel for polyacrylamide (PAM) in that it is more favorable from environmental point of view. It is understandable that if the crosslinking density becomes greater, then such crosslinked PVOH will no longer be water-soluble. The polymer gel formation reaction is illustrated in Scheme I.
As described in Chapters 3, 4 and 5, GH tends to be absorbed into latex particles and the GH-AAEM crosslinking reaction is the dominant reaction inside of latex particles; while GTDA likes to be adsorbed on latex particle surface and the reaction of GTDA-PVOH is the dominant crosslinking mechanism in latex. The GTDA crosslinked films showed much lower water sensitivity than did films crosslinked with GH. This finding implies that the surface water sensitivity of PVAc latex particles is more critical than crosslinked structure inside of latex particles. This finding may drive the research interest for future focus on water sensitivity of PVAC latex.

The shrinking-core model (SCM) has been reported for latex film formation studies. Boyars studied an AAEM-containing polyacrylate/Amine-containing latex blend system and reported that the SCM can be used to accurately predict the
crosslinking reaction activation energy\(^7\). Osifo \textit{et al.} reported using SCM for studies of the influence of the degree of cross-linking on the adsorption properties of chitosan beads\(^8\).

The focus in this Chapter is to study the lap-shear mechanical performance of the crosslinked latex films. The details of the second-order SCM for chemical reaction are derived and it is successfully used to calculate the crosslinking reaction constant and for diffusion coefficient prediction. The reaction rate constant calculated from SCM and the film formation control factor from deGenne’s scaling theory\(^12,16\) are compared with experimental results.

6.2 Mechanical Performance of Crosslinked PVAc Films

6.2.1 Lap-Shear Modulus of Crosslinked Latex Films

Latex was cast as described in Chapter 2 (section 2.3) and Chapter 3 (section 3.3) and the lap shear strength after room temperature curing was measured with an Instron. The 20\% AAEM-containing copolymer has a glass transition temperature 19 \(^\circ\)C (< room temperature) which is calculated by the Fox equation. Hence, the modulus from Instron test can be considered as the rubbery modulus of the crosslinked films. Assuming that the crosslinked film is in the rubbery state and the Poisson’s ratio is 0.5, \(n\) is the active network chains per unit volume. Then equation \(E = 3nRT\) can be used for crosslinking density determination. The effective crosslinking density is the sum of
both physical entanglements and chemical crosslinking reactions. The actual chemical crosslinking density cannot be obtained from the crosslinked film since PVOH-stabilized PVAc usually has a high degree of grafting and the grafted PVAc film is insoluble in THF and toluene solvent\textsuperscript{9-11}. The linear polymer trapped in the film cannot be separated easily by extraction with any solvent especially for high solids content latex. Hence, the swollen measurement for crosslinking density did not work. The actual value for chemical crosslinking density shall be lower than the data obtained from Young’s modulus.

Young’s modulus and the active network chain per unit volume, n, are listed in Table 6.1.

**Table 6.1:** Young’s Modulus and Effective Crosslinking Density of Cured Films*  

<table>
<thead>
<tr>
<th>GH/AAEM mole ratio</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (MPa)</td>
<td>15.87</td>
<td>28.24</td>
<td>33.32</td>
<td>34.58</td>
<td>32.92</td>
</tr>
<tr>
<td>Effective crosslinking density n (mole/cm(^3))</td>
<td>2.33x10(^{-4})</td>
<td>4.15x10(^{-4})</td>
<td>4.89x10(^{-4})</td>
<td>5.08x10(^{-4})</td>
<td>4.83x10(^{-4})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GTDA/AAEM mole ratio</th>
<th>0.25</th>
<th>0.75</th>
<th>1.25</th>
<th>1.75</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (MPa) (Instron)</td>
<td>14.28</td>
<td>16.25</td>
<td>16.32</td>
<td>21.06</td>
<td>22.77</td>
</tr>
<tr>
<td>Effective crosslinking density n (mole/cm(^3))</td>
<td>2.10x10(^{-4})</td>
<td>2.39x10(^{-4})</td>
<td>2.40x10(^{-4})</td>
<td>3.09x10(^{-4})</td>
<td>3.34x10(^{-4})</td>
</tr>
</tbody>
</table>

*The cast films have dimension 0.25-0.30 mm in length and 0.1-0.15 mm in width.
Table 6.1 shows that the modulus increases with crosslinker/AAEM mole ratio. The effective crosslinking density $n$, from rubber elasticity theory, increases with crosslinker/AAEM ratio as well. In all cases, the effective crosslinking density or active network chains per unit volume, $n$, is in the order of $10^{-4}$ (mole/cm$^3$). The crosslinking density is the sum of molecular entanglement and actual chemical crosslinking. Molecular entanglements include the effect of chain grafting since high grafting levels occur in PVAc when PVOH is used as stabilizer. The GTDA crosslinked films exhibited lower modulus than GH crosslinked films, which is because GTDA is flexible due to its 3 methylene groups present in the molecule.

### 6.2.2 Wet Strength of Crosslinked Latex Films

The latex control and crosslinked latex film lap-shear performance on maple substrates are to be discussed in this Chapter. The reason of maple wood was used for film strength test is that water can be quickly absorbed by wood and then strength of latex film can be determined with crosslinking reaction time. The mixed latex-crosslinker can served as an “adhesive” to bond two pieces of wood substrate together and the cured substrates then were subject to water immersion before lap-shear test. The lap-shear results from Instron test are called “wet strength” of adhesives, which is used to characterize the latex film water sensitivity closer to reality. Substrates such as European Beech, Maple wood board or other types of wood species can be bonded with
crosslinker-containing latex. According to European standard, DIN EN204, the latex obtained from the master batch was mixed with GH or GTDA crosslinkers in specific mole ratios and the “adhesive” is then coated on wood boards, clamped, cut, 4-days water immersion and then tested by Instron right out of water immersion. The set-up of the test is shown in Figure 6.1. The wet strength is directly related to the water sensitivity of crosslinked latex films.

Figure 6.1: Wet lap shear strength test set-up illustration (European standard DIN EN204). Note: substrate used for this test was maple boards.
4 g “adhesives” were coated on 6 x 6 square inches maple boards. The double-sided coated substrates were clamped at 210 psi pressure and then cured 1 week in ambient condition. The cured boards were trimmed to 0.787 inches in width (or 20 mm) x 5 inches in length first and then two cuts were made in center of the specimen with cut lines between 0.394 inches (or 10 mm) apart (see Figure 6.1). 5-8 pieces bonded specimens were used on each sample to obtain the standard deviation.

The lab shear strength after 4 days of water immersion is shown in Figure 6.2. The left bar is the lap shear strength of the control (20% AAEM-containing latex from master batch), the center bar is the lap shear strength of the GH crosslinked “adhesive” and right side bar is the strength of GTDA crosslinked “adhesive”. It can be seen that after the 4 day water soak, the bonded substrates with the GH and GTDA both exhibited higher lap shear strength than the control. The GTDA crosslinked latex showed the highest strength even at a lower mole ratio than GH cured boards. The bonded substrates with crosslinkers exhibited better water resistance or lower water sensitivity of the crosslinked films. The effectiveness of GTDA was same as that found from low water absorption of the neat crosslinked films, which have been discussed in Chapters 3 and 4.
The GH-crosslinked adhesive on maple substrates showed lower wet strength than GTDA crosslinked adhesive, which is opposite to the results of crosslinked neat films shown in Table 6.1. The reason for the lower wet strength is linked to its reversible crosslinking reaction under wet conditions, which has been discussed previously (in Chapter 4 section 4.4 and Chapter 5 section 5.3). As a result, even the GH-crosslinked films showed higher modulus values compared to GTDA in dry condition, the effectiveness of GH as crosslinker in wet condition is lower.
6.2.3 Lap-Shear Strength versus Crosslinking Time

The latex film formation (with and without crosslinkers) can be characterized by strength built-up with curing time at given temperature. The strength built-up approaches with reaction time at given temperature can also be used to determine the efficiency of crosslinking. The second order chemical reaction shrinking-core model (SCM) is another kinetic model that can be used to predict for reaction efficiency (conversion verse reaction time). The mechanical performance of the crosslinked films depends on the competition between molecular interdiffusion and chemical crosslinking reactions. The time to reach maximum strength due to a purely physical diffusion process is defined as \( t_{\text{diffusion}} \) (\( t_d \)), while the time to reach maximum strength due to purely chemical crosslinking reaction is defined as \( t_{\text{reaction}} \) (\( t_r \)). The film formation control parameter, \( \alpha \), was defined by deGennes\(^{12} \). The value of \( \alpha \) is related to the physical-chemical properties of the polymer and the crosslinker. The control factor, \( \alpha \), is used to characterize the final state of the polymer interface. The definition of \( \alpha \) is:

\[
\alpha = \frac{t_{\text{diffusion}}}{t_{\text{reaction}}} \tag{6.1}
\]

20% AAEM-containing latex with/without GTDA (GTDA/AAEM = 1.0) was prepared and coated on both sides of maple wood surfaces. The procedure to prepare bonded substrates was described in section 6.2.2. The necessary press time is needed in order to dry out water through the wood substrate before mechanical strength can be
measured. The results are shown in Figures 6.3, 6.4 and 6.5 with varied reaction temperatures 23 °C, 50 °C and 80 °C, respectively.

**Figure 6.3:** Lap shear strength of latex films vs curing time at RT. Upper curve: GTDA-cured film; and lower curve: GTDA-free film (control).

Without GTDA present, the latex shows a similar maximum strength as a function of curing time for all of the tested temperatures (23 °C to 80 °C). This is because the T_g of the polymer is 19 °C which is lower than room temperature and molecular diffusion can occur easily at this temperatures. The diffusion time to achieve maximum lap shear strength of the control sample is exhibited in Figure 6.3 (lower curve) where \( t_d = 2.5 \) hours. With GTDA present in the latex, the time \( t_r \) to achieve
maximum lap shear strength is delayed compared to \( t_d \) from the control. The time needed to achieve maximum strength for GTDA-containing latex (upper curve), \( t_r = 7.5 \) hours, is greater than \( t_d \). Here, control factor \( \alpha = t_d/t_r = 2.5/7.5 = 0.33 < 1 \) which means that the mechanism of film formation was reaction-controlled, since the slow step controls the film strength built-up with reaction time.

![Graph showing lap shear strength vs curing time at 50 °C.](image)

**Figure 6.4:** Lap shear strength of latex films vs curing time at 50 °C. Upper curve: GTDA-cured film; and lower curve: GTDA-free film (control).

Figure 6.4 shows 50 °C lap shear strength *versus* reaction time. The control factor \( \alpha = t_d/t_r = 2.5/4.4 = 0.57 < 1 \), so, film formation at 50 °C is still reaction controlled.
Figure 6.5: Lap shear strength of latex films vs curing time at 80 °C. Upper curve: GTDA-cured film; and lower curve: GTDA-free film (control).

Figure 6.5 shows 80 °C lap shear strength versus reaction time. Here, the control factor $\alpha = t_d/t_r = 2.5/2.7 = 0.93$, which is close to 1.0. At 80 °C, the latex with or without GTDA both reached maximum strength at nearly the same time, which implies that a reaction temperature of 80 °C is the optimized condition which will ensure the system to reach its maximum strength with minimum reaction time when the GTDA/AEM mole ratio is between 0.0-1.0. The control factor $\alpha = 1$ is very useful in applications since it gives an optimized crosslinking reaction condition.
Chapter 5 showed the GTDA-PVOH reaction is the main crosslinking reaction in latex. The reaction of GTDA-latex occurs on the latex surface. The dominant crosslinking mechanism is the GTDA-PVOH reaction rather than the GTDA-AAEM reaction ($k_{\text{GTDA-PD}} >> k_{\text{GTDA-EAA}}$). In all of the Chapters, the GTDA level in latex was represented as GTDA/AAEM mole ratios rather than GTDA/OH molar ratios, because it is convenient for comparison with GH level used in crosslinked system.

Lap shear strength of GH-latex bonded substrates were measured in the same manner as GTDA crosslinker as described above. The results are shown in Figure 6.6 with reaction temperature at 23 °C, 35 °C and 45 °C, respectively. The reason for employing the lower reaction temperature is because the boiling point of GH is around 50 °C.

![Figure 6.6: Lap shear strength of latex films vs curing time at 23 °C, 35 °C (not show in Figure) and 45 °C. The GH/AAEM mole ratio is 2.0. In all conditions, $t_d$ is greater than $t_r$.](image)

*Figure 6.6:* Lap shear strength of latex films vs curing time at 23 °C, 35 °C (not show in Figure) and 45 °C. The GH/AAEM mole ratio is 2.0. In all conditions, $t_d$ is greater than $t_r$. 
According to deGennes’s definition, the GH crosslinking reaction is diffusion controlled since the ratio of \( t_d/t_r > 1 \) in all reaction conditions. In fact, since the \( T_g \) of the latex film is lower than room temperature, diffusion has less influence on strength development with time. The shorter value \( t_r \) was due to the fast reaction between GH and AAEM, which can be explained by the kinetics described in Chapter 5 \( (k_{GH-EAA} >> k_{GH-PD}) \). Again, the GH-latex reaction mechanism is the GH-AAEM reaction inside of the latex particle.

### 6.3 Second-Order Chemical Reaction of Shrinking-Core Model (SCM)

The original kinetic model, shrinking-core model (SCM)\(^{13}\), was derived based on an assumption of first order reaction between a solid surface and gas molecule, where the gas concentration was constant in bulk. According to Chapter 5, all four model reactions showed pseudo-first-order reaction for crosslinking. However, the entire reactions in this study were second order reaction since concentration of \([\text{OH}]\) or \([\text{AAEM}]\) changes with time. The crosslinking reaction (GTDA-PVOH reaction) was assumed within 3 nanometer layer on latex particle surface. Hence, it is necessary to derive an adequate second-order SCM for kinetic comparison and for data fitting.

Figure 6.7 is the shrinking-core model for an isothermal spherical particle reaction with gas A, where solid reactant B is initially a sphere of radius \( r_s \). When the reaction occurs, an ash layer of product forms around the unreacted core of reactant B. For further reaction, this ash layer is assumed porous, so that the reaction occurs by diffusion of A through the ash layer to react at the interface between ash layer and
unreacted core. In the case of latex-GTDA reaction, the GTDA is used in place of gas A and the latex sphere is used in place of solid reactant B, hence, second order SCM can be derived in detail as described below.

\[ \text{Figure 6.7: Reprint from the Chemical Reaction Engineering book of the scheme of shrinking-core model for an isothermal spherical particle concentration profile with reaction time } t. \ C_{Ag}, C_{As} \text{ and } C_{Ac} \text{ are the gas-phase concentration in bulk layer, in ash layer (porous layer) and on particle surface of the unreacted core respectively. } C_{B0} \text{ is the mole density of the solid B.} \]
In this derivation, it is assuming that the entire reaction of A with reactant B is a 2nd order reaction (but 1st order for reactant A if assume $C_B \gg C_A$). There are three rate equations, 6.2, 6.2 and 6.4, expressed as moles of A disappearing per unit time per particle (mole/s):

$$A(g) + b(B(s) \rightarrow E(G) + F(S)$$

$$-\frac{dN_A}{dt} = 4\pi r_s^2 k_m[(C_A)_b - (C_A)_s] \text{ external diffusion, unit of } k_m \text{ is:} \quad (6.2)$$

$k_m$ is external mass-transfer coefficient.

$$-\frac{dN_A}{dt} = 4\pi r_c^2 D_e \left(\frac{dC_A}{dr}\right)_{r=r_c} \text{ diffusion through product, } D_e \text{ is: } \left(\frac{cm^2}{s}\right) \quad (6.3)$$

$$-\frac{dN_A}{dt} = \frac{4}{3}\pi r_c^3 k(C_A)_c (C_B)_c \text{ reaction at } r_c, \text{ unit is: } \left(\frac{L}{smole}\right) \quad (6.4)$$

$k$ is reaction constant for the 2nd order reaction.

$$-\frac{dN_A}{dt} = \frac{4}{3}\pi r_c^3 k'(C_A)_c \quad (6.5a)$$

$k' = k(C_B)_c; \text{ for } C_B \gg C_A, \text{ for low conversion,} \quad (6.5b)$

$$(C_B)_c \approx (C_B)_0; \text{ } k' = k(C_B)_0 \quad (6.5c)$$

At steady-state mass conservation expression for A in this layer is:

$$-(\pi r^2 D_e \frac{dC_A}{dt})_r - (\pi r^2 D_e \frac{dC_A}{dt})_{r+\Delta r} = 0, \quad (6.6)$$
or \( \frac{d}{dt} \left( r^2 D_e \frac{dC_A}{dr} \right) = 0 \), which can be integrated twice (6.7)

\[ r^2 D_e \frac{dC_A}{dr} = \text{constant } C \] (6.8)

\[ \int_{(C_A)_s}^{(C_A)_c} D_e \, dC_A = \int_{r_s}^{r_c} \frac{C}{r^2} \, dr \]

\[ D_e \left[ (C_A)_c - (C_A)_s \right] = C \left( \frac{1}{r_s} - \frac{1}{r_c} \right) \] (6.9)

\( C_A = (C_A)_s \) at \( r = r_s \) and \( C_A = (C_A)_c \) at \( r = r_c \) or

\[ D_e \left[ (C_A)_c - (C_A)_s \right] = \frac{C}{r_c} \left( \frac{r_c}{r_s} - 1 \right) \] or

\[ D_e \left[ (C_A)_s - (C_A)_c \right] = \frac{C}{r_c} \left( 1 - \frac{r_c}{r_s} \right) \] (6.10)

also Eq. 6.5b can be integrated as

\[ \int_{(C_A)_c}^{C_A} D_e \, dC_A = \int_{r_c}^{r} \frac{C}{r^2} \, dr \]

\[ D_e \left[ C - (C_A)_c \right] = C \left( \frac{1}{r_c} - \frac{1}{r} \right), C_A = C \text{ at } r = r \text{ and } C_A = (C_A)_c \text{ at } r = r_c \text{ or} \]

\[ D_e \left[ C - (C_A)_c \right] = \frac{C}{r_c} \left( 1 - \frac{r_c}{r} \right) \] (6.11)

From Eqs. 6.10 and 6.11 we have:
\[
\frac{[C_A - (C_A)_c]}{((C_A)_s - (C_A)_c)} = \frac{\left(1 - \frac{r_c}{r}\right)}{\left(1 - \frac{r_c}{r_s}\right)} \tag{6.12}
\]

or differentiated with respect to \( r \) and then evaluated at \( r = r_c \) to give:

\[
\frac{dC_A}{dt}_{r=r_c} = \frac{(C_A)_s - (C_A)_c}{r_c\left(1 - \frac{r_c}{r_s}\right)} \tag{6.13}
\]

so from Eq. 6.3, \(-\frac{dN_A}{dt} = 4\pi r_s^2 D_e \frac{dC_A}{dr}_{r=r_c} \)

\[
= 4\pi r_s^2 D_e \frac{(C_A)_s - (C_A)_c}{r_c\left(1 - \frac{r_c}{r_s}\right)} \tag{6.14}
\]

Now \((C_A)_s\) and \(\frac{dC_A}{dt}\) can be eliminated from Eqs. 6.2, 6.4 and 6.14. From Eqs 6.2 and 6.14:

\[
4\pi r_s^2 D_e \frac{(C_A)_s - (C_A)_c}{r_c\left(1 - \frac{r_c}{r_s}\right)} = 4\pi r_s^2 k_m [(C_A)_b - (C_A)_s] \tag{6.15}
\]

\[
\left(\frac{r_c}{r_s}\right)^2 \frac{D_e}{k_m} \frac{(C_A)_s - (C_A)_c}{r_c\left(1 - \frac{r_c}{r_s}\right)} = (C_A)_b - (C_A)_s \tag{6.16a}
\]
Use Eqs. 6.2, 6.4 and 6.17 and we can get \((C_A)_c\) in terms of \((C_A)_b\) and \(r_c\).

\[
\begin{align*}
\frac{(r_c/r_s)^2 D_e}{r_c \left(1 - \frac{r_c}{r_s}\right)} (C_A)_s &= \frac{(r_c/r_s)^2 D_e}{r_c \left(1 - \frac{r_c}{r_s}\right)} (C_A)_c = (C_A)_b - (C_A)_s \\
(1 + \frac{(r_c/r_s)^2 D_e}{r_c \left(1 - \frac{r_c}{r_s}\right)}) (C_A)_s &= (C_A)_b + \frac{(r_c/r_s)^2 D_e}{r_c \left(1 - \frac{r_c}{r_s}\right)} (C_A)_c \\
(C_A)_b + \frac{(r_c/r_s)^2 D_e (C_A)_c}{r_c \left(1 - \frac{r_c}{r_s}\right)} \\
(C_A)_s &= \frac{r_c (C_A)_b \left(1 - \frac{r_c}{r_s}\right) + \left(\frac{r_c}{r_s}\right)^2 \frac{D_e}{k_m} (C_A)_c}{r_c \left(1 - \frac{r_c}{r_s}\right) + \left(\frac{r_c}{r_s}\right)^2 \frac{D_e}{k_m}} \\
\end{align*}
\]

\(6.16b\)

\[
\begin{align*}
4 \frac{\pi r_c}{3} k'(C_A)_c &= 4 \pi r_s^2 k_m \left( (C_A)_b - (C_A)_s \right) \\
4 \frac{\pi r_c}{3} k'(C_A)_c &= 4 \pi r_s^2 k_m \left[ (C_A)_b - \frac{r_c (C_A)_b \left(1 - \frac{r_c}{r_s}\right) + \left(\frac{r_c}{r_s}\right)^2 \frac{D_e}{k_m} (C_A)_c}{r_c \left(1 - \frac{r_c}{r_s}\right) + \left(\frac{r_c}{r_s}\right)^2 \frac{D_e}{k_m}} \right] \\
\end{align*}
\]

\(6.18a\)

\(6.18b\)
\[
\frac{\frac{r_c}{3} \left( \frac{r_c}{r_s} \right)^2 k'}{k_m} (C_A)_c = (C_A)_b - \frac{\frac{r_c}{2} (C_A)_b \left( 1 - \frac{r_c}{r_s} \right) + \left( \frac{r_c}{r_s} \right)^2 \frac{D_e}{k_m} (C_A)_c}{r_c \left( 1 - \frac{r_c}{r_s} \right) + \left( \frac{r_c}{r_s} \right)^2 \frac{D_e}{k_m}}
\]

(6.18c)

\[
\frac{r_c (\frac{r_c}{r_s})^2 k'}{k_m} (C_A)_c = (C_A)_b - \frac{r_c (C_A)_b \left( 1 - \frac{r_c}{r_s} \right) + \left( \frac{r_c}{r_s} \right)^2 \frac{D_e}{k_m} (C_A)_c}{r_c \left( 1 - \frac{r_c}{r_s} \right) + \left( \frac{r_c}{r_s} \right)^2 \frac{D_e}{k_m}}
\]

(6.18d)

\[
\frac{r_c k'}{3 k_m} (C_A)_c = \frac{\frac{D_e}{k_m} [(C_A)_b - (C_A)_c]}{r_c \left( 1 - \frac{r_c}{r_s} \right) + \left( \frac{r_c}{r_s} \right)^2 \frac{D_e}{k_m}}
\]

(6.18e)

\[
(C_A)_c = \frac{\frac{r_c}{3} k' \left[ (C_A)_b - (C_A)_c \right]}{\frac{D_e}{k_m} \left[ r_c \left( 1 - \frac{r_c}{r_s} \right) + \left( \frac{r_c}{r_s} \right)^2 \frac{D_e}{k_m} \right]}
\]

(6.18f)

So, we have:
\[(C_A)_c = \frac{(C_A)_b}{1 + \frac{r_c}{3D_e}k'[r_c\left(1 - \frac{r_c}{r_s}\right) + \left(\frac{r_c}{r_s}\right)^2 \frac{D_e}{k_m}]}
\]

\[= \frac{(C_A)_b}{1 + \frac{r_c}{3} \left(\frac{r_c}{r_s}\right)^2 k' + \frac{k' r_c^2}{3D_e} \left(1 - \frac{r_c}{r_s}\right)} \quad (6.19)\]

\[- \frac{dN_A}{dt} = - \frac{dN_B}{bdt} = - \frac{d}{bdt} \left(\frac{4}{3} \pi r_c^3\right) = - \frac{\rho_{Bm} 4 \pi r_c^2 dr_c}{bdt} \quad (6.20)\]

Here \(\rho_{Bm}\) is mole density (mole/L) of reactant B. From Eqs 6.4 and 6.20,

\[- \frac{dN_A}{dt} = \frac{4}{3} \pi r_c^3 k'(C_A)_c = - \frac{\rho_{Bm} 4 \pi r_c^2 dr_c}{bdt} \quad (6.21)\]

Substituting Eq. 6.19 in Eq. 6.21 to give

\[\frac{dr_c}{dt} = - \frac{bk' r_c (C_A)_c}{3 \rho_{Bm}}
\]

\[= - \frac{bk' r_c (C_A)_b}{3 \rho_{Bm} \left[1 + \frac{r_c}{3} \left(\frac{r_c}{r_s}\right)^2 k' + \frac{k' r_c^2}{3D_e} \left(1 - \frac{r_c}{r_s}\right)\right]} \quad (6.22)\]

\[- \frac{bk'(C_A)_b}{3 \rho_{Bm}} \int_0^t dt = \int_{r_s}^{r_c} \left[1 + \frac{r_c}{3} \left(\frac{r_c}{r_s}\right)^2 k' + \frac{k' r_c^2}{3D_e} \left(1 - \frac{r_c}{r_s}\right)\right] dr_c \quad (6.23)\]

Integrate with Eq. 6.22

\[- \int_0^t \frac{bk'(C_A)_b}{3 \rho_{Bm}} dt = \int_{r_s}^{r_c} \left[1 + \frac{1}{3} \left(\frac{r_c}{r_s}\right)^2 k' + \frac{k' r_c^2}{3D_e} \left(1 - \frac{r_c}{r_s}\right)\right] dr_c\]
\[
\frac{bk(C_A)_b}{3\rho_B m} t = \left\{ \ln \frac{r_c}{r_s} + \frac{r_c^3 - r_s^3}{9r_s^2} \frac{k'}{k_m} + \frac{k'(r_c^2 - r_s^2)}{6D_e} - \frac{k'(r_c^3 - r_s^3)}{9D_e r_s} \right\}
\]

(6.24a)

\[
\frac{bk(C_A)_b}{3\rho_B m} t = \left\{ -\ln \frac{r_c}{r_s} + \frac{r_c^3 - r_s^3}{9r_s^2} \frac{k'}{k_m} + \frac{k'r_s^2(r_c^2 - r_s^2)}{6D_e r_s^2} - \frac{k'r_s^2(r_c^3 - r_s^3)}{9D_e r_s^3} \right\}
\]

(6.24b)

\[
\frac{bk(C_A)_b}{3\rho_B m} t = -\ln \frac{r_c}{r_s} + \frac{r_s(r_c^3 - r_s^3)}{9} \frac{k'}{k_m} + \frac{k'r_s^2(1 - \frac{r_c^2}{r_s^2})}{6D_e} - \frac{kr_s^2(1 - \frac{r_c^3}{r_s^3})}{9D_e}
\]

(6.24c)

If \(r_c/r_s\) close to (low conversion), then \(-\ln(r_c/r_s) \approx 1 - r_c/r_s\); so we have

\[
-\ln \frac{r_c}{r_s} + \frac{r_s(1 - \frac{r_c^3}{r_s^3})}{9} \frac{k'}{k_m} + \frac{kr_s^2(1 - \frac{r_c^2}{r_s^2})}{6D_e} - \frac{kr_s^2(1 - \frac{r_c^3}{r_s^3})}{9D_e}
\]

\[
= \left(1 - \frac{r_c}{r_s}\right) + \frac{r_s k'}{9k_m} \left[ \frac{1 - \frac{r_c}{r_s}}{1 + \frac{r_c}{r_s} + \left(\frac{r_c}{r_s}\right)^2} \right] + \frac{k'r_s^2}{6D_e} \left(1 + \frac{r_c}{r_s}\right) - \frac{k'r_s^2}{9D_e} \left[1 + \frac{r_c}{r_s} + \left(\frac{r_c}{r_s}\right)^2\right]
\]

\[
= \left(1 - \frac{r_c}{r_s}\right) \left[1 + \frac{r_s k'}{9k_m} \left[1 + \frac{r_c}{r_s} + \left(\frac{r_c}{r_s}\right)^2\right] + \frac{k'r_s^2}{6D_e} \left(1 + \frac{r_c}{r_s}\right) - \frac{k'r_s^2}{9D_e} \left[1 + \frac{r_c}{r_s} + \left(\frac{r_c}{r_s}\right)^2\right]\right]
\]

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\[
= \left(1 - \frac{r_c}{r_s}\right) \left\{ 1 + \frac{r_c k'}{3k_m} \left[ 1 + \frac{r_c}{r_s} \left( \frac{r_c}{r_s} \right)^2 \right] + \frac{k' r_s^2}{6D_e} \frac{r_c}{r_s} - \frac{k' r_s^2}{9D_e} \frac{r_c}{r_s} - \frac{k' r_s^2}{9D_e} \left( \frac{r_c}{r_s} \right)^2 \right\}
\]

\[
= \left(1 - \frac{r_c}{r_s}\right) \left\{ 1 + \frac{r_c k'}{3k_m} \left[ 1 + \frac{r_c}{r_s} \left( \frac{r_c}{r_s} \right)^2 \right] + \frac{k' r_s^2}{6D_e} \frac{r_c}{r_s} - \frac{k' r_s^2}{9D_e} \frac{r_c}{r_s} - \frac{k' r_s^2}{9D_e} \left( \frac{r_c}{r_s} \right)^2 \right\}
\]

\[
= \left(1 - \frac{r_c}{r_s}\right) \left\{ 1 + \frac{r_c k'}{3k_m} \left[ 1 + \frac{r_c}{r_s} \left( \frac{r_c}{r_s} \right)^2 \right] + \frac{k' r_s^2}{18D_e} \frac{r_c}{r_s} - \frac{k' r_s^2}{18D_e} \frac{r_c}{r_s} - \frac{2k' r_s^2}{18D_e} \left( \frac{r_c}{r_s} \right)^2 \right\}
\]

\[
= \left(1 - \frac{r_c}{r_s}\right) \left\{ 1 + \frac{r_c k'}{3k_m} \left[ 1 + \frac{r_c}{r_s} \left( \frac{r_c}{r_s} \right)^2 \right] + \frac{k' r_s^2}{18D_e} \left[ 1 + \frac{r_c}{r_s} - 2 \left( \frac{r_c}{r_s} \right)^2 \right] \right\}
\]

\[
\frac{bk' (C_A) b}{3\rho_B m} t = \left(1 - \frac{r_c}{r_s}\right) \left\{ 1 + \frac{r_c k'}{3k_m} \left[ 1 + \frac{r_c}{r_s} \left( \frac{r_c}{r_s} \right)^2 \right] + \frac{k' r_s^2}{18D_e} \left[ 1 + \frac{r_c}{r_s} - 2 \left( \frac{r_c}{r_s} \right)^2 \right] \right\}
\]

(6.25)

\[
x_B = \frac{\frac{4}{3} \pi r_s^3 \rho_B m - \frac{4}{3} \pi r_s^3 \rho_B m}{\frac{4}{3} \pi r_s^3 \rho_B m},
\]

\[
\rho_B m \text{ is constant, which imply } C_B \text{ is constant, see (6.5c)}
\]

or \[x_B = 1 - \left( \frac{r_c}{r_s} \right)^3 \text{ or } \frac{r_c}{r_s} = (1 - x_B)^{\frac{1}{3}}\] (6.26)
\[ t = \frac{3\rho_{Bm}}{bk'(C_A)_b}(1 - (1 - x_B)^{1/3})(1 + \frac{r_s k'}{3k_m}[1 + (1 - x_B)^{1/3} + (1 - x_B)^{2/3}]) \]
\[ + \frac{k'r_s^2}{18D_e}\left[1 + (1 - x_B)^{1/3}2(1 - x_B)^{2/3}\right] \] (6.27a)

or

\[ t = \frac{3\rho_{Bm}}{bk(C_B)_b(C_A)_b}(1 - (1 - x_B)^{1/3})(1 + \frac{r_s k(C_B)_b}{3k_m}[1 + (1 - x_B)^{1/3} + (1 - x_B)^{2/3}]) \]
\[ + \frac{k(C_B)_b r_s^2}{18D_e}\left[1 + (1 - x_B)^{1/3}2(1 - x_B)^{2/3}\right] \] (6.27b)

Eq. 6.27a or 6.28 is the global rate for reaction.

Rewrite Eq. 6.27a

\[ t = K(1 - (1 - x_B)^{1/3})(1 + \frac{r_s k(C_B)_b}{3k_m}[1 + (1 - x_B)^{1/3} + (1 - x_B)^{2/3}]) \]
\[ + \frac{Y}{6}\left[1 + (1 - x_B)^{1/3}2(1 - x_B)^{2/3}\right] \] (6.28)

For a liquid-solid particle chemical-controlled reaction system, external-diffusion resistance may be very high \(K_m\) is the external mass transfer coefficient, very large) and \(k\) is relatively low. At low conversion Eq. 6.28 can be simplified as:

\[ t = K(1 - (1 - x_B)^{1/3})(1 + \frac{Y}{6}\left[1 + (1 - x_B)^{1/3}2(1 - x_B)^{2/3}\right]) \] (6.29)

\[ K = \frac{3\rho_{Bm}}{bk'(C_A)_b} = \frac{3\rho_{Bm}}{bk_r(C_B)_b(C_A)_b} \]
or

$$K = \frac{3P_{bm}}{bk_r(C_B)_b(C_A)_b}$$

(6.30)

$$Y = \frac{k_r(C_B)_b \mu_s^2}{3D_e}$$

(6.31)

K and Y are two parameters in SCM model. In the case of GTDA-Latex reaction, $k_r$ is 2nd order reaction constant (volume based) with unit: (L.s$^{-1}$mole$^{-1}$), $b=2$, $P_{bm}$ is the [OH] mole density in particle (constant), $(C_A)_b$ is GTDA concentration (mole/L) in reaction zone, $(C_B)_b$ is OH concentration assumed on latex particle surface within 3 nm.

6.4 Shrinking-Core Model (SCM) and Applications

6.4.1 Fitting the Shrinking-Core Model (SCM) with Experimental Data

Using nonlinear regression fitting, the experimental data from the lap-shear tests can be fitted into the second-order shrinking-core model (SCM) which is derived as above. Assume that the complete reaction time is the time for the lap shear strength to reach a maximum. At this point the GTDA conversion (fully crosslinked) is assumed to be 100%. The curves of experimental conversion and SCM predicted conversion versus reaction times are shown in Figures 6.8a-d.
Figure 6.8a: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength at 23 °C (latex with GTDA).

Figure 6.8b: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength at 50 °C (latex with GTDA).
Figure 6.8c: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength at 50 °C (latex with GTDA).

Figure 6.8d: Nonlinear regression fit of second-order SCM to the experimental data based on lap-shear strength of the GTDA-latex blend at 23 °C, 50 °C and 80 °C.
Figures 6.8a-d show that the predicted data obtained from the second order SCM (solid lines) fit the experimental data very well. The SCM parameters K and Y can also be used for kinetic studies. The reaction constant and diffusion coefficient can be calculated from a proper fitting experiment.

When the GTDA/AAEM mole ratio is 1, the concentration of GTDA in the mixture was 0.29 mole/L while the [OH] concentration in 3 nm the outer particle shell layer from the surface is 29.43 mole/L. Here the OH concentration means the unit mole from PVOH on the latex particle surface per volume. One mole of GTDA will at least react with two mole of [OH]. The available equivalent OH concentration for reaction is much higher than the GTDA concentration. Hence, the [OH] can be assumed to be constant during the GTDA crosslinking reaction. This assumption makes above derivation of SCM valid for calculation. The reaction of GTDA-OH is pseudo–first order reaction which agrees with the model reactions derived in Chapter 5. The entire reaction is 2\textsuperscript{nd} order reaction where the pseudo-first order reaction constant \( k' = k_r C_{[OH]} \), and \( k_r \) is the real second-order reaction constant and \( C_{[OH]} \) is the surface hydroxyl group concentration in 3 nanometer outer shell of the latex particles.

6.4.2 Kinetic Comparison of Experimental Data to Shrinking-Core Model

The latex particle size of the master batch and particle size of the GTDA-containing latex with mixing time were measured by SEM. Figure 6.9 shows that the
particle size of AAEM-containing latex is same as the particles size of the control latex (see A in Figure 6.9). The value of $D_w \approx D_n$ (PDI = 1.03). As discussed in Chapter 4, the GTDA tends to be adsorbed on the surface of the latex particles and the theoretical coverage of GTDA is about 110\% if the GTDA/AAEM mole ratio is 1.0 which is close to monolayer coverage. GTDA adsorption on latex particles does not change the particle size in a measurable way. The narrow particle size distribution allows SCM to be better used for the kinetic study.

**Figure 6.9**: Particle size of latexes (GTDA/AAEM = 1.0): (A) Control; (B) 1 hour mixing time; (C) 2 hour mixing time and (D) 3 hour mixing time.
The second kinetic model SCM is shown in eq. 6.29 and K and Y are given as Eqs 6.30 and 6.31. Table 6.2 shows the parameters of the GTDA-crosslinked system for the calculation of the reaction constant $k_r$ and the diffusion coefficient $D_e$. The value of the frequency factor K and parameter Y were obtained from nonlinear regression fits.

**Table 6.2: Parameters Used for Shrinking-Core Model Calculation**

<table>
<thead>
<tr>
<th>Latex $D_s$ (nm)</th>
<th>Latex $r_s$ (nm)</th>
<th>Latex $r_s$ (dm)</th>
<th>Total # PS</th>
<th>$\rho_{B(AAEM)}$ (mole/L)</th>
<th>$C_B(OH)$ (mole/L) in 3 nm</th>
<th>$C_{GTDA}$ (mole/L)</th>
<th>$\rho_{B(OH)}$ (mole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>150</td>
<td>1.50E-04</td>
<td>2.56E+15</td>
<td>0.86</td>
<td>26.50</td>
<td>5.00</td>
<td>14.12</td>
</tr>
</tbody>
</table>

*GTDA/AAEM = 1.0, Total particle number was calculated based on 100 g latex.

$$K = \frac{3\rho_{Bm}}{b k_r C_{GTDA} C_B(OH)} \quad \text{and} \quad Y = \frac{k_r C_B(OH) r_s^2}{3D_e}$$

Here $b = 2$ due to 2 functional groups per GTDA molecule. $\rho_{Bm}$ is the moles of OH functional groups per volume before reaction. $C_B(OH)$ is the concentration of surface OH in the reaction zone where its loci is considered to be within 3 nm of the surface of the latex particles. $C_{GTDA}$ is the concentration of GTDA in the reaction zone. $r_s$ is the average radius of latex particle and $k_r$ is the second order reaction constant (L/s/mole). The calculated reaction constant $k$ values are shown in Table 6.3.
Table 6.3: Reaction Constant k calculated from Shrinking-Core Model

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>K from fitting</th>
<th>$K = \frac{3\rho_{Bm}}{2k_rC_{GTDA}C_{B(OH)}}$</th>
<th>Reaction constant $k_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 °C</td>
<td>19573</td>
<td>$\frac{3\rho_{Bm}}{2C_{GTDA}C_{B(OH)}} = 1.62^{-2}$</td>
<td>$1.66 \times 10^{-6}$</td>
</tr>
<tr>
<td>50 °C</td>
<td>7398</td>
<td>$K = 1.62 \times 10^{-2}/k_r$</td>
<td>$4.38 \times 10^{-6}$</td>
</tr>
<tr>
<td>80 °C</td>
<td>4802</td>
<td></td>
<td>$6.75 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The values of $k_r$ obtained from SCM in Table 6.3 are similar to the values determined from experiments (see Chapter 5). The SCM parameters $K$ and $Y$ can be used for the determination of the GTDA diffusion coefficient ($D_e$) and the values are shown in Table 6.4.

Table 6.4: Diffusion Coefficient $D_e$ Calculated from Shrinking-Core Model

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Reaction constant $k_r$</th>
<th>$Y = \frac{k_rC_{B(OH)}r_s^2}{3D_e}$</th>
<th>$De = \frac{\rho_{Bm}r_s^2}{2k_rYC_{GTDA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 °C</td>
<td>1.66 x 10^{-6}</td>
<td>4.18</td>
<td>3.89E-13</td>
</tr>
<tr>
<td>50 °C</td>
<td>4.38 x 10^{-6}</td>
<td>19.38</td>
<td>2.22E-13</td>
</tr>
<tr>
<td>80 °C</td>
<td>6.75 x 10^{-6}</td>
<td>18.05</td>
<td>3.67E-13</td>
</tr>
</tbody>
</table>

The gellation of GTDA in PVOH and GTDA self diffusion were probed through NMR. Hansen et al.\textsuperscript{14} reported that the GTDA diffusion coefficient $D_e$ is in the range of $10^{-12}$ to $10^{-14}$ cm$^2$/s, which is similar to the finding from the SCM above.

It must be mentioned that the $K$ and $Y$ from SCM fitting are not the only pair which will meet the minimum residual sum square (RSS) shown in Eq. 6.32\textsuperscript{7}. In other
words, the RSS may not be the global minimum for a pair of $K$ and $Y$. Hence, different results may be obtained on the initial guesses for $K$ and $Y$.

$$RSS = \sum_{k=1}^{n} [t_{i, exp} - t(K, Y)]^2 \quad (6.32)$$

To validate the value predicted from SCM, the known $D_c$ from Hansen is very helpful. The diffusion coefficient can be measured directly by small angle neutrum scattering (SANS)$^{15}$.

For the reaction of GTDA-latex at 80 °C, the $K$ and $Y$ have the relationship shown in Figure 6.10. The straight line fits in the X-Y plane which indicates that there is a ridge or valley in the response surface and therefore no global minimum. Because there are an infinite number of local minima, the values of $K$ and $Y$ cannot be uniquely determined to calculate the diffusion coefficient and rate constant. However, with prior knowledge of one of the parameters $k_r$ or $D_c$, the rest can be determined.
Figure 6.10. Level curves of the residual sum of square (RSS) response surface for the GTDA-latex reaction at 80 °C (see Figure 6.8c).

It was noted that the value of $D_e$ obtained from SCM (Table 6.4) does not change with temperature, which is unusual for glassy polymers. In this work, the vinyl acetate-AAEM copolymer has a $T_g$ lower than ambient temperature. Hence, the temperature has little influence on the diffusion coefficient for the small molecule GTDA under the experimental conditions.
6.4.3 Comparison of Experimental Results with Shrinking-Core Model and Scaling Theory

Table 6.5 shows very good agreement in the reaction constant $k_r$ between the experimental results and those calculated from the SCM. The $k_r$ value obtained from SCM is in the same order of magnitude as $k_r$ determined from experiments. This result implies that the SCM is correct and the $K$ and $Y$ values from the data fitting is correct.

**Table 6.5: Comparison of Reaction Constant $k_r$ from SCM and Experimental Data**

<table>
<thead>
<tr>
<th>GTDA as crosslinker</th>
<th>$k_r$ (exp) (L/s.mole)</th>
<th>$k_r$ from SCM</th>
<th>$k_{model}/k_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 °C</td>
<td>1.44E-06</td>
<td>1.66E-06</td>
<td>1.15</td>
</tr>
<tr>
<td>50 °C</td>
<td>2.89E-06</td>
<td>4.38E-06</td>
<td>1.52</td>
</tr>
<tr>
<td>80 °C</td>
<td>5.55E-06</td>
<td>6.75E-06</td>
<td>1.22</td>
</tr>
</tbody>
</table>

The control parameter (control factor), $\alpha$, can be used for a mechanistic study in film formation when crosslinker is used. In the case of the GTDA-latex system, the values of the control factor $\alpha$ determined from the lap shear test in Section 6.2.3 are listed in Table 6.6.
Table 6.6: Relationship of Control Factor ($\alpha$) versus Reaction Temperature from Experiments

<table>
<thead>
<tr>
<th>Reaction Temperature (°C)</th>
<th>GTDA/AAEM = 1.0</th>
<th>GH/AAEM = 2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23 °C</td>
<td>50 °C</td>
</tr>
<tr>
<td>$\alpha_{exp} = t_d/t_r$</td>
<td>0.33</td>
<td>0.57</td>
</tr>
</tbody>
</table>

The film strength build-up results show that the GTDA-crosslinked system is a chemically controlled process, while the GH-crosslinked system is diffusion-controlled. deGennes’s scaling theory presents an approach to describe the film formation of the homogenous and symmetric polymer-polymer interface with addition of an external crosslinker$^{12,16}$. deGennes defined the competition of molecular interdiffusion and chemical reaction by the control factor, $\alpha$, shown in Eq. 6.1. The reaction time is presented as:

$$t_{reaction} = \frac{N_c}{N} \frac{1}{Qb^3A_0^*}$$  \hspace{1cm} (6.33)

Where $A_0^*$ is the active functional group [OH] concentration and $Qb^3$ is the corresponding reaction constant $k_r$ ($k_r = Qb^3$). $N_c$ is the number of monomer units between two cross-links, and $N$ is total number of monomer units per chain. Eq. 6.33 can be rewritten as:

$$t_{reaction} = \frac{N_c}{k_rA_0^*N}$$  \hspace{1cm} (6.34)
The diffusion time is represented as:

\[ t_{\text{diffusion}} \approx t_{\text{reptation}} \]  \hspace{1cm} (6.35)

Wool’s definition of reptation time can be applied for the calculation:\textsuperscript{17}

\[ t_{\text{diffusion}} \approx t_{\text{reptation}} = \frac{6R_g^2}{3\pi^2D_e} \]  \hspace{1cm} (6.36)

Here \( R_g \) is the radius of gyration (Å) that is related to the weight-average molecular weight, \( M_w \), in the relaxed state. Combining Eqs. 6.1, 6.34 and 6.36, the final modified analytical control factor \( \alpha \) can be expressed as:

\[ \alpha = \frac{6R_g^2k_rA_o^*N}{3\pi^2D_eN_c} \]  \hspace{1cm} (6.37)

Assuming that PVOH polymer has similar \( R_g \) as poly(ethylene oxide), \( R_g =0.343 \) (\( M_w \))\(^{1/2} \), Eq. 6.37 then becomes:

\[ \alpha = 2.39 \times 10^{-18} \frac{M_wk_rA_o^*N}{D_eN_c} \]  \hspace{1cm} (6.38)

\( M_w \) is the weight-average molecular weight of PVOH (Mowiol 28-99), \( N \) and \( N_c \) can be calculated from \( M_w \) and the effective crosslinking density \( n \). When GTDA/AAEM = 1.0, [OH] =29.43 mole/L and [GTDA] = 0.293 mole/L. Eq. 6.38 can be further simplified as Eq 6.39. The values of control factor \( \alpha \) from scaling theory are calculated and compared in Table 6.7.
\[ \alpha = 3.18 \times 10^{-9} \frac{k_r}{D_e} \quad (6.39) \]

**Table 6.7: Control Factor \(\alpha\) Comparison of Scaling Theory and Experimental Data**

<table>
<thead>
<tr>
<th></th>
<th>23 (^{\circ})C</th>
<th>50 (^{\circ})C</th>
<th>80 (^{\circ})C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_w) of PVOH (g/mol)</td>
<td>145000</td>
<td>145000</td>
<td>145000</td>
</tr>
<tr>
<td>(M_0) of PVOH (g/mol)</td>
<td>44</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>(N=M_w/M_o)</td>
<td>3.30E+03</td>
<td>3.30E+03</td>
<td>3.30E+03</td>
</tr>
<tr>
<td>Crosslinking density (mole/cm(^3)), (n)</td>
<td>2.39E-04</td>
<td>2.39E-04</td>
<td>2.39E-04</td>
</tr>
<tr>
<td>(A_o^*[OH]) in 3 nm (mole/L)</td>
<td>29.43</td>
<td>29.43</td>
<td>29.43</td>
</tr>
<tr>
<td>(Mc = 1/n) (assume particle density g/cm(^3))</td>
<td>4.18E+03</td>
<td>4.18E+03</td>
<td>4.18E+03</td>
</tr>
<tr>
<td>(N_c = Mc/M_o)</td>
<td>9.51E+01</td>
<td>9.51E+01</td>
<td>9.51E+01</td>
</tr>
<tr>
<td>(D_e) from SCM (cm(^2)/s)</td>
<td>3.89E-13</td>
<td>2.22E-13</td>
<td>3.67E-13</td>
</tr>
<tr>
<td>(k_r) from SCM</td>
<td>1.66E-06</td>
<td>4.38E-06</td>
<td>6.75E-06</td>
</tr>
<tr>
<td>(\alpha) from scaling theory</td>
<td>1.50E-03</td>
<td>6.96E-03</td>
<td>6.49E-03</td>
</tr>
<tr>
<td>(\alpha) from experimental</td>
<td>0.33</td>
<td>0.57</td>
<td>0.93</td>
</tr>
<tr>
<td>(\alpha_{exp}/\alpha_{scaling})</td>
<td><strong>221.73</strong></td>
<td><strong>81.60</strong></td>
<td><strong>142.72</strong></td>
</tr>
</tbody>
</table>

Table 6.7 shows that the control factor, \(\alpha\), calculated from the deGennes’s theory is 80-220 times different between the two methods. The reasons for these differences could be:

(1) The scaling theory was derived based on a polymer-polymer system while latex-GTDA system is the polymer-small molecular system which is totally different. In our system, the reaction starts soon after the crosslinker was mixed to latex which make
difficult to distinguish the exact value of $t_{\text{reaction}}$. The $t_{\text{reaction}}$ value is actually the mixture of diffusion and reaction. Hence, the actual $t_{\text{reaction}}$ value may be larger or $\alpha$ is smaller. The smaller the value of $\alpha$ from experiment, the closer of value of $\alpha_{\text{exp}}$ and $\alpha_{\text{scaling}}$.

(2). Radius gyration of PVOH is estimated same as poly(ethylene oxide), which may cause some deviation. The concentration $A_o^*$ or [OH] in Eq 6.37 may be much higher which means the real reaction loci may be less than 3 nm on surface due to the PVOH is a stabilizer on latex particle surface. Hence, the value of $\alpha$ from calculation may be larger which will make the ratio $\alpha_{\text{exp}} / \alpha_{\text{scaling}}$ closer.

6.5 Summary

The second-order shrinking-core model (SCM) was derived and successfully used for nonlinear regression fitting. The predicted conversion-reaction time curve fits the experimental data very well.

The parameters, K and Y, obtained from SCM fitting were used for kinetic studies. It was found the calculated reaction constant $k_r$ matches the data from experiments and the calculated GTDA diffusion coefficient $D_c$ from SCM is close to the literature value.

The control factor, $\alpha$, derived from deGennes’s theory for film formation (strength build-up) was used to predict the mechanism of film formation. If the $\alpha$ value
is less than 1 then the film formation process is chemical reaction controlled (i.e., GTDA-Latex); if the $\alpha$ value is greater than 1 then the film formation process is diffusion controlled (i.e., GH-latex). The slow step controls the film formation process. An analytical expression of control factor was derived. The values of the control factor calculated from scaling theory are 80-220 times higher than the experimental results. The main reason why the two models are very different is that the GTDA-latex system is not a polymer-polymer system as described by deGennes. In the latex-GTDA system, the crosslinking and diffusion both take place soon they are mixed together, which differs from deGennes’s model. It needs to be noted that, in general, the film formation control factor obtained from the scaling theory is a useful tool to predict the kinetics and reaction mechanism. Like the shrinking-core model, if a known diffusion coefficient is reliably measured and the reaction constant $k_r$ can then be determined, and vice versa. In this work, the SCM and experimental results are close to matching.

6.6 References


7. Boyars, B. Ph.D. Dissertation, Lehigh University, **2004**.

8. Osifo, P. O.; Webster A.; van der M. H.; Neomagus H.; van der Gun M. A; Grant D. M. *Bioresource Technology, 2008*, 90(15) 7377.


Chapter 7

Conclusions and Recommendations for Future Work

7.1 Conclusions

7.1.1 Latex Film Water Sensitivity

AAEM monomer can be copolymerized with VAc in any ratio in semi-batch processes with t-BHP-SFS as the initiation system. A longer feeding time (8 hour monomer feeding in master batch) gives smaller particle size and particle size distribution \( (D_w = 313 \text{ nm} \text{ and PDI} = 1.03) \) compared to a shorter feeding time (2.5 hour feeding time \( (D_w = 461 \text{ nm and PDI} = 1.68) \)). The designed latex solids content is 36% since higher solids content in latexes is more suitable for mechanical performance experiments. The AAEM-containing latex was used successfully throughout this research program for crosslinking reaction studies and water sensitivity studies.

Water sensitivity of poly(vinyl acetate)-based latex is impacted by two factors: 1) surface chemistry and 2) latex polymer backbone. It was found that, with or without using crosslinkers, the surface of the latex particles has a high impact on latex film water sensitivity compared to the polymer backbone. The use of different PVOH (fully-hydrolyzed, carboxylated or acetoacetylated) systems in the same latex recipe exhibited
different water sensitivities of the derived latex films. Two crosslinkers, glyoxal (GH) and glutaric dialdehyde (GTDA), were used for latex film water sensitivity, kinetics and mechanism studies. Crosslinked latex films exhibited lower water sensitivities compared to the latex control (latex from the master batch without crosslinker). The GTDA-crosslinked films more effectively reduced water sensitivity than the GH-crosslinked latex films. The water sensitivity of GTDA-crosslinked films is closer to the water sensitivity of neat PVAc films. The minimum water sensitivity of latex film is always higher than a neat PVAc film which is cast from solution since more entanglement occurs in solution polymers than from emulsion latex films. The water sensitive stabilizers on latex particle surfaces always have a negative influence on film water sensitivity even after crosslinking.

7.1.2 Kinetics and Mechanism of GH and GTDA of Crosslinking in Latex

Four competitive model reactions were studied in detail and it was found that the GH-PD reaction is a reversible reaction. A reversible reaction kinetic model was established which fits the experimental data very well. The reversible reaction was also confirmed from leaching experiments where the majority of GH was leached out to the aqueous phase when the crosslinked films were immersed in water. All of the model reactions are pseudo-first-order reactions. This finding allows the shrinking-core-model (SCM) model to be used for further kinetic studies.
A partitioning study suggested that GH tends to be absorbed into the interior of latex particles. The partitioning of GTDA in latex suggested that GTDA tends to be adsorbed on the latex particle surfaces. When GTDA is mixed with latex, 40% of GTDA was found in the aqueous phase and 60% was absorbed on the latex particle surface. When GH is mixed with latex, 60% of GH was present in the aqueous phase, while 40% was absorbed into the interior or the latex particles. Due to its high reactivity and absorption mechanism, the GH concentration in the latex does not show an equilibrium state.

The ranking of the model reaction constant $k_r$ is used to predict the real crosslinking reaction as given below:

$$k_{GH-AEEM} >> k_{GH-PVOH} \approx k_{GTDA-PVOH} >> k_{GTDA-AEEM}$$

The kinetic and crosslinking mechanisms suggest that GTDA reacts with hydroxyl-functional groups present from the PVOH (stabilizer) and the crosslinking reaction occurs on the latex particle surface. The dominant GTDA-latex crosslinking reaction is the GTDA-PVOH reaction. GH reacts with the acetoacetyl functional group from AAEM and the crosslinking reaction occurs in the latex particle. The dominant GH-latex crosslinking reaction is actually the GH-AAEM reaction.

The GTDA-crosslinked films exhibited much lower water sensitivity than films crosslinked with GH. This finding implies that the water sensitivity of the surface of PVAc latex particles is more critical than crosslinked structure inside of the latex
particles. This finding may drive the research interest for future focus on the water sensitivity of PVAC latex. Currently, most research described in the literature pays more attention to reactions with functional monomers within the latex system rather than the functional stabilizer. The findings from this work point out that surface chemistry plays a larger role for PVAc latex water sensitivity than the chemistry in the latex backbone.

7.1.3 Shrinking-Core Model and Scaling Theory

It is assumed that the real reaction of GTDA and PVOH is also a first-order reaction like the model reaction of GTDA with PD. When \( C_{[OH]} \gg C_{[GTDA]} \), the second-order chemical reaction Shrinking-Core Model was derived and it was successfully used for nonlinear regression data fitting, the expected values from the SCM fit the experimental data very well. The calculated reaction constant, \( k_r \), matches that from kinetic studies. The GTDA diffusion coefficient obtained from SCM is close to the value in the literature.

The film formation control factor \( \alpha (t_d/t_e) \) from deGenne’s theory was used to determine the mechanism of film formation. During the GTDA-latex reaction, the ratio \( \alpha (t_d/t_e) \) decreases with increasing temperature. When the ratio is close to 1, then the reaction temperature becomes the ideal film formation temperature for a given crosslinked system. At this temperature, the uncrosslinked or GTDA-crosslinked films
both respectively reach their maximum strength. This is a useful tool to predict the optimized crosslinking conditions. The GTDA-latex film formation is a chemically controlled reaction. During the GH-latex reaction, the ratio $\alpha (t_d/t_r)$ increases with increasing temperature due to the fast reaction between GH and AAEM. This reaction is a diffusion-controlled reaction.

The analytical control factor, $\alpha$, of the film formation model was derived based on deGenne’s theory and it was compared with the experimental results. It was found that the $\alpha$ value of the experimental data differed from the $\alpha$ value of the scaling theory by a factor of 80-220, which results from several reasons. The most important reason is that the system that studied was based on a rubbery polymer which used small molecular crosslinkers, while the scaling theory was based on polymer-polymer interface reactions and diffusion across the interface. Small molecules such as GTDA are more easily diffused into the rubbery polymer compared to the polymer chain diffusing from one latex sphere to another.

### 7.2 Recommendations for Future Work

1. Use non-reactive anionic surfactant as stabilizer (OH free) in the PVAc latex polymerization and then compare the results with the PVOH-stabilized PVAc-based latex (both are 20% AAEM-containing PVAc latex). In this way, the GH
and GTDA crosslinking behavior can be studied without competing reactions. This will simplify the understanding or the individual crosslinking reaction. Precise kinetics and mechanism for surfactant-stabilized system can be studied and the results can be compared with the findings obtained from this work;

2. Use reactive surfactant as stabilizer, for example, Hitenol KH series surfactants from Dai-ichi Kogyo Seiyaku Co, Ltd, Japan, for PVAc-based latex preparation. The latexes can be used to compare with non-reactive surfactant-stabilized latexes from recommendation #1 and compare with PVOH-stabilized latex from this work in performance studies, such as water sensitivity of latex film, mechanical properties of latex film and water resistance in real coatings or adhesive applications (i.e., lab shear test on substrates);

3. Study the Z-polymer to understand why the latex prepared from these types of stabilizers (20% equivalent AAEM in Z-polymer) exhibited much lower water sensitivity (even in the absence of crosslinkers) compared to the PVOH stabilized latex. The mechanism of Z-polymer in polymerization is unknown and needs to be addressed. It will be very informative to compare these results with the 20% AAEM-containing latex since no impact of water sensitivity of the AAEM-containing was observed, if without crosslinking reaction. This research may lead to future real world applications, if:

   a. The polymerization process is under good control;

   b. Higher solids such as 45-55% can be obtained with a semi-batch process;
c. The stability and rheology of the latex in storage can be balanced.

4. Find different ways to study the kinetics and mechanism of film formation during crosslinking reaction. It was reported that ellipsometry is a new tool to analyze latex film formation. The instrument may be used for kinetic study by monitoring the film density changes \textit{versus} crosslinking reaction time, or measuring the thickness changes \textit{versus} crosslinking reaction time.

5. Consider different small molecules, diamines, as crosslinkers to compare with GH or GTDA (i.e., adipic acid dihydrazide). This kind of crosslinker may only react with acetoacetyl functional group with AAEM monomer in latex particles. These results can be used to compare the crosslinking efficiency with GH crosslinker since all of the crosslinking reactions are inside of latex particles (when AAEM-containing latex is stabilized by surfactant).
Appendix 1

Water Sensitivity of VAc-VeoVa10 (VV10) Copolymer

A1.1 Copolymerization of VAc and VV10

The water sensitivity of latex films is related to both the colloidal stabilizer and the polymer chemical structure. Farwaha et al.\textsuperscript{1} reported that nBA-VV10 based coatings showed great promise in scrub resistance and also alkaline resistance (low saponification, see Chapter 1 in Figure 1.3\textsuperscript{1}). Long chain vinyl ester monomer, VV10, is one of the most popular monomers in coatings because of its water repelling properties. This monomer can be copolymerized with VAc in almost any ratio because of their similar reactivity. This current study aims to characterize the water sensitivity of the copolymer dry film and mechanical performance of the films.

Fully-hydrolyzed poly(vinyl acetate-co-ethylene) (PVEOH) was used as stabilizer and the stabilizer/monomer ratio is 6\% during the latex preparation. It was found that stable latex could be prepared with a minimum of 6\% PAEOH colloidal stabilizer. The strain-stress behavior of the latex with 6\% or higher PVOH exhibited properties of a Newtonian fluid (see Figure A1.1).
Figure A1.1: Shear stress vs shear rate (run with a Hercules HI-Shear Viscometer, HHSV) (fully-hydrolyzed PVEOH was used as stabilizer, the stabilizer/monomer ratio is 6%).

Excess PVEOH stabilizer is not desirable because of the negative impact on water sensitivity of the latex film. The VAc-VV10 copolymerization procedure is the same as VAc-AAEM master batch process described in Chapter 2. The VV10 monomer was from Hexion and was used as received. All other raw materials were same as described in Chapter 2, section 2.1.3. The weight ratio of VV10/total monomer varied from 0% up to 70% and the films were prepared as described in Chapter 2, section 2.3.2. The dry latex films were characterized for water sensitivity from water immersion tests, and the film modulus analyzed using an Instron. The latex surface tension was measured with a Kruss Surface Tension instrument.
A1.2 Latex Film Water Sensitivity

The latex samples were prepared with an adhesive applicator as described in Chapter 2, section 2.3.3. The wet latex was drawn down with this applicator for 8 mil on a mylar film which was on a glass plate. These films were dried at ambient temperature for 7-days before water immersion test. The thickness of dried films was about 0.1mm measured by a digital caliper. The impact of VV10 on water uptake is shown in Table A1.1.

<table>
<thead>
<tr>
<th>VV10 (%wt.)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry film (mm) thickness</td>
<td>0.09</td>
<td>0.10</td>
<td>0.12</td>
<td>0.13</td>
<td>0.10</td>
<td>0.10</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Water absorption (%wt.)</td>
<td>27.2%</td>
<td>22.1%</td>
<td>20.0%</td>
<td>19.1%</td>
<td>20.6%</td>
<td>19.2%</td>
<td>20.1%</td>
<td>20.8%</td>
</tr>
</tbody>
</table>

Without the long chain monomer VV10 present in the polymer backbone, the film exhibited higher amount of water absorption (see A-1 sample). Water absorption decreased with increasing VV10 in latex. However, this trend disappears when the VV10 level is over 30%. Table A1.1 and Figure A1.2 show that the water sensitivity was the same when VV10 is greater than 30%, which means that there is no further impact on water sensitivity if VV10 higher than 30% by weight. The results cannot be explained simply by the polymer structure. The possible explanation is that water
sensitivity of latex films may not be only related to chemical structure but also related to the morphology of dry film, such as porosity and roughness.

Figure A1.2: Impact of VV10 on water absorption (fully-hydrolyzed-PVEOH was used as stabilizer, the stabilizer/monomer ratio is 6%).

The excess vinyl ester, VV10, in the polymer compositions may be restricted in actual industrial applications due to its higher cost and negative impact on the glass transition temperatures of the film. It was found that when the VV10 to VAc ratio is over 50% by weight, the film is slightly tacky in wet conditions. (see section A1.3).
A1.3 Surface Tension

The surface tension of the dry latex was measured with a Kruss Surface Tension instrument. The films were dried at ambient temperature for 7 days and then at 50 °C for 7 days before the test. Contact angles were measured with two liquids, water and diiodomethane, on the dry films. The surface energy is calculated and averaged with repeated tests.

Calculation process for $\gamma$, $\sigma$ and $\theta$:

(1). Surface contact angle with diiodomethane ($\sigma_L^D = \sigma_L = 50.8$ mN/m) which only has a dispersive component to its surface tension.

\[
\gamma_s^D = \sigma_L^* (\cos \theta +1)^2 /4
\]

(2). Surface contact angle with water ($\sigma_L^D = 26.0$ mN/m, $\sigma_L^P = 46.8$ mN/m, $\sigma_L = 72.8$ mN/m) which has both a polar and a dispersive component to its surface tension.

\[
(\sigma_L^D \gamma_s^D)^{1/2} + (\sigma_L^P \gamma_s^P)^{1/2} = \sigma_L (\cos \theta +1)/2
\]

Overall surface energy (mJ/m$^2$) $\gamma_s = \gamma_s^D + \gamma_s^P$ and Surface Polarity (%) = $\gamma_s^P / \gamma_s$

The measured and calculated data contact angle and surface tension are shown in Table A1.2 and Figure A1.3.
Table A1.2: Latex Film Surface Tensions (mJ/m²)

<table>
<thead>
<tr>
<th>%VV10</th>
<th>Static Contact Angle</th>
<th>Calculated Surface Energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Diodomethane</td>
</tr>
<tr>
<td>A, 0%</td>
<td>76.9 ± 3.4</td>
<td>45.4 ± 1.3</td>
</tr>
<tr>
<td>B, 10%</td>
<td>81.0 ± 2.0</td>
<td>45.7 ± 0.9</td>
</tr>
<tr>
<td>C, 20%</td>
<td>86.3 ± 1.3</td>
<td>47.8 ± 1.8</td>
</tr>
<tr>
<td>D, 30%</td>
<td>83.5 ± 2.1</td>
<td>50.0 ± 1.5</td>
</tr>
<tr>
<td>E, 40%</td>
<td>84.5 ± 3.3</td>
<td>51.6 ± 1.4</td>
</tr>
<tr>
<td>F, 50%</td>
<td>89.6 ± 2.1</td>
<td>53.0 ± 0.9</td>
</tr>
<tr>
<td>G, 60%</td>
<td>90.4 ± 2.3</td>
<td>60.2 ± 4.1</td>
</tr>
<tr>
<td>H, 70%</td>
<td>86.2 ± 1.8</td>
<td>51.8 ± 1.5</td>
</tr>
</tbody>
</table>

Figure A1.3: The impact of VV10 level on surface tension fully-dyedolized-PVEOH was used as stabilizer, the stabilizer/monomer ratio is 6%).

\[ R^2 = 0.9328 \]
Table A1.2 and Figure A1.3 show that surface tension of the latex film decreases with increasing VV10 ratio. A near linear relationship between surface tension and monomer ratio is observed. The lower is the surface tension, the lower is the water absorption in the latex film. Hence, films with lower surface tension should have better water resistance. The lower surface tension of VV10-containing latex film is because the long hydrophobic side chain in VV10 and this long soft chain serves like an umbrella for VAc. In theory, samples B through H should have progressively better water resistance or lower water sensitivity. However, the water absorption on Figure A1.1 does not show this trend when VV10 level is higher 30%. The possible explanation was as in section A1.2.

**A1.4 VAc-VV10 Latex Film Modulus**

Thick films of the VAc-VV10 latex films were prepared as described in Chapter 3 (section 3.3.1). The samples were cut into 1x3 inches for testing. The thickness of the dried film samples were around 1 mm. The tensile modulus data are shown in Table A1.3 and Figure A1.4.
Table A1.3: Impact of VV10 on Latex Film Modulus and $T_g$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (inch)</th>
<th>Modulus (psi)</th>
<th>Average (psi)</th>
<th>Modulus (KPa)</th>
<th>$T_g$(DMA) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.043</td>
<td>2574</td>
<td>2025</td>
<td>13966</td>
<td>60.5</td>
</tr>
<tr>
<td>B</td>
<td>0.046</td>
<td>1876</td>
<td>3004</td>
<td>20714</td>
<td>53.5</td>
</tr>
<tr>
<td>C</td>
<td>0.046</td>
<td>2028</td>
<td>2259</td>
<td>15577</td>
<td>48.9</td>
</tr>
<tr>
<td>D</td>
<td>0.041</td>
<td>1467</td>
<td>1403</td>
<td>9675</td>
<td>44.3</td>
</tr>
<tr>
<td>E</td>
<td>0.045</td>
<td>804</td>
<td>767</td>
<td>5289</td>
<td>40.4</td>
</tr>
<tr>
<td>F</td>
<td>0.043</td>
<td>606</td>
<td>616</td>
<td>4284</td>
<td>N/A</td>
</tr>
<tr>
<td>G</td>
<td>0.042</td>
<td>574</td>
<td>533</td>
<td>3675</td>
<td>32.1</td>
</tr>
<tr>
<td>H</td>
<td>0.038</td>
<td>526</td>
<td>495</td>
<td>3415</td>
<td>27.5</td>
</tr>
</tbody>
</table>

Figure A1.4: Impact of VV10 on Latex Film Modulus and $T_g$ (VV10 level changes from 10% to 70% based on total monomer).
Lap shear tests were performed at 20 °C. Tables A1.3 and Figure A1.4 show that the film modulus decreases sharply with increasing VV10 in the latex (see sample B(10%) to E(40%)). The VV10 impact on modulus of the films become less when its level is over 40%. Beyond this point, the soft monomer segments (long side chain in VV10) in the polymer backbone has a larger influence on the modulus compared to VAc. Table A1.3 also show the changed in glass transition temperature with VV10 level. The higher is the VV10, the lower is the $T_g$ of the latex films.

In general, the addition of VV10 lowers the water sensitivity of the latex films and, provides relatively low surface energy. However, it has a negative impact on the latex film modulus and it lowers film glass transition temerature.

**A1.5 Summary**

The water absorption of VAc-VV10 latex films were studies. It is found that the VV10 in latex film reduces water absorption and surface tension. However, it has negative impact to modulus of the films.

The VAc-VV10 latex film reaches to minimum water absorption when VV10 level is 30% by weight. At this ratio, the water absorption is still as high as 20% in 8 hours water absorption, which implies that copolymerization with long chain monomer is limited for high demand of water resistance of films, unless the PVAc-based latex is chemically crosslinked.
A1.6 Reference

Appendix 2

Oxygen Permeability of GH-crosslinked Latex Films

A2.1. Sample Preparation for Oxygen Permeability

Carbon dioxide as a probe gas has been used to characterize residual porosity in polymer latex films\(^1\). It was believed that the porosity of crosslinked latex films may have an influence on water sensitivity. This is the reason why permeation experiments were carried out for studies of GH- and GTDA-crosslinked films. Normally, the higher the porosity in the film, the higher the permeation should be. Oxygen gas was used for this test.

Latex film preparations were described in Chapter 2 (section 2.3.3). All GH-crosslinked films were cured at room temperature for two weeks and then the cured films were put in desiccators for two more weeks in order to remove any adsorbed moisture before the test. Another set of GH-crosslinked films were annealed at 80 °C for four hours then the permeability was compared with room temperature cured films. The gas permeability test was started after 10 minutes in a vacuum at 27 mm Hg.
A2.2. Principle of Permeation from Experiments

The permeability of oxygen can be calculated with Eq. A2.1:

\[ \rho_E = \frac{\Delta V}{A X P_0} \times ss \delta \]  
(A2.1)

\( \rho_E \): permeation parameter with unit [cm\(^2\) (STD) s\(^{-1}\) atm\(^{-1}\)]

\( (\frac{\Delta V}{\Delta t})_{ss} \): Steady state volume changes

\( (\frac{\Delta V}{\Delta t})_{ss} = (\frac{\Delta P}{\Delta t})_{ss} \times \frac{273V_c}{T} \)

\( P_o \): pressure used during test

\( V_c \): cell volume of the test chamber

\( \Delta \): thickness of the tested films

A2.3 Crosslinked Latex Film Oxygen Permeability

The dried films were placed on a calibrated sealed testing cell to allow oxygen gas pass from one side to the other side of the film. The pressure differences were recorded for calculation as described in eq. A2.1. The permeability of room temperature-cured films and 80 °C annealed films is shown in Table A2.1 and Figure A2.1.
Table A2.1: Oxygen Permeability of GH- and GTDA-Crosslinked Latex Films

<table>
<thead>
<tr>
<th>GH ( %wt.)</th>
<th>$P_E$(RT) [cm$^3$(STD)cm/cm$^2$.s.atm]</th>
<th>$P_E$(80 °C) [cm$^3$(STD)cm/cm$^2$.s.atm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>8.97E-08</td>
<td>9.65E-08</td>
</tr>
<tr>
<td>5%</td>
<td>1.04E-07</td>
<td>2.26E-07</td>
</tr>
<tr>
<td>10%</td>
<td>1.21E-07</td>
<td>2.90E-07</td>
</tr>
<tr>
<td>15%</td>
<td>1.74E-07</td>
<td>1.03E-06</td>
</tr>
<tr>
<td>20%</td>
<td>1.79E-07</td>
<td>2.05E-06</td>
</tr>
</tbody>
</table>

Figure A2.1: Oxygen permeability of GH- and GTDA-crosslinked latex films.
Table A2.1 and Figure A2.1 showed that there was little difference in oxygen permeation with room-temperature cured films. The GH concentration based on latex (or GH/AAEM mole ratio) made no difference in permeability. The permeability value of GH-crosslinked film is close to that of a control film. However, the 80 °C annealed films exhibited much higher $\rho_E$ values. The higher the concentration of GH in film, the higher the oxygen permeation was observed.

Significantly, higher oxygen permeation values with the 80 °C annealed films implied that the films were more porous than those dried only at room temperature. Unlike GH-crosslinked films, GTDA-crosslinked films exhibited no differences in permeability under conditions (see Table A2.1 and Figure A2.1). This suggests that the annealing temperature or curing temperature for both crosslinkers has different influences on the morphology of the crosslinked films, which will be discussed in section A2.4.

Table A2.2 and Figure A2.2 show that the oxygen pressure had a large impact on permeation if the GH-containing films were annealed at 80 °C. Higher pressure resulted in higher permeation (top curve in Figure A2.2). The permeation of 20% GH-containing film (annealed at 80 °C) was 11.5 times higher than that of room temperature cured films. However, the pressure showed less impact on permeability if the films were all annealed at 80 °C (bottom curve in Figure A2.2). Here the ratio of permeation $\rho(340\text{Kpa})/\rho_E(200\text{KPa})$ is close to unity.
Table A2.2: Impact of Pressure on Oxygen Permeability of GH-crosslinked Latex Films (80 °C annealed films)

<table>
<thead>
<tr>
<th>%GH in film</th>
<th>$\rho_E (80 \degree C)/\rho_E (RT)$ 200KPa pressure</th>
<th>$\rho_E (340Kpa)/\rho_E (200KPa)$ (80 °C annealed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>5%</td>
<td>2.2</td>
<td>0.6</td>
</tr>
<tr>
<td>10%</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>15%</td>
<td>5.9</td>
<td>1.2</td>
</tr>
<tr>
<td>20%</td>
<td>11.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure A2.2: Impact of pressure on oxygen permeability of GH crosslinked latex films (top: permeability of 80 °C annealed film vs room temperature cured films; bottom: permeability of 340 KPa vs 200 KPa on 80 °C annealed films).
It can be assumed that the annealing temperature (80 °C) of GH-cured films imparted more porosity to the films. The higher the GH level in the film, the higher was the porosity, which gave a high ratio of $\rho_E(80^\circ C)/\rho_E(RT)$. If the tests were performed with the same films then the impact of pressure on permeation was diminished (bottom curve in Figure A2.2).

**A2.4 Characterization of the GH Crosslinked Films with SEM and AFM**

In order to understand why the GH-crosslinked films exhibited high permeability after 80 °C annealing, the SEM and AFM were used to examine the cross-section and surface roughness of the films. Figure A2.3 shows that the film prepared with high amount of GH exhibited more porosity or rougher structure in the cross-section of the film. The cross-section of the control film showed a very dense surface. The results imply that GH evaporated during annealing at 80 °C since boiling point of GH is only 50 °C which is much lower than the annealing temperature.
Figure A2.3: Optical micrographs of cross-section of GH-crosslinked latex films (A) 0%; (B) 5% GH; (C) 10% and (D) 15%. The master batch latex was used and all cured films were annealed at 80 °C before test.

The evaporation of GH from the film during high temperature annealing can be explained by the weak GH-latex bonding. As discussed in chapter 5, the GH-latex crosslinking reaction is a reversible reaction. The chemical bond becomes de-associated during heating. The evaporation of GH during annealing causes more porosity in the film. The high the GH level in the film, the rougher cross-section was
observed. Therefore, higher oxygen permeability was observed compared with the control film.

Figure A2.4 shows the water absorption of latex films with/without crosslinkers. The GH-crosslinked film (dotted line) shows a higher initial water absorption rate than the control film because of high porosity or roughness in the film. After the peak water absorption, the curve decreases with immersion time and then increases with additional immersion time after passes the lowest water absorption. This process was related to GH diffusion to water. After GH the leaching process is over, the water absorption increases with immersion time once again which is due to higher internal surfaces from the porosity or roughness which makes the water absorption higher with immersion time.
Figure A2.4 indicates that the efficiency of crosslinkers and process of film formation all have impact to latex film water sensitivity. As discussed in Chapter 3, Figure A2.4 also showed that the GTDA-crosslinked film exhibited much lower water absorption compared to GH-crosslinked films. The GTDA crosslinking reaction is a permanent and films annealed at any temperature showed no differences in permeation (no show).

Table A2.3 and Figure A2.5 show the surface roughness (lower side of film surface) versus GH level and annealing conditions. In general, the presence of GH reduces the roughness of the films since the small molecular crosslinker served as a
coalescence agent and assists in film formation. 80 °C and 60 °C annealed films showed different surface roughness results. The GH-crosslinked latex films become smoother with GH when annealing temperature was 60 °C. However, the films become rougher with GH when annealing temperature was increased to 80 °C. This is because 80 °C is far above GH boiling temperature. 60 °C annealing temperature shows smoothest surface and this temperature can be considered as maximum curing condition for application.

**Table A2.3:** Roughness of GH Crosslinked Latex Films

<table>
<thead>
<tr>
<th></th>
<th>Roughness of RT cured film (RMS, µm)</th>
<th>Roughness of 60°C annealed film (RMS, µm)</th>
<th>Roughness of 80°C annealed film (RMS, µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% GH</td>
<td>19.43</td>
<td>9.42</td>
<td>5.26</td>
</tr>
<tr>
<td>5% GH</td>
<td>14.95</td>
<td>6.13</td>
<td>12.38</td>
</tr>
<tr>
<td>10% GH</td>
<td>10.85</td>
<td>2.32</td>
<td>14.98</td>
</tr>
<tr>
<td>15% GH</td>
<td>10.75</td>
<td>1.33</td>
<td>17.02</td>
</tr>
</tbody>
</table>

RMS: Root-Mean-Square
Figure A2.5: Optical micrographs of GH crosslinked latex films (60°C annealed, lower film surface was measured). (A) control 0% GH; (B) 5% GH; (C) 10% GH and (D) 15% GH.

Section A2.3 indicated that the permeation of GH and GTDA crosslinked films is independent of crosslinker level. This can be explained that Permeability = Solubility x Diffusion coefficient. Kobayashi et al.\textsuperscript{2} reported that the PVAc film has a free volume of 80-90 Å\textsuperscript{3} which is much larger than the oxygen molecule in size (only 1.2 Å in length).
A2.5 Summary

GH- and GTDA-crosslinked films, cured at room temperature, showed no difference in oxygen. The high permeability of GH-annealed films is caused by evaporation of GH in annealing process at 80 °C. The water absorption behavior of GH-crosslinked film (GH/AAEM = 2.84) was explained, which is the sum of GH diffusion and water absorption processes both during the immersion time. It can be concluded that the oxygen permeability and water absorption of the GH-crosslinked films were not only related to crosslinkers but also related annealing temperature.

A2.6 References


Vita

Zhijin Chen was born in Jiang Yan City, Jiang Su Province, P. R. China on October 14, 1958. He graduated from Nanjing University of Science and Technology in 1982 with a Bachelors degree in Polymer Chemical Engineering. He then started his career working at the same University as a faculty member teaching polymer science, as well as performing polymer related research. In 1990, Zhijin received his Masters degree from the same University, also in Polymer Chemical Engineering.

Zhijin came to Florida State University as a research fellow in 1991 where he worked on water soluble polymer synthesis in FSU’s Chemistry Department. In 1993 he was admitted as a student to University of Detroit Mercy seeking his life-long dream of earning a Ph.D. In 1995, Zhijin earned a second Masters degree at UDM in Polymer Chemistry. However, to support his family and following the advice of his friends, Zhijin started his first job at PPG industries before he could attain his Ph.D. He then moved on to his second chemist position at Sovereign Specialty Chemicals in Cincinnati, Ohio, where in 2001 he started the Material Science Ph.D program at the University of Cincinnati. However, after one year’s study at UC, Zhijin once again had to put his dream on hold because his company’s merger required him to relocate to the East coast. Unwilling to uproot his family once again, Zhijin instead decided to take a position as a R&D chemist at Franklin International in Columbus, Ohio.
In 2005, Zhijin came to Lehigh’s EPI short course where he found that Lehigh was the perfect destination for a real Ph.D study. With the support of his employer and also a lot of support from Ray Pearson from Lehigh, Zhijin enrolled as a part time student in Lehigh’s Polymer Science and Engineering doctorate program. After registering in August of 2005 and while working full time as a research chemist, Zhijin finished all required course work as well as two qualification exams and an oral presentation in just two years. Zhijin found the same commitment to academic achievement from his current employer, IFS Industries. IFS provided Zhijin one year residence time at Lehigh to finish his academic research in 2009. After a long journey, Zhijin finally had the support to attain his dream.

Zhijin started his journey to earning a Ph.D two times before arriving at Lehigh University where he is a straight A student. As a many years industrial polymer chemist who has worked on polyurethane synthesis, emulsion polymer synthesis and formulations. To date, Zhijin has received 9 offers from different companies since 1995 but he has only worked for a few of them. He views the research work as fun because of his love for polymer science, and he enjoys his academic work as well. Zhijin’s lifelong pursuit of scholastic success is firmly driven by his desire to learn. It is because of this philosophy that Zhijin has maintained a good position in the polymer industry and kept his knowledge current and fresh.