EPI-HALOHYDRIN MODIFIED POLYAMINES AS MORDANT AGENTS FOR ALKALINE ROSIN SIZING

A Dissertation Submitted by

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3. Abstract

Many grades of paper have shifted from acid to alkaline production conditions. This change excludes the usage of traditional alum-rosin sizing chemistry. In some cases however, rosin sizing could prove beneficial if it could be used under neutral to alkaline paper making conditions. One effort toward this goal has been the use of epi-halohydrin modified polyamine/polyaminoamide in place of alum. The optimum sizing conditions, as well as the mechanism that modified polyamines/polyaminoamides use to size rosin, is investigated. Polyethyleneimine modified with epi-chlorohydrin was used in these studies.

Rosin dosage was found to be the main variable that controlled the degree of sizing achieved. As the only hydrophobic material added, this was expected. In addition to rosin dosage, the polymer and pH had significant impacts on this sizing chemistry.

Laboratory data shows that the synthesis procedure for and structure of polyethyleneimine-epi-cholohydrin (PEI-epi) impacts the degree of sizing achieved. Use of different modification techniques and degrees of modification illustrated several key factors regarding the polymer as a rosin sizing mordant. Prevention or removal of by-products from epi-chlorohydrin improves the sizing efficiency of PEI-epi with rosin. A critical molecular weight of the PEI-epi was found to be important

to sizing. Higher charge density on PEI-epi provides better the sizing efficiency. In addition to the polymer, other important factors where examined.

The pH of the stock impacted the degree of sizing and permanency of the sizing achieved. Varying stock pH showed changes in sizing that are consistent with effects seen for rosin retention and of PAE as a wet strength agent. Low and high pH levels also caused reversion of the sizing effect.

A pilot trial of the PEI-epi-rosin sizing chemistry was conducted at the Herty Foundation. The pilot trial shows that PEI-epi-rosin can reach the required level of sizing for linerboard. Trial results showed that calcium carbonate filled sheets could be sized by this chemistry. No significant impact on strength is seen from the sizing chemistry at the required dosage levels. As would be expected, addition of filler diminishes sheet strength. No sizing reversion was seen from any samples of this trial.

Size reversion at low stock pH indicated that acid catalytic cleavage of an ester bond could have been occurring. Addition of acid or base to permanently sized sheets showed significant levels of reversion, similar to that seen for low stock pH sheets. This provides further supporting evidence for the formation and importance of an ester bond between rosin and PEI-epi.

FTIR spectra were collected for model compounds to further examine the presence and importance of ester bonds. An ester bond was found to form at room temperature

with aging or immediately with drying. Further, the ester bonds were found to decrease when the sample was subjected to acidic or basic environments.

Solid state NMR was run to demonstrate the presence and importance of ester bonds to sizing in handsheets. Use of a ^{13}C labeled fatty acid showed that the ester bond peak dominated when sizing was present. After treatment with sodium hydroxide, the sizing disappeared and much of the ester bond signal shifted to a carboxylic acid or salt. Further solid state NMR of a non-reactive cationic polymer or a fully pre-reacted PEI-epi polymer shows retention of the fatty acid, but no ester bond and no sizing.

The sizing mechanism of PEI-epi-rosin sizing appears to be connected to an ester bond formed during drying or with aging. While the amount of rosin retained controls the degree of sizing, retention alone is not enough to give sizing. The most effective pH for this sizing chemistry is near neutral, pH 6-8. FTIR and solid state NMR shows that an epichlorohydrin modified polyamine can form ester bonds with fatty acids in handsheets under conditions comparable to papermaking. The presence of residual acid or base in handsheets destroys the sizing effect achieved. Destruction of the sizing by addition of sodium hydroxide parallels the cleavage of many of the ester bonds present. PEI-epi appears to function as a mordant for rosin by creating an ester bond to anchor and help orient the hydrophobic portion of rosin.

4. Background

4.1. Sizing

The sizing of paper is done to impede the penetration of fluids into the paper. Sizing agents can be added internally or on to the surface of paper. The focus of this research is on internal sizing agents. Many chemicals have been used to size paper. Today most internal sizing is done with these chemical agents: alum-rosin, alkyl ketene dimers (AKD), and alkyl succinic anhydride (ASA). Alum-rosin sizing came into use in the early 1800's.[1,2] Alum-rosin sizing was the primary internal sizing agent until the invention of AKD in 1953[3].

In certain grades of paper, shifts to alkaline papermaking or a need for higher degrees of sizing have given preference to AKD and ASA over the older alum-rosin chemistry. Under alkaline papermaking conditions, alum becomes anionic and alum-rosin additions alone no longer achieve sizing. Drawbacks of AKD and ASA sizing have encouraged research into finding new ways of using rosin in alkaline conditions.

Before proceeding, some terminology must be clearly defined. Reversion will be used here as Neimo defines it. "Size **reversion** is when paper is in specification at the reel and, upon aging, the sizing level decreases to a level where it then remains constant".[4]

Retention refers only to keeping material in the fiber web during sheet formation with no regard to how it is oriented, generally through charge neutralization. The term **mordant** is used here to describe a chemical that orients a sizing agent so that the hydrophobic portion of the material is facing away from the fiber surface and the hydrophilic portion is facing toward the fiber surface. The difference of these last two terms is important because of their similarity and also because in some cases the same chemical carries out both functions.

4.2. Alum-Rosin Sizing Mechanism

In order to create a liquid barrier, a sizing agent has to turn the hydrophilic surface of paper into a hydrophobic surface. Rosin has both a hydrophilic and a hydrophobic end. The hydrophilic end allows for stability in the headbox and for bonding to the fiber surface. The hydrophobic end allows for creation of a fluid barrier.

The hydrophobic end of rosin consists of aromatic rings. The hydrophilic end is formed by carboxylic acid(s). Figure 4.1 shows the structure of a common rosin acid, levopimaric acid, in its natural form and a fortified form. The number of carboxylic acids can be increased through a process called fortification. Fortification can be accomplished through a Diels-Alder reaction between a conjugated diene in rosin and maleic anhydride, fumaric acid, or through reaction with glycerol. Figure 4.2 shows

the mechanism of the Diels-Alder reaction. There are different ways in which the rosin is prepared for application on paper machines.

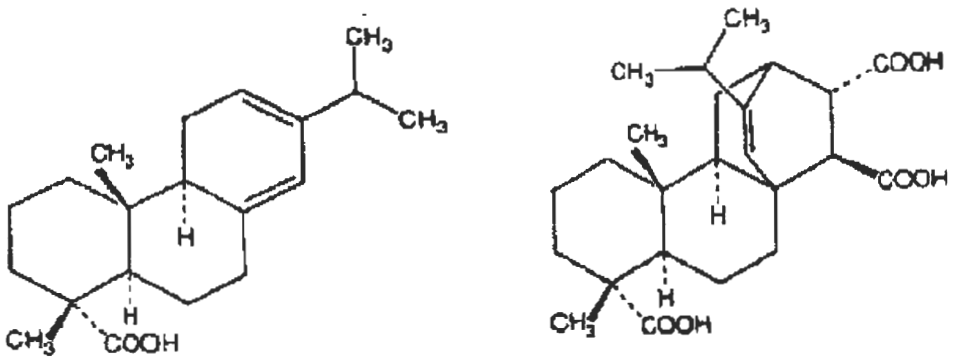


Figure 4.1 – Structure of a rosin acid on the left, levopimaric acid, and on the right the same rosin acid fortified.[5]

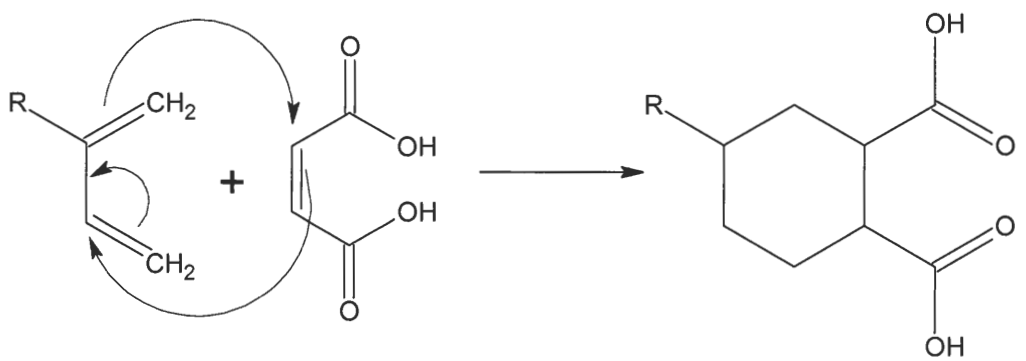


Figure 4.2 - Diels-Alder reaction mechanism.

The two most common forms of rosin available are rosin soap and dispersed or emulsified rosin. Rosin soap is formed by reacting rosin with sodium hydroxide, a process known as saponification. Saponified rosin is water-soluble and when made in

a liquid form it can be added directly into the papermachine's wet-end. Emulsifying rosin acid with a surfactant gives dispersed rosin. Dispersed rosin can also be added directly into the papermachine's wet-end. Once added to the system, the rosin needs to be retained.

Rosin soap and dispersed rosin are retained in different ways. Rosin soap reacts with alum in solution, forming an alum- rosin particle about 0.1 μm in diameter. The alum imparts a positive charge to the alum-rosin soap particle surface. This positive charge retains rosin on the anionic fiber surface.

In contrast, dispersed rosin sizing involves the alum and rosin attaching to the fiber separately. This requires the use of a retention aid to retain the dispersed rosin, commonly starch, or the use of cationic dispersed rosin. Figure 4.3 demonstrates both of the rosin sizing mechanisms. The reactions between alum and rosin impact decisions on the chemical addition order chosen. Also, the difference in retention mechanism allows dispersed rosin sizing to be used at a slightly higher pH.

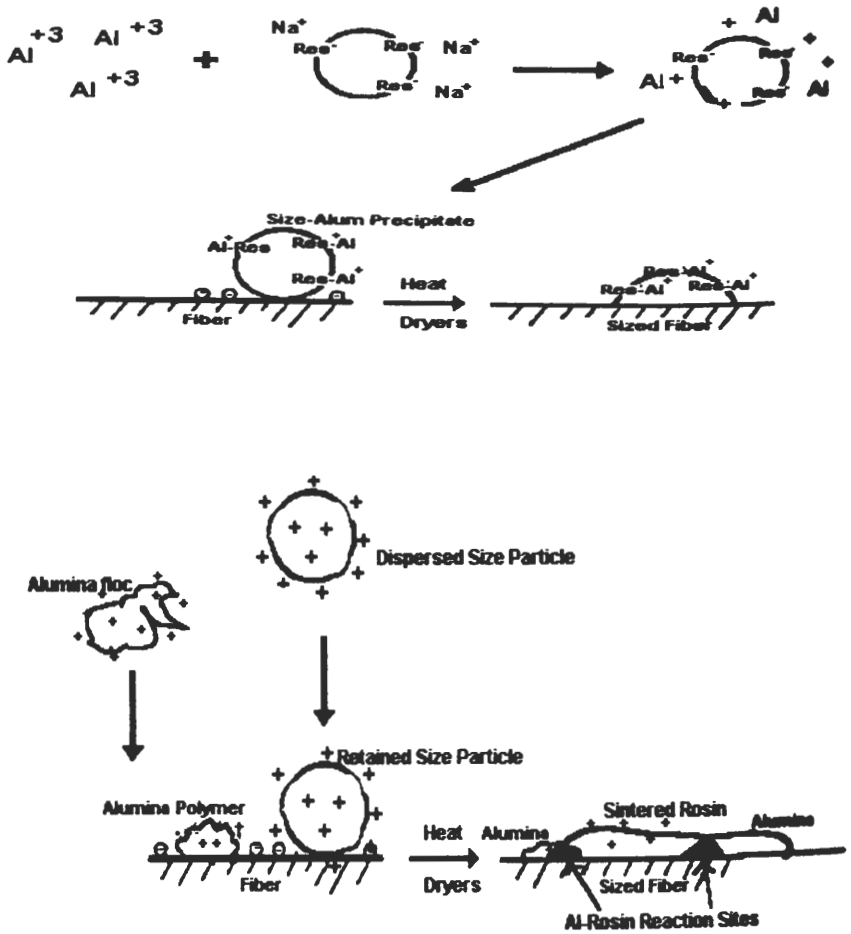


Figure 4.3 - Alum-soap rosin mechanism (top) and alum-dispersed rosin mechanism (bottom). [6]

Alum's structure varies with pH. Figure 4.4 shows the non-complex forms of alum at different pH values. The pH has to be controlled in rosin sizing to get the desired form of alum. A pH of 4.0 to 4.8 is typically used for optimal soap sizing.[7] This pH puts alum predominately in the Al^{3+} form. Alum in this form is highly cationic and has a small molecular size. A pH of 4.2 to 5.5 is commonly used for anionic dispersion sizing.[7]

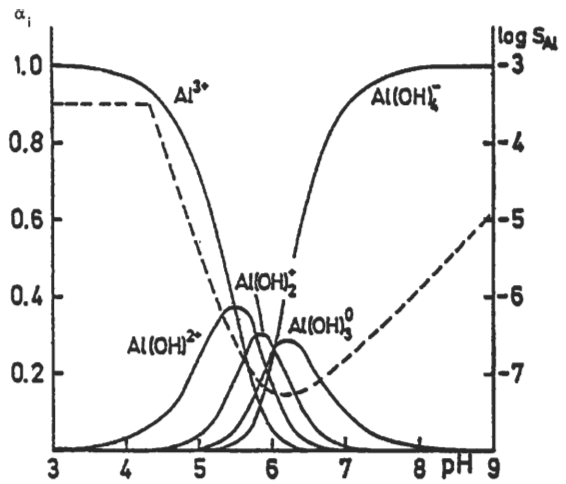


Figure 4.4 – A diagram showing Al-hydrolysis species versus pH.[8]

The pH range for dispersed rosin appears to produce a polynuclear aluminum hydroxide complex of $Al_{13}O_4(OH)_{24}^{7+}$ or $Al_8(OH)_{20}^{4+}$.[9] The higher charge of the complexes provides a better retention of alum on fibers. Dispersed rosin sizes are used in higher pH than rosin soaps and benefit from this better retention of alum.

Rosin soaps perform best at a pH in which the Al^{3+} form of aluminum dominates. The more cationic complexes of aluminum appear to form larger alum-rosin particles than the Al^{3+} form.[10] In which case, a larger particle would tend to be less evenly distributed over the surface of the fiber. This gives a lower surface coverage by rosin. Once the alum and rosin are on the fiber, a water-insoluble bond needs to be formed between rosin and the fiber.

The alum bond between rosin and the fiber is formed in the dryer section. This process is often referred to as sintering. The dispersed rosin particles are about five

times larger in diameter than the rosin soap-alum particles. Dispersed size particles have a melting point of 71-110^{0}C, at or below typical dryer temperatures.[11] In the dryer section, this low melting point allows the relatively large dispersed particles to spread over the fiber surface, coming into contact and reacting with alum, see Figure 4.3 bottom. The spreading of the dispersed rosin also helps to increase the fiber surface coverage area.

Alum-rosin soap particles have a melting point higher than typical dryer temperatures. The melting point of rosin soap is 138-154^{0}C.[11] Rosin soap is thus dependent on uniform distribution in the wet-end to achieve adequate fiber coverage. Thus, a fiber becomes sized with alum and rosin in acidic conditions.

Under acid conditions alum has two important roles in sizing. One purpose of alum is retention. The retention may be of alum alone or alum and rosin. The other purpose of alum is to anchor rosin to the fiber and orienting the hydrophobic end away from the fiber surface. The retention functionality of alum is lost when papermaking conditions move into neutral to alkaline conditions.

4.3. Move Toward Alkaline Papermaking

Fine paper is now made almost exclusively under neutral to alkaline conditions. The typical pH range used is 7.2-8.0.[12] At this pH, the $Al(OH)_4^-$ specie of alum dominates.

In this form, alum does not retain on fibers and can not retain rosin soap. Also, rosin sizing provides a lower degree of sizing than AKD or ASA. For these reasons, rosin has largely been replaced by synthetic sizes in fine paper, food and liquid packaging, neutral/alkaline linerboard, and some other smaller applications. Most linerboard is still made under acidic conditions to allow for use of the alum-rosin sizing chemistry.

Several factors have influenced and been gained by shifting to neutral/alkaline papermaking conditions, see Table 4.1. The main factor that drove the shift from acid to neutral/alkaline papermaking relates to the ability to make paper with calcium carbonate filler. The better appearance/printing properties of calcium carbonate along with the increased strength of neutral/alkaline paper provide great benefits for printing grades.

One of the biggest changes that the shift to neutral/alkaline papermaking has brought about is the need to use synthetic sizing agents. Due to alum's pH sensitivity, traditional alum-rosin sizing can not be used in the pH required for calcium carbonate. Synthetic sizing agents present some significant difficulties and drawbacks over alum-rosin sizing. However, the benefits of neutral/alkaline papermaking have out weighed the problems with synthetic sizes.

Table 4.1 - Benefits and drawbacks of neutral/alkaline papermaking.[13]

Process Benefits	**Product Benefits**
Calcium carbonate can be used	Improved strength properties
Reduced energy consumption	HW substitution because of strength gain
Higher drainage rate	Higher filler content
Less buildup of inorganic solids	Good printability
Specific water consumption reduced	Calendering at higher moisture content
Cheaper furnish (filler substitution)	Improved paper permanence
Less corrosion	Improved chemical resistance
Process Drawbacks	**Product Drawbacks**
Synthetic internal sizes required	Size curing can be difficult to control
Temperature limitations on wet end	Size reversion and fugitivity
Acid chemical pulps can be a problem	Fine filler required for opacity
High load of anionic trash with mechanical pulps	Yellowing with mechanical pulps if pH > 7.5
Deposit and picking problems	Insufficient toner adhesion in copying
High microbiological activity, slime	Slippery sheet surface at hard sizing
Difficult to optimize retention systems	Large dosage of OBA can hurt marketing
Chemical incompatibility (w/ alum and some dyes, wet strength agents, & OBAs)	

4.4. Synthetic Sizing Mechanisms

4.4.1. Alkyl Ketene Dimer (AKD)

Downey developed alkyl ketene dimer for use in papermaking in 1953.[3] Figure 4.5 shows the structure and generally accepted reactions of AKD. The dimer in AKD can react with water to form a β keto acid. A ketone is formed by decarboxylation of the acid. The dimer can also react with cellulose hydroxyls and form a β keto ester.[14]

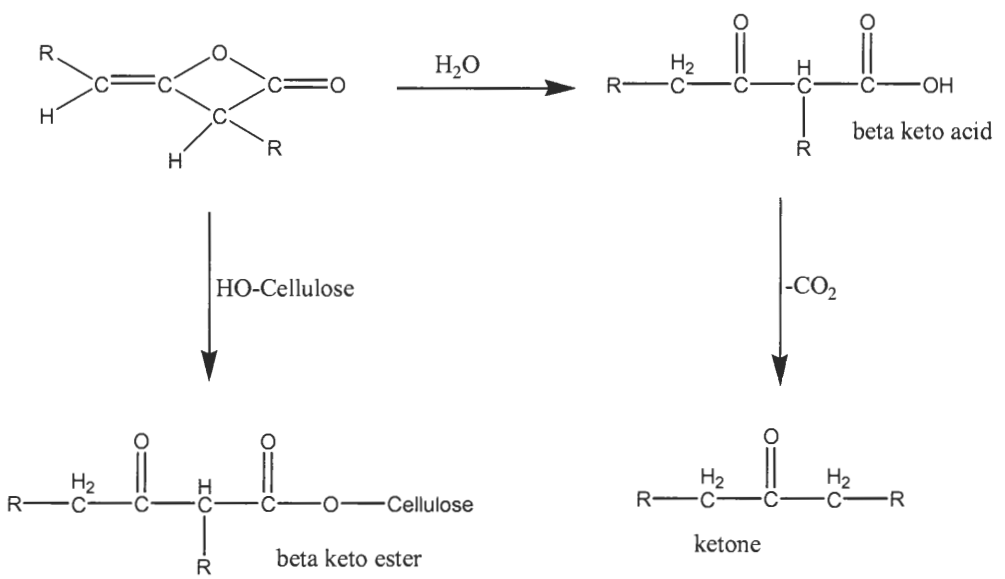


Figure 4.5 - AKD structure and reactions with water and cellulose hydroxyls.

Most attribute AKD sizing to the formation of a β-keto ester bond to a cellulose hydroxyl.[15,16,17] Others have argued that no β-keto ester bond is present in AKD sized

paper.[18,19] The importance of bound or unbound AKD becomes apparent when it is realized that excessive heat from drying can cause AKD to migrate within the roll during storage.[19,20,21]

Migration of unbound AKD can cause over or under sizing of the paper. Paper over sized with AKD is extremely slippery. Further, removal of the unbound AKD, 80-90 percent of added AKD, only causes a slight drop in the degree of sizing.[15,16] The hydrolyzed AKD provides a sizing effect, but not nearly as strong as the bound AKD.

AKD reacts slowly with either water or cellulose. A major benefit of this slow rate is that AKD can be stored in ready to use solutions for long periods of time. AKD tends to not react with water during sheet forming. The slow reaction rate also impacts the bond formed between AKD and cellulose. Because of this slower rate, AKD does not set up much of the sizing effect until long after winding. This makes process control of the final degree of sizing difficult.

4.4.2. Alkenyl Succinic Anhydride (ASA)

Wurzburg patented the use of alkenyl succinic anhydride for use in papermaking in 1974.[22] Figure 4.6 shows the structure of ASA and its reactions with water and cellulose hydroxyls.[23,24] The anhydride in ASA can form an ester bond with the cellulose hydroxyls. ASA also hydrolyzes rapidly with water under papermaking conditions. There is little debate that ester bound ASA is key to the sizing mechanism.

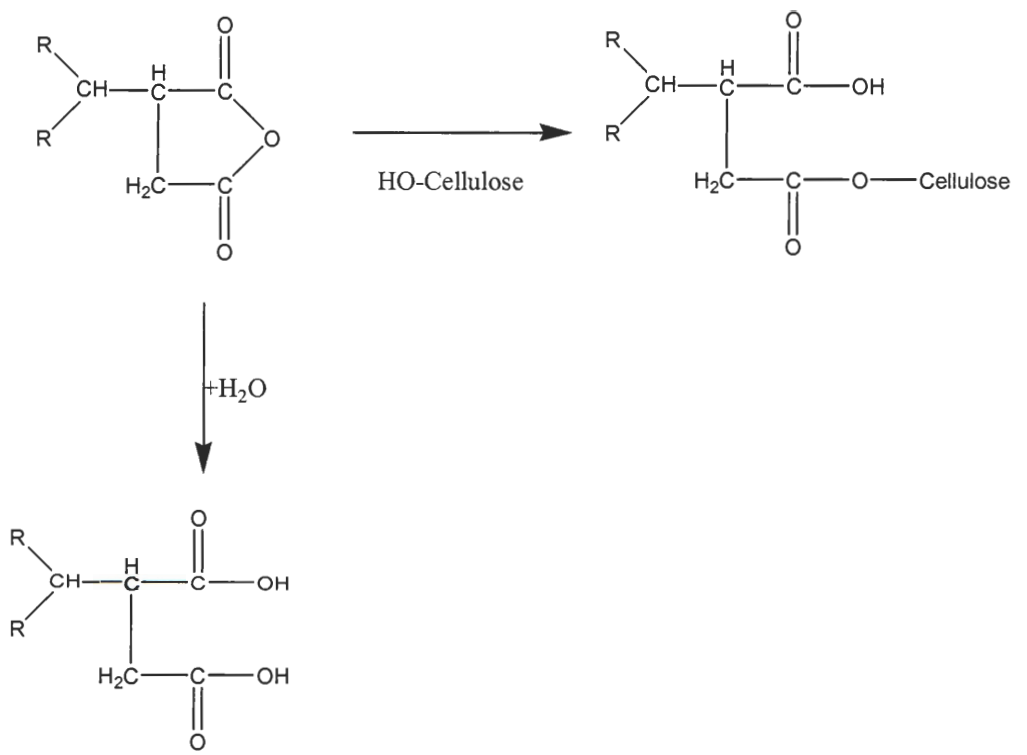


Figure 4.6 - ASA structure and reactions with water and cellulose hydroxyls.

The main reason for acceptance of this mechanism for ASA is that the hydrolyzed form of ASA inhibits sizing.[25,26] Roberts and Wan Daud[27] further showed that solvent extraction of ASA sized sheets removes hydrolyzed ASA and increases the degree of sizing. The explanation of this effect is that removal of the unbound, hydrolyzed ASA left a more hydrophobic fiber surface.

Roberts and Wan Daud[27] also found that ASA reacts much faster than AKD. Because of this, ASA must be made down on site. Further, ASA tends to hydrolyze significantly during sheet formation. Additionally, hydrolyzed ASA forms extremely

tacky salts on the machine when Ca^{2+} or $Mg^{2+}$is present.[28] Poor first pass retention of ASA will cause a build up of the hydrolyzed product. A major benefit of the faster reaction rate is that ASA creates a sizing effect on machine. ASA can even provide sizing without heat treatment.[27]

4.5. Size Reversion

All of the commonly used sizing agents can undergo reversion. The cause of reversion is not fully understood in all cases, but a brief summary of what is known will be discussed here. Often, reversion occurs because conditions prevent or break the sizing agent's bond to the fiber.

As discussed previously, rosin requires a mordant, traditionally alum, to properly orient the hydrophobic portion away from the fiber surface. The presence of Ca^{2+} or Mg^{2+} salts, from hard water, can interfere with the alum-rosin interaction. These divalent ions can initially after heating react with rosin to size paper. However, within a few days the sizing effect vanishes.[29] Addition of alum before or simultaneously with the rosin is generally practiced to reduce the chance of this interference.

Dispersed rosin retained in paper but not fixed by alum can be oriented with the hydrophobic portion facing out after drying and provide an initial sizing effect. Exposure to a penetrating fluid causes the 'unfixed' dispersed rosin to turn over,

placing the hydrophilic tail toward the fluid and destroying the sizing effect. Dispersed rosin that is not in a proper complex with alum can also be vaporized at extreme drying conditions.[30] The vaporized rosin can leave the paper, giving no size effect. Alternatively, the vaporized rosin can redeposit on another portion of the sheet and give the false sizing effect mentioned at the beginning of this paragraph.

Several sources of AKD reversion have been identified. As discussed in section 4.4.1, page 21, AKD can migrate in the sheet. Conditions that promote AKD esterification appear to reduce the occurrence of reversion. AKD reverts faster in the presence of precipitated calcium carbonate (PCC) than ground calcium carbonate (GCC). There are different thoughts on why PCC causes a more rapid reversion. The pore structure of PCC may lead to AKD being absorbed into pores over time, where AKD provides no sizing effect.[31] PCC may cause hydrolysis of the AKD with time, leaving a ketone that is less hydrophobic. PCC may be breaking or preventing ester bounds between AKD and fiber carboxyl groups.[32] Solutions to AKD reversion include excess dosage of AKD, addition of 'catalytic' agents to accelerate ester bond formation, and use of retention aids to keep more AKD on the sheet.

ASA sizing can be reverted in a number of ways. Hydrolysis of unreacted ASA in the sheet forms a diacid. The diacid is hydrophilic and can easily desize the sheet.[14] Oxidation of double bonds in the alkenyl chains of ASA can lead to formation of hydrophilic groups that destroy the sizing effect.[33] The ester bond between ASA and the fiber can get hydrolyzed. This unbound size molecule can turn over, reducing the

sizing effect.[34] Good emulsification and first pass retention of ASA is key to minimizing hydrolysis related reversion.

4.6. Comparison of Synthetic Sizes to Alum-Rosin

One of the biggest drawbacks of shifting to neutral/alkaline papermaking is the need to change from alum-rosin sizing agents to synthetic sizing agents. ASA and AKD both have drawbacks of higher cost, difficult to control degree of sizing, and greater reversion problems when compared to alum-rosin. ASA can also cause severe precipitates on machine. AKD does not cure on machine and creates a slippery sheet when over sized. A new sizing agent that has the benefits of rosin sizing but works at higher pH could improve existing alkaline paper products. A more controllable alkaline sizing agent would make it possible to move some acid products to alkaline conditions, such as linerboard.

ASA and AKD share some common disadvantages when compared to alum-rosin sizing. Synthetic sizes cost more both in raw material and delivery equipment. Synthetic sizes tend to have a sharp increase in degree of sizing with only a small increase in the amount of size added.[2] A comparison of increasing degree of sizing with dosage of synthetic sizes and alum-rosin is shown in Figure 4.7. This rapid increase of synthetic sizes makes adjusting the degree of sizing difficult to control with synthetic sizing agents. Reversion is an embarrassing and costly problem that

still plagues synthetic size agents. In addition to these common problems, ASA and AKD have specific drawbacks when compared to alum-rosin.

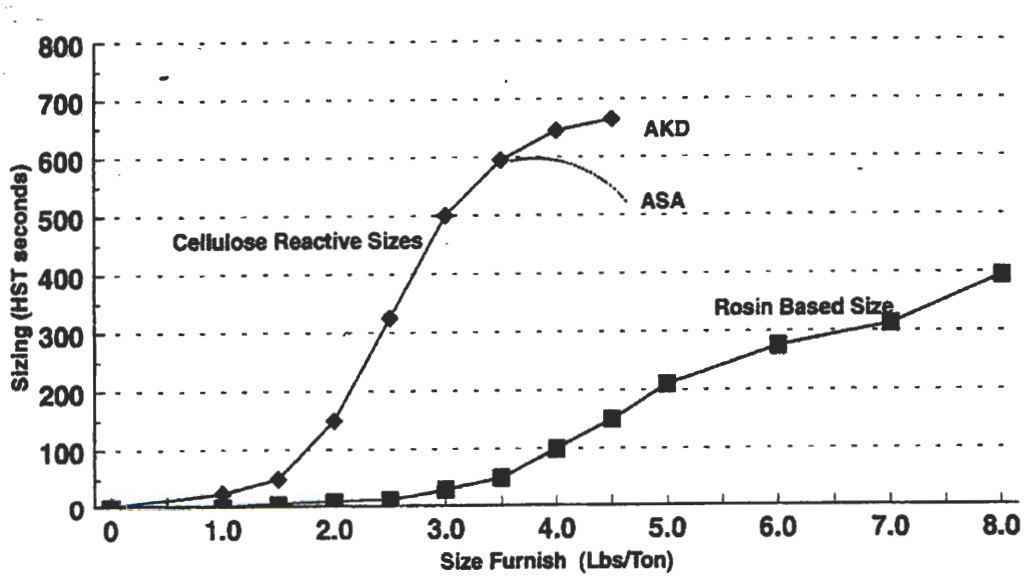


Figure 4.7 - Sizing response of synthetic and rosin sizes.[35]

Hydrolysis of ASA in the white water can lead to severe precipitation problems. Retention aids and even alum can be used to limit this problem. This extra chemical further increases the cost of the ASA sizing chemistry. Alum used at high pH can potentially worsen the precipitation problem if the white water chemistry is not carefully controlled.

AKD is not cured until after aging. This makes it hard to predict the final sizing level. This also prohibits the use of AKD on applications such as on-line coating that require a sizing effect after drying. Sheets oversized with AKD become slippery, causing severe problems with converting and end use operations. Given that one

solution to AKD reversion is over dosing and the steep response curve in Figure 4.7. Combined with the slipping issue, AKD dosing requires a delicate balance to achieve a good product.

These disadvantages of synthetic sizing agents have encouraged researchers to find ways of using rosin size in alkaline conditions. There have been several approaches to raise the operational pH of rosin sizing. Researchers have modified the structure of rosin, modified alum, added a retention aid for alum in the traditional alum-rosin sizing chemistry, and used non-alum retention/anchor compounds.

4.7. Alkaline Rosin Sizing Research

4.7.1. Esterified Rosin Sizing

One approach of moving rosin into alkaline papermaking has been to modify rosin. Advances related to this technique can be found in the literature.[36,37,38,39] In addition to difficulties in using alum at high pH, the carboxyl groups of rosin can react with calcium carbonate filler. This causes a loss of hydrophobicity at higher pH. Therefore, modification of rosin's carboxyl groups has attracted much interest. Rosin esters are the most popular modification of rosin for this purpose. Rosin esters have been used for a number of years for alkaline rosin sizing and have proven to be successful.

Ronge et al.[40] claim that the fortified rosin sizes, partially esterified by polyvalent alcohols, can be used for sizing in acidic to alkaline conditions, preferably in a pH range of 6-9. Figure 4.8 illustrates the esterification of rosin. A comparison of a rosin ester and a dispersed rosin size is shown in Figure 4.9. Rosin ester sizing is nearly independent of pH in acid to weak alkaline conditions. Esterification of rosin also requires less alum than traditional rosin sizing and does not react with calcium carbonate.

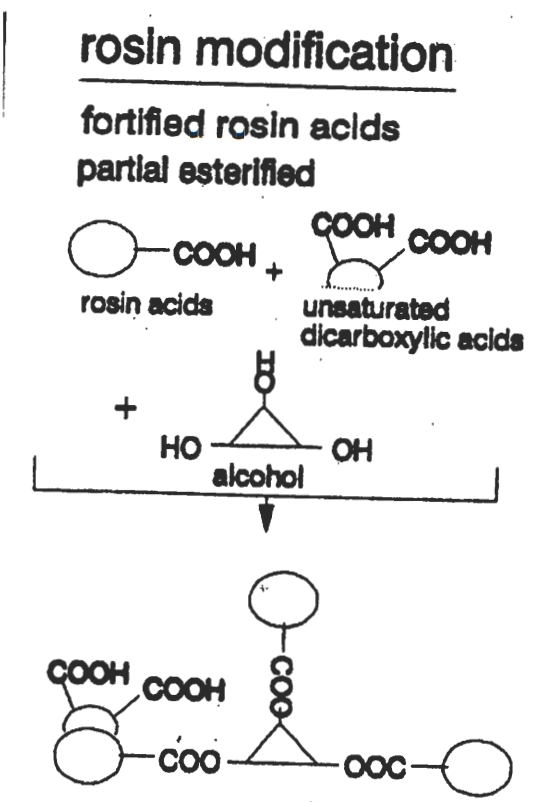


Figure 4.8 - Modification of rosin with esterification.[41]

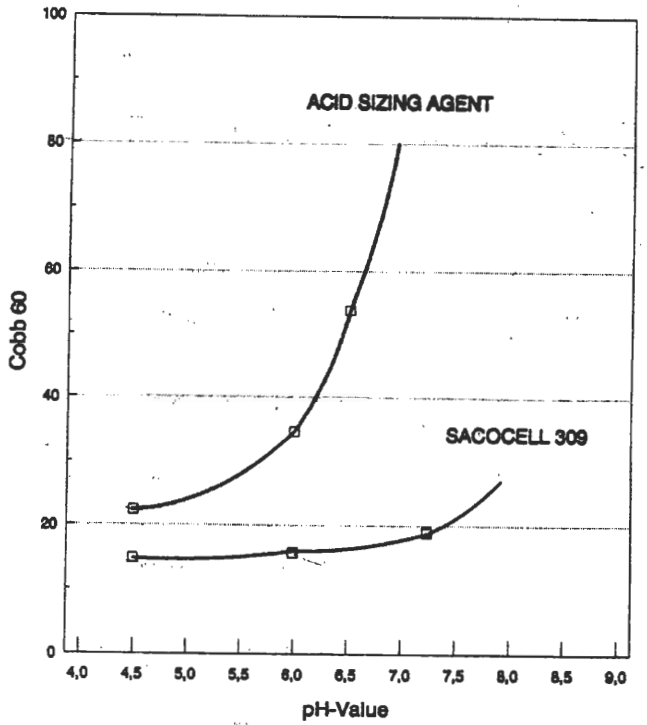


Figure 4.9 - Sizing comparison of a rosin ester (Sacocell 309) and a dispersed rosin (rosin acid).[41]

Curing treatment is important for rosin ester sizing.[36,42] Ito et al. reports that there is little change in the degree of sizing between handsheets dried at 20^{O}C and those cured at 100^{O}C for 20 minutes for AKD, ASA, and dispersed rosin sizing. Rosin ester sizing however shows no sizing effect when dried at 20^{O}C. Figure 4.10 shows the effect of curing on rosin ester sizing.[43] Ito et al. also observed melting and spreading of rosin esters on the fiber surface using SEM. They attribute the increasing sizing effect with curing to the melting and spreading they observed.

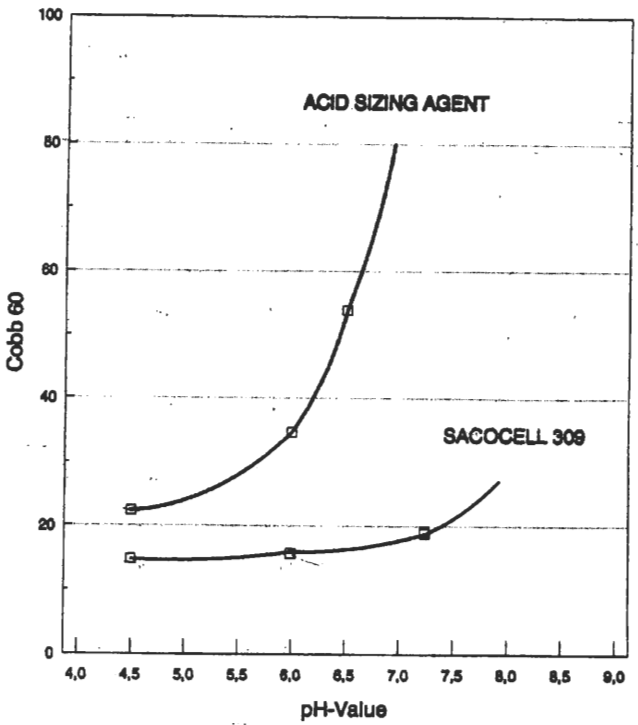


Figure 4.10 - Effect of curing temperature on sizing degree of handsheets prepared with rosin ester size.[43]

Rosin esters achieve much higher degrees of sizing than the traditional alum-rosin chemistry. Unfortunately, the ability to control to a targeted sizing level with rosin esters is nearly as difficult as with AKD or ASA.[44] In essence rosin esters are just an alternative to AKD and ASA, not a shift of traditional rosin sizing to higher pH. Rosin esters are not a good solution for paper grades that require controlled sizing.

4.7.2. Retention Aid for Alum using Traditional Alum-Rosin Sizing

The traditional alum-rosin sizing can be used at higher pH with the use of a retention aid for the alum as well as the rosin.[45,46,47] While alum's charge and thus its self-retention are pH sensitive, alum's sizing mechanism is not. The mordant function of alum appears to be at least partially independent of pH.

Alum-rosin sizing with a retention polymer at alkaline conditions achieves similar sizing results to that seen for traditional acid alum-rosin sizing.[45] Under alkaline conditions, however, alum is more likely to precipitate onto the machine. Aluminum precipitates are extremely difficult to remove from machinery. Gess[48] theorizes that the aluminum species at higher pH form weaker bonds with rosin. The weaker alum-rosin bonds may lead to greater reversion issues for this sizing chemistry. For these reasons, alum has not found wide spread acceptance for use under alkaline papermaking conditions.

4.7.3. Non-alum Retention/Mordant Compounds

The use of metals other than aluminum has been examined. Biermann and co-workers[45,49,50] have studied various metal ions, including Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, and Zn^{2+}. They showed that sizing could be achieved at alkaline conditions if the proper metal ions were used. They propose that the pK_1 value of a metal ion is a good indication of its pH for maximum sizing efficiency.

Zhang and Biermann[45] also studied the combination of polyethyleneimine (PEI) and metal ions. They found that Fe^{2+} with PEI is very effective at pH below 7 and Cu^{2+} with PEI is effective up to a pH of 9. They conclude that polyamines can improve the rosin sizing efficiency by the formation of a complex between the mordants (polyamines or metal ions) and rosin molecules.

Polyamines have been found to perform rosin sizing without alum or other metal ions.[45,47,51] Among the polyamines studied, polyallylamine performed the best.[45] Other polyamines also proved effective at alkaline rosin sizing, such as polyvinylamine and poly(dimethylaminoethyl methacrylate). Polyamine-rosin sizing is comparable to traditional alum-rosin sizing. It was found that primary amines ($-NH_2$) are the best for sizing with rosin, secondary amines (-NH-) have only a marginal sizing effect, and quaternary amines do not contribute to the rosin sizing development. Biermann[47] concluded that the key to the sizing effect seen are the protonated amines present in the polymer chain.

4.7.4. Improved Alkaline Rosin Sizing by Epi-chlorohydrin Modification

Polyamines can also increase the wet strength of paper. Large improvements in wet strength gains from polyamines are seen when the polyamines are modified with epi-chlorohydrin.[52,53] This modification has been tested for sizing as well.

Epi-chlorohydrin modification of polyamines and polyaminoamides has been examined in an effort to improve upon polyamine-rosin sizing.[46,5455] In previous work[54], sizing was done with polyethyleneimine (PEI) modified with epi-chlorohydrin (epi). It is unclear what effect the epi modification had on sizing.

Some clues were seen of the PEI-epi rosin sizing mechanism. Addition of rosin and PEI-epi to water yields a water insoluble bond. This indicates that PEI-epi is reactive with rosin. PEI-epi rosin addition does not increase sheet dry strength. However, addition of PEI-epi alone does increase sheet dry strength. The lack of strength gain shows that the PEI-epi is interacting with the rosin and/or fiber in some way during formation.

Sheet wet strength increased with PEI-epi addition, but this appears to be related to a sizing effect and not increased crosslinking. Increasing anionic material in the pulp slurry negatively impacted the degree of sizing.[56] This result most likely is due to a change in rosin retention, but retention was not measured.

Isogai[57] and Kitaoka et al.[58] studied systems of cationic emulsions of fatty acid anhydrides in the presence of PAE resin. Isogai indicated that although polyaminoamide-epichlorohydrin resin can form a chemical bond with fatty acid, he claims this reaction did not contribute to the sizing. In other studies[59,60] including the systems of alum-rosin, AKD, and ASA, they concluded that bonding was not important to sizing.

Although Isogai's studies conclude that no chemical bonds contribute to sizing, there are still many arguments in this area.[61,62,63,64] Furthermore, in Isogai's studies, the paper sheets were dried at 20°C before curing. The air-dry process may impact the chemical-bond formation in the post curing process because the molecules cannot move and react with each other if no water is present. Additionally, Isogai used a commercially available PAE, which are typically crosslinked. This reduces the number of azetidinium groups available to retain and form ester bonds to the fatty acids. Isogai also treated his samples with cellulase before collecting solid state NMR spectra. This was done to remove cellulose and hemicellulose in order to improve the fatty acid signal intensity and reduce the scan time. He assumed that the cellulase caused no change to the fatty acid anhydride present.

Isogai's work involved a fatty acid anhydride as the sizing agent. Due to its higher hydrophobicity, the anhydride alone may size while a fatty acid could require an anchoring mechanism. He claims that the ester bond formed with PAE in his study does not contribute to sizing because there is no ester bond in his sample with only fatty acid anhydride and no PAE. Further, Isogai claims that fatty acids alone provide a sizing effect. Others argue that fatty acids alone do not give sizing.[47]

These clues, however, do not fully explain how PEI-epi rosin sizing works. Prior work indicates that an ester bond can form between carboxylic acids and epi-chlorohydrin modified polymers.[72,73] The presence of a bond between the fatty acid

and the polymer is debated. Some additional insight can be gained by looking at work done on epi-chlorohydrin modified polymers for use to improve paper wet strength.

4.8. Improved Wet Strength by Epi-chlorohydrin Modification

Reaction of polyamines or polyaminoamides with epi-chlorohydrin greatly improves the wet strength achieved. The epi-chlorohydrin modification reaction of secondary amines is shown in Figure 4.11. The chlorohydrin structure attaches to the polyamines through opening of the epoxide by the amine. The azetidinium structure is then formed by an intramolecular cyclization in which the nitrogen displaces the chlorine.

Occurrence of the intramolecular amine cyclization has been known since 1888.[65] The rate of formation of the azetidinium ring is substantially lower than for similar amino rings, but it does form.[66] Figure 4.12 shows the intramolecular reaction along with relative rates for different ring sizes. Because of the slow rate of formation, epi-chlorohydrin modification is typically carried out at elevated temperature and/or for an extended period of time.

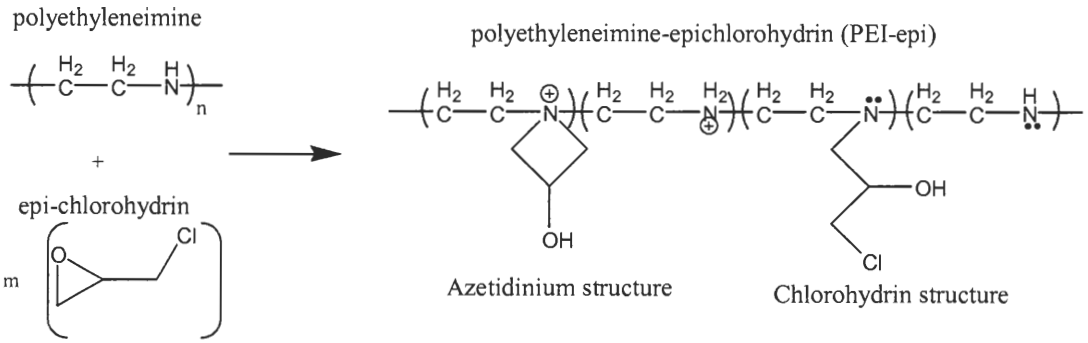
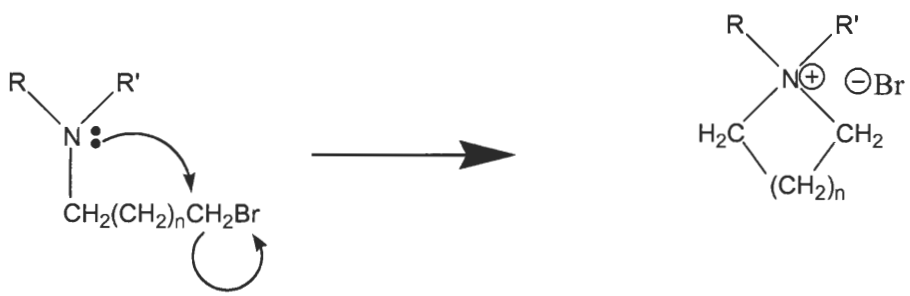


Figure 4.11 - Reaction of epi-chlorohydrin with secondary amines.



Structure:		Relative rate
Aziridine	n=0	1
Azetidine	n=1	0.014
Pyrrolidine	n=2	800
Piperidine	n=3	14
Azacycloheptane	n=4	0.02

Figure 4.12 - Intramolecular amine cyclization of amino halides.

Ross et al.[67] has confirmed the formation of the azetidinium structure from this reaction through exact molecular weight, IR and NMR analysis using diethylamine as the base material. They also found that the hydrogen on the azetidinium hydroxyl could be identified from the modified polymer by proton NMR. The hydrogen on the azetidinium hydroxyl has a proton NMR peak at 8.2 ppm, with a polyaminoamide backbone. Devore and Fischer have confirmed this hydrogen peak.[68]

A polyaminoamide backbone is typically used in the paper industry for wet strength. Once modified, polyaminoamide epi-chlorohydrin polymers are commonly referred to as PAE resins. The azetidinium structure can under go two reactions that may contribute to wet strength. Figure 4.13 shows these reactions: ester bonding to fiber carboxylic groups and crosslinking with secondary or tertiary amine groups on the polymer.

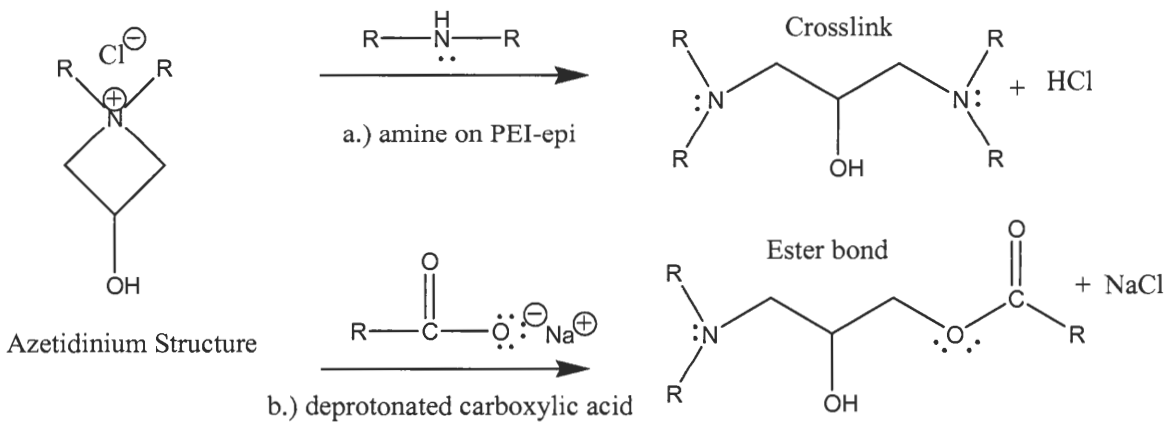


Figure 4.13 - Reactions of PAE in paper: a.) crosslinking b.) with carboxylic groups.

There are two mechanisms presented in the literature for how PAE resins provide wet strength to paper. The mechanisms are (1) reinforcement of the fiber-fiber bonds by a network of crosslinked PAE molecules or (2) crosslinking of fibers by the formation of PAE-fiber chemical bonds. Both bonds are resistant to water under the conditions of sheet saturation.

4.8.1. Wet Strength by PAE Crosslinked Network

In the first mechanism, wet strength is gained through reinforcement of fiber to fiber bonds by network of crosslinked PAE. The crosslinking reaction is shown in Figure 4.13a. According to this mechanism, crosslinked PAE is attached to the fiber by only electrostatic forces. When the sheet is saturated with water, these electrostatic forces will dissipate. The wet strength gained is argued to be from the reinforcement of the fiber-fiber bonds by being completely surrounded by a water insoluble network of crosslinked PAE.

Evidence supporting a mechanism involving only the crosslinked network comes from several sources. Espy[69] found that equal dosages of PAE give similar percentages of wet/dry strength in different pulp furnish, covering a wide range of dry strengths. This suggests that the pulps and their carboxylic groups do not directly relate to the development of wet strength. Bates[70] using methyl β-glucoside as a model for the anhydroglucose units of cellulose showed that PAE does not react with hydroxyl groups under paper making conditions. His model compound, however, does not address ester linkages with fiber carboxylic acid groups.

Devore and Fischer[68] found evidence from NMR and handsheet data supporting the presence of only the PAE crosslinked network mechanism. Using the proton NMR peak of the azetidinium hydroxyl, they calculated the rate constant of PAE reacted with several model compounds. Devore and Fischer found that model carboxylic acid

and hydroxyl compounds impeded the PAE crosslinking and formed model-PAE covalent bonds at a slower rate than crosslinking. Their work also shows that addition of PAE alone follows an additivity rule consistent with the behavior of resin networks that work independently of the fibers. Further, this additivity rule did not apply when CMC was added to the furnish.

4.8.2. Wet Strength by PAE-Fiber Ester Bond

The second mechanism proposes that wet strength is contributed from an ester bond between PAE and paper carboxylic groups, Figure 4.13b. Evidence supporting this mechanism includes reaction with model compounds, calculation of bond strength, and evidence of ester bonds from sheets dosed with large amounts of PAE on carboxymethylated pulps. This is not an ester formation from reaction of a carboxylic acid with an alcohol, which involves an acid catalyst or high-energy intermediate steps. The ester formed is proposed to be a reaction between the carboxylic and opening of the azetidinium ring, Figure 4.13b. Therefore, no high-energy barriers are expected and the presence of a catalyst should not be required to drive this reaction under paper making conditions.

Espy and Rave[71] found that handsheet strength data and solubility tests support the formation of an ester bond between PAE and cellulose carboxyl groups. Their results show that model compounds of the reactive PAE structures form insoluble ester bonds to carboxyl groups on the cellulose. They also tested a similar model

compound with the only functional group being a quaternary amine. The quaternary amine remained soluble. This shows that the bond between cellulose and the other model compounds is more than a salt effect.

Espy and Rave also demonstrated that the rate of wet strength gain has two distinct phases when compared to the amount of PAE retained on the fiber. The first phase is rapid and ends at the point when all available fiber carboxyl groups are neutralized by the PAE. Strength gained in the second phase requires about four times more PAE per unit strength gained than in the first phase. Espy and Rave surmise that the more rapid strength gain in the first phase is due to stronger fiber-PAE ester bonds. They propose the strength gained in the second phase come from PAE-PAE crosslinked network that reinforce fiber-fiber bonds.

Ester bonds have a distinct IR peak around 1735 cm^{-1}. If an ester bond is present, it should show this IR peak. Wagberg and Bjorklund[72] were able to demonstrate the presence of such an ester peak in handsheets. They increased the number of ester bonds by using carboxymethylated pulps. By subtracting spectra of a blank sheet from one reacted with PAE, Wagberg and Bjorklund show that an ester peak is present. This ester peak is not present in the PAE or the pulp; therefore it must be from a bond formed between the fiber and PAE.

4.9. Summary

The debate over the presence and contribution of these ester bonds in PAE wet strengthened paper has revolved around some analysis problems. Direct analysis of chemical additives on paper sheets at normal concentrations is difficult to measure accurately. The number of potential ester bonds is lowered because the PAE resins used for wet strength are crosslinked before addition to the papermaking process. It is difficult to accurately simulate the conditions of a paper machine on model compounds. The study of reactions of these polymers with rosin may provide ways to overcome these difficulties.

Monitoring reactions of epi-chlorohydrin modified polymers-rosin interactions present some advantages for analysis over polymer-fiber interactions. Linear fatty acids with 16 or more carbons also size with alum and epi-chlorohydrin modified polymers. Chemical labeling of these fatty acids is easier to do than the polymers or fibers. With the labeled fatty acids, inaccuracies of modeling can be avoided. This may allow for better direct analysis of paper sheets.

Initial findings indicate that epi-chlorohydrin polymer crosslinking hinders the sizing effect.[55] With little or no crosslinking before addition, there will be a greater number of potential ester bonds. Additionally, the fatty acid will greatly increase the number and availability of carboxylic acids in the system for reaction with the polymer. Reaction of the epi-chlorohydrin polymers with sizing agents in solution forms a

precipitate. This may present a way for more accurate modeling of paper machine conditions without the presence of fibers. Studying epi-chlorohydrin modified polymer-rosin sizing may provide insight into the PAE wet strength mechanism as well as the sizing mechanism.

It is desirable to use rosin sizing for alkaline papermaking. The use of epi-chlorohydrin modified polymers presents a possible way in which rosin could be used for alkaline sizing. The sizing mechanism of epi-chlorohydrin modified polymers is not well understood. Further, rapid reversion seems to present a limitation to this method. A better understanding of the mechanism for epi-chlorohydrin modified polymer-rosin sizing may provide a solution to the reversion problem and provide a greater sizing effect. Additionally, information on the sizing mechanism may provide useful information on the wet strength mechanism of similar polymers. This project attempts to develop a better understanding of the mechanism of epi-chlorohydrin modified polymer-rosin sizing.

5. Problem Analysis

A series of studies have led to experiments using modified polyamines for alkaline rosin sizing. Table 5.1 shows a summary of the progression that led to the testing of modified polyamines/polyaminoamides. Simple retention of rosin is not enough to provide sizing, as seen by use of polyDADMAC and polyacrylamide (PAM). Alum rosin sizing does not work under alkaline conditions. Polyamines are partially protonated under alkaline papermaking conditions. Further, polyamines have multiple charges per molecule. Testing of polyamines was done with the thought that these features may lead to retention and sizing with rosin under alkaline conditions. Earlier work with polyamines did not examine a permanent sizing effect. Use of modified polyamines and polyaminoamides achieved both temporary and permanent sizing effects. Understanding what is causing the different results with these modified polymers may help explain how they provide sizing with rosin.

Table 5.1 - Progression leading up to the testing of polyamines for alkaline rosin sizing.

Chemistry	Effect seen under alkaline conditions
Rosin alone	No permanent sizing
Rosin with polyDADMAC or PAM	No sizing, even with retention of rosin
Rosin with alum	No sizing
Rosin with polyamines	Temporary sizing reported[45,47]
Rosin with polyamine and alum	Permanent sizing[73]
Rosin with modified polyamine/polyaminoamides	Permanent[55] and temporary[54] sizing reported

Why does size reversion occurs with modified polyamines in some cases but not all? Do modified polyamines function only as retention aids or do they also provide a mordant effect? How do modified polyamines/polyaminoamides provide sizing with rosin while quaternary amines do not? Answering these questions is the central goal of this research project. Research has been done on the use of modified polyamines and polyaminoamides for alkaline rosin sizing. The prior work has recommended that more research needs to be done. However, knowing how these polymers work is important in deciding if these polymers warrant further research and, if so, what direction should that research take.

If modified polyamines/polyaminoamides are to be used industrially, how they function needs to be understood. If these polymers function only as retention aids,

then other approaches are clearly better candidates. If these polymers also work as mordants for rosin, then there are advantages for using them. Building on prior works with modified polyamines and polyaminoamides, a series of tests will be done to examine if those polymers are mordants or just retention aids. The next section will discuss the testing to be done.

6. Research Objectives

Rosin alkaline sizing has recently attracted great research interests. Traditionally, the rosin molecules are bonded to the fiber surface through rosin/aluminum/fiber complexion. Because the aluminum forms a negatively charged complex in alkaline conditions, the alum-rosin system cannot be used alone as an alkaline sizing agent. Some recent studies show that some functional polymers may be able to provide sizing with rosin in alkaline conditions. Previous work indicates that epi-chlorohydrin modified polyamines and polyaminoamides can effectively enhance the sizing efficiency at neutral to alkaline conditions without using alum. However, the mechanism is unclear. It is of great interest to know the mechanism of this polymer mordant for rosin alkaline paper sizing because this fundamental understanding will greatly help people to develop polymer mordant systems for alkaline rosin sizing.

The questions that remain unanswered:

1. What characteristics of the epi-chlorohydrin modified polymers are important to this sizing chemistry?
2. How does epi-chlorohydrin modified polymer size with rosin?

Objectives:

1. Choose and test possible polymers for rosin alkaline sizing.
2. Perform a sizing mechanism study using an elected polymer.

3. Study the effect of polymer properties and other factors on the sizing performance of rosin polymer chemistries. Draw a conclusion from your study about if there is an effective functional polymer that can be used as rosin alkaline sizing mordant.

7. Experimental Approach

If the mechanism involves charge neutralization retention and an ester, then charge neutralization and ester bonds are important to the epi-chlorohydrin modified polymer-rosin sizing chemistry.

The importance of charge neutralization can be analyzed by examining factors that impact:

- Fiber surface charge
- Rosin charge (rosin soaps)
- Polymer charge density
- Dissolved charged material

The importance of ester bonds can be analyzed by examining the bond formed between the epi-chlorohydrin modified polymer and rosin. The two proposed bonds, ester or electrostatic, have different IR and NMR spectra. Also, ester bonds can be cleaved by catalytic amounts of acid or base. Neutral conditions should have no impact on ester bonds.

Figure 7.1 contains an overview of the experimental approach used in laboratory portion of this research. Figure 7.2 contains an overview of the experimental approach used in a pilot trial at the Herty Foundation.

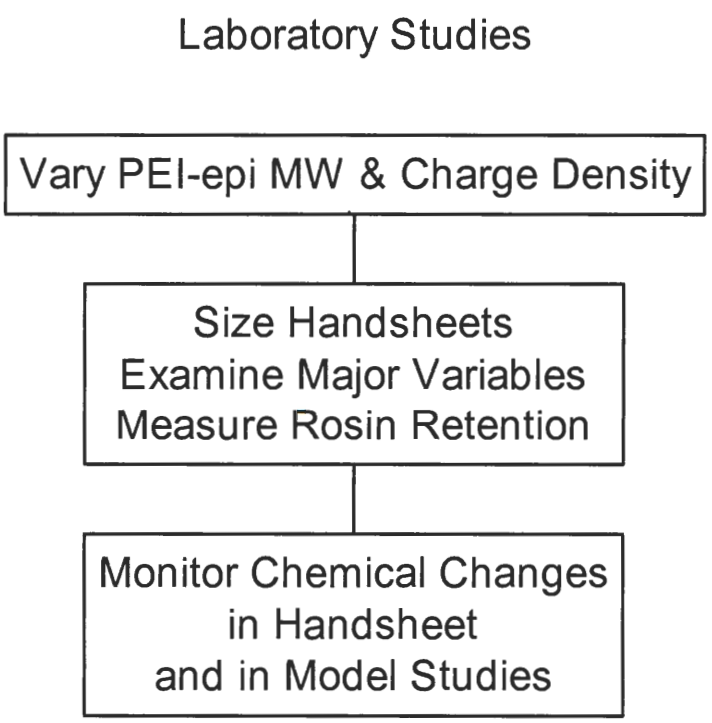


Figure 7.1 - Overview of laboratory portion of experimental approach.

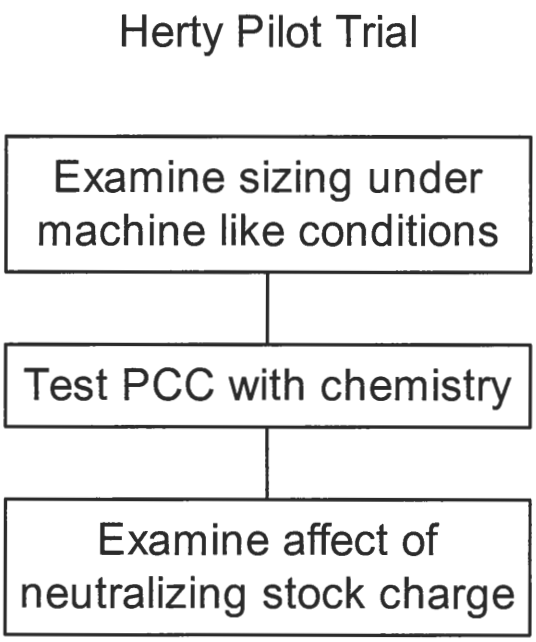


Figure 7.2 - Overview of pilot trial portion of experimental approach.

Modification with the epi-chlorohydrin will be done under two different methods for comparison. The first modification method will be done all in water. The second modification will use a newer method, adding the epi-chlorohydrin to a water immiscible solvent and the backbone polymer to water. This method is claimed to reduce side reactions of epi-chlorohydrin, reducing impurities.[55] In both cases, PEI will be used as the backbone because it has simpler IR and NMR spectra than other polymer choices. The sizing effect of different degrees of modification will be compared for the method that performs the best. Structural analysis and sizing comparisons will need to be done.

The next step will be to confirm the epi-chlorohydrin modification occurred under the new synthesis technique. Molecular weight and charge density will be measured as

well as proton NMR. The azetidinium hydroxyl has a detectable proton NMR peak at 8.2 ppm for PAE resins.[67] The modified polymer should also impact sheet strength in a similar fashion as PAE resins do. Once the structure is confirmed, comparisons and reactions of the polymers can be done.

Laboratory sizing with the sample polymers will then be done. The laboratory data can then be used to set conditions for a pilot trial. The chemistry will be simplified in the laboratory to eliminate interference from other chemicals. No retention aids or charge neutralization chemicals will be used. This is because the modified polymer is charged and can perform both functions without need of other chemicals that may interfere with analysis. Rosin soap or sodium oleate will be used as the sizing agent. Use of soaps presents less complexity for analysis. Sodium oleate provides sizing like rosin and will be used for IR and NMR analysis samples because of its simpler spectra.

A never-dried bleached kraft pulp will be used for the laboratory studies. Bleached kraft has less lignin, providing simpler IR and NMR spectra. Removal of the lignin will also reduce the amount of anionic material in the pulp slurry, reducing charge interference for a charge retention mechanism. A never-dried pulp will provide a greater number of exposed carboxylic acids for better charge retention and ester bond of the proposed mechanism. Laboratory results will be used to analyze the importance of charge, degree of polymer modification, and determine conditions and samples to be used for a pilot trial as well as samples for IR and NMR analysis.

Several approaches will be used to identify the bond formed between the epi-chlorohydrin modified polymer and sodium oleate. Surface scanning of sized handsheets with ATR-FTIR and Raman spectroscopy will be used. Subtraction of blank samples should leave only the added chemicals. The presence of an ester bond will show up clearly around 1735 cm^{-1}. Raman spectroscopy is less commonly used than IR, but due to their complementary relation Raman spectroscopy can analyze some samples better than IR.

Solid state NMR with 1-^{13}C labeled sodium oleate will also be used. The carbon 13 NMR shift between an ester and carboxylic salt should be distinct. For a fatty acid, carboxylic salts or acids will give a peak around 178-182 ppm. An ester of a fatty acid will give a peak around 170-172 ppm.

In addition to these direct sheet measurements, a model reaction of the polymer and sodium oleate will be examined. Addition of the polymer and sodium oleate to water forms a precipitate in the same pH range used to make sized handsheets. This precipitate can then be collected and treated to similar conditions used for sizing handsheets and then analyzed by FTIR without any interference from fibers. Use of these methods should provide evidence of the type of bond formed between epi-chlorohydrin modified polymers and rosin/sodium oleate under the conditions used to size paper.

A pilot trial of the epi-chlorohydrin modified polymer-rosin sizing will provide data under conditions that are closer to those seen on a paper machine. Unbleached kraft linerboard and calcium carbonate filler will be examined. Reasons for using linerboard include that it is a potential grade for use of this sizing chemistry and that unbleached kraft has a greater number of surface carboxylic groups than bleached kraft. Neutralization of anionic material will be done because of the higher content of such materials in an unbleached pulp. Calcium carbonate filler will be examined to see if it is compatible with this sizing chemistry.

8. Materials and Methods

8.1. Materials

8.1.1. Chemicals

Tables 8.1 to 8.3 list the chemicals purchased or donated from chemical suppliers. Tables 8.1 and 8.2 lists the chemicals used in laboratory experiments and Table 8.3 lists those chemicals used for the Herty pilot trial. All chemicals were used as received.

Table 8.1 - Chemicals donated by chemical companies used in laboratory experiments.

Chemical	Description	Company
Polymin SKA	PEI-epi retention aid, fully reacted as shipped	BASF
Malros ®	Fortified Rosin Soap	Eka Chemicals, Akzo Nobel
cationic Polyacrylamide	high molecular weight, moderate charge density	Eka Chemicals, Akzo Nobel

Table 8.2 - Chemicals purchased from chemical suppliers used in laboratory experiments.

Chemical	Description	Company
Poly(ethyleneimine)	~60,000 MW	Sigma-Aldrich
epi-chlorohydrin	99.9% pure	Sigma-Aldrich
Diethylamine	99.9% pure	VWR
1-octanol	99% pure	VWR
Deturated dimethyl sulfoxide	99% D_6	Sigma-Aldrich
Sodium Oleate	powder, 99% pure	Sigma-Aldrich
1-^{13}C Oleic Acid	99% 13C	Sigma-Aldrich
2% & 88% Formic Acid	For HST tests	VWR
Diethyl ether	GC/MS solvent	VWR
Heptadecanonic acid	GC/MS standard	VWR
Methanol	GC/MS solvent	VWR
Sodium Hydroxide	Pellets	VWR
Hydrochloric Acid	Concentrated	VWR

Table 8.3 - Chemicals donated by chemical companies used in the Herty pilot trial.

Chemical	Description	Company
modified Polymin SKA	PEI-epi sample pulled early in production for Herty Trial	BASF
Hi-Phase 35 ®	Dispersed Rosin	Hercules Incorporated
Fennofix 40	PolyDADMAC, Charge neutralizer	Kemira
Albacor HO	1μm precipitated calcium carbonate	Specialty Minerals
eXtend	3μm precipitated calcium carbonate	Specialty Minerals

Polymin SKA is manufactured as an epi-chlorohydrin modified polyamine with all azetidinium structures pre-reacted. For the purposes of the pilot trial, a sample of Polymin SKA was collected prior to the reaction step of the azetidinium structures.

8.1.2. Pulp

Pulp for Laboratory Testing

The Chillicothe, Ohio mill of Mead/MeadWestvaco donated the pulp used for the laboratory testing. A bleached, kraft hardwood pulp was used. The pulp was pulled from the production line after refining and shipped for testing as wet slurry. The shipped stock consistency was approximately four-percent solids. Canadian Standard

Freeness (CSF) was between 450-mL and 500-mL for all samples received. No additional refining was done.

Pulp for the Herty Pilot Trial

Pre-consumer recycled double-lined Kraft (DLK) was used for the Herty pilot trial. An undisclosed company donated the DLK. The estimated percent of white top DLK was five percent. The base stock used on the Herty trial was one hundred percent DLK. This presented a problem, because DLK normally contains a very high amount of wet strength additive, which made it very difficult to pulp without chemical additives. The stock preparation began by loading 3500 OD pounds of recycled DLK linerboard into a Black Clawson hydropulper. The stock was pulped for approximately 2-3 hours at 150°F. Then, it was pumped to a holding tank where it would await refining.

For the Herty pilot trial, the preliminary CSF of the stock before refining was 570-mL CSF. The objective was to drop the freeness about 50-mL. At the Herty Foundation, a single disc refiner was used with a no-load power of 65 kW. The intent for refining was actually to break up the clumps of fibers caused by the wet strength additive present in the stock rather than modifying the individual fiber surface. As a result the refiner gap was fairly open between the plates and only applied approximately 8 kW of power to the stock, which raised our gross power consumption up to 73 kW. The flow rate of stock through the refiner was roughly 120-gpm. By knowing the flow rate

and the volume of pulp in the holding tank, it would take approximately 40 minutes for one complete revolution of the stock to cycle through the refiner. Each batch of stock was refined for approximately two hours and forty minutes. During this time, freeness tests were performed, but no significant drop in freeness was seen.

It was determined that refining alone would not be sufficient to break up the clumps due to the wet strength additive in the DLK. The solution was to run the stock through the pressure screens. After the pressure screens, a pronounced drop in the freeness value was achieved by reaching 520-mL CSF. As a result of running the stock through the pressure screens, the overall amount of pulp obtained was about 2500 pounds OD. This loss resulted in a possible shorter run time on the paper machine then originally assumed.

8.2. Methods

8.2.1. Laboratory Preparations of PEI-epi

Single phase preparation of PEI-epi

PEI-epi was synthesized in the laboratory by reacting epichlorohydrin with PEI in deionized water. Procedures for PEI-epi synthesis are as follows. To 100 ml deionized water, 5% PEI that had been cooled to a temperature of $5^{O}C$ in an ice bath, a

prescribed amount of epichlorohydrin was added slowly. The amount of epichlorohydrin was determined according to a desired substitution ratio of 1:1. The mixture stirred on an ice bath for 8 h. Hydrochloric acid was then added to adjust the pH below 4.0 for storage. The finished product was diluted to a concentration of 5% and stored in a refrigerator.

Two-phase preparation of PEI-epi

A two-phase method developed by Hercules[74] was also used to synthesize PEI-epi in the laboratory. The prescribed amount of epi-chlorohydrin was added to a water immiscible solvent, 1-Octanol was used. The prescribed amount of PEI was added to deionized water. The two solvents were then mixed together and placed in a flask in a heated oil bath with stirring for a specified time. The octanol solvent phase was then removed.

To introduce additional crosslinking, some samples were then heated to $70^{O}C$ and stirred for an additional time period. The reaction in the water solvent was quenched with water and hydrochloric acid to between a pH of 3.5-4.0. Samples were stored in a refrigerator.

Epi-chlorohydrin was added at a 1:1 molar ratio to the repeat unit of PEI. Samples quenched immediately after separation of the octanol and water phases are referred to as 'non-crosslinked' because only a little crosslinking, if any, occurs under these

conditions. Samples given additional reaction time after removal of the octanol phase are referred to as 'crosslinked' samples.

A crosslinked commercial PEI-epi sample, Polymin SKA, was used and the reaction conditions are not available for publication. This sample is manufactured as a retention aid and was donated by BASF. The BASF sample serves as a control sample of PEI-epi with quaternary amines and no azetidinium structures present.

Washing of prepared PEI-epi samples

Unless specified otherwise, samples were washed with octanol to remove impurities and unreacted epi-chlorohydrin. Octanol, 30-mL, was added to the PEI-epi sample, approximately 100-mL. The octanol/PEI-epi was then mixed thoroughly by hand. The octanol was separated and discarded. This was repeated twice more.

Characterization of prepared PEI-epi samples

Molecular weight and charge density were collected of the prepared PEI-epi samples. Molecular weight of prepared polymers was measured by light scattering on a Wyatt Technology's DAWN EOS using a Varian ProStar 350 reflective index detector. Charge density titration was done using a Mutek PCD 03 m particle charge monitor with a Mutek PCD-titrator two auto titration system.

8.2.2. Handsheet Method

Handsheets were formed in a British handsheet mold. A bucket of deionized water was adjusted to the desired pH and added to the mold. Before addition to the mold, the desired amount of pulp was diluted to 0.3 percent in 400-mL deionized water. To this, the needed amount of rosin was added and mixed by hand with a stirring rod. The pulp-rosin stock pH was adjusted toward the desire pH. Then the PEI-epi was added and the pH was adjusted to the target value and stirred for 30 seconds. The stock was then added to the mold and more pH adjusted water added, filling to the etched mark in the mold. The handsheet was then formed and pressed following the TAPPI standard method T 205 SP-02. After pressing, the handsheets were dried on a steam heated drying drum at 105-110^{O}C for one minute.

8.2.3. TAPPI Standard Test Methods

The TAPPI standard test methods used for laboratory or pilot trial paper are listed in Table 8.3.

Table 8.4 - TAPPI standard test methods employed.

TAPPI Method Number	Test Use
T 211 OM-93	Ash Content at 525^{O}C
T 227 OM-99	Canadian Standard Freeness
T 414 OM-98	Internal Tearing Resistance (Elmendorf)
T 441 OM-98	Water Absorbency Test (Cobb Test)
T 494 OM-96	Dry Strength Tensile
T 494 OM-96	Wet Strength Tensile (soaked samples for 48 hours)
T 489 OM-99	Bending Resistance / Stiffness (Taber)
T 509 OM-02	pH of Paper Extracts (Cold Extraction)
T 530 OM-02	Size Test by Ink Resistance - Hercules Size Test (HST)
T 541 OM-99	Internal Bond Strength of Paperboard (Z-direction tensile)
T 807 OM-99	Bursting Strength of Paperboard and Linerboard
T 818 CM-97	Ring Crush of Paperboard

8.2.4. Herty Pilot Machine Specifications

The trial was performed on the No.1 Paper Machine at the Herty Foundation's facilities. This paper machine is a 36" conventional Fourdrinier, manufactured by Sandy Hill Corporation. Figure 8.1 shows the headbox and forming section of the No. 1 Paper machine used for the Herty pilot trial. Figure 8.2 shows the dryer section of the No. Paper Machine used for the Herty pilot trial. The production on this machine may vary from 500 to 6,000 pounds per day with sheet basis weights of 20-600 lbs/1000 ft^2. The machine can be run between 20-200 ft/min.

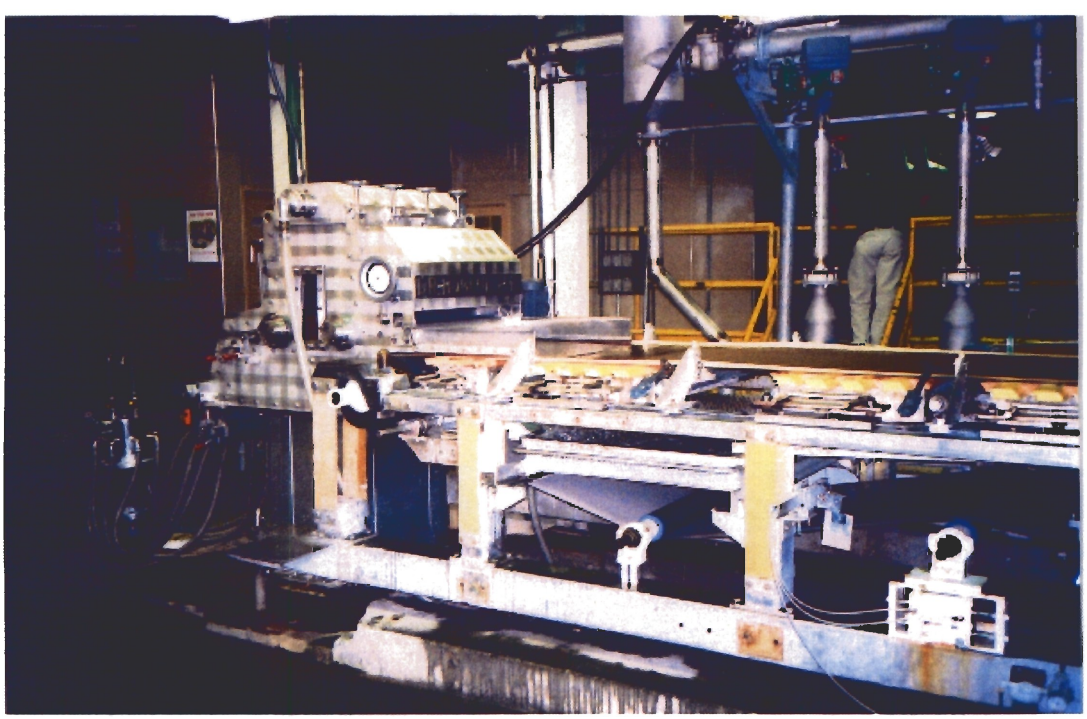


Figure 8.1 - Forming Section of the No. 1 Paper Machine at the Herty Foundation.

Figure 8.2 - Drying Section of the No. 1 Paper Machine at the Herty Foundation.

Many machine settings were to be established by the operators of the machine, including flows to the headbox, slice openings, headbox pressures, hydrofoil pressures, sheet width, dryer operations, and wind-up operations. With the experience of the operators, these settings were to be optimized by Herty personnel to produce the targeted basis weight sheet.

The machine speed was estimated to be 75 ft/min, proportionate to the 42 lb/1000ft^2 basis weight desired. Using Figure 8.1, the addition points were as follows: point 1: charge neutralizer, point 5: PCC, point 7: rosin, point 6: PEI-epi, point 9: caustic.

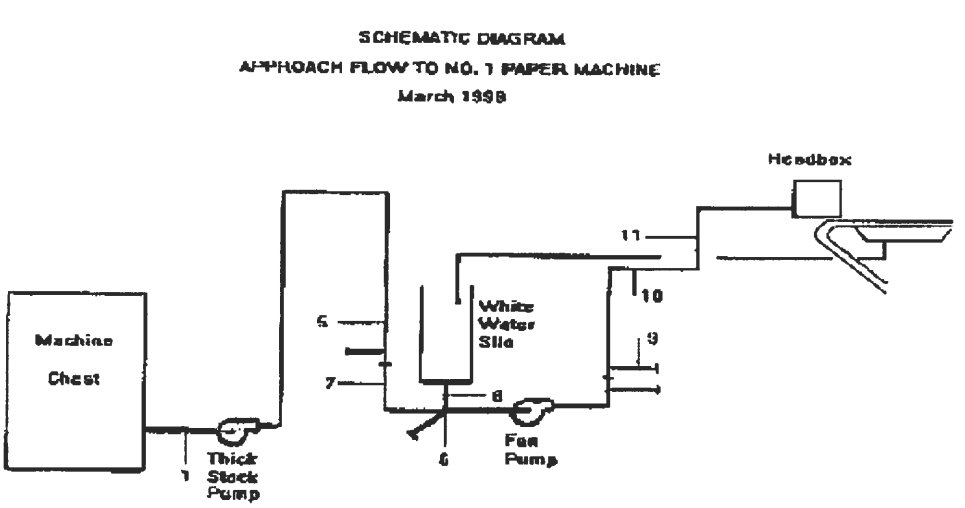


Figure 8.3- Schematic diagram of Herty pilot machine No. 1 approach flow.

Each addition point was assigned a tank and pump combination. The charge neutralizer, PEI-epi, and rosin were to be diluted in 50-gallon tanks using 2–45-gph metering pumps. The two PCC slurries were to be diluted into separate 600-gallon filler slurry tanks using a 0.5-3-gpm variable speed Moyno pump. This pump would be switched between the two tanks when necessary.

8.2.5. Solid State Nuclear Magnetic Spectroscopy (SS NMR)

Solid state NMR experiments were recorded on a Bruker DSX300. The experiment was a CP-MAS experiment with TOSS (total suppression of spinning sidebands). The spinning speed was 4 kHz. Repetition delay was 4 seconds. Contact pulse length was 1 ms. The 90 degree pulse length was 5 microseconds. Handsheets were made according to the described method. Finely cut handsheet samples were packed in 7mm rotors. Talc was added to fill void spaces, providing better balance for spinning.

Data were recorded at room temperature. Approximately 20,000 scans were used for each sample, collected in about 23 h.

8.2.6. Solution Nuclear Magnetic Spectroscopy (NMR)

Solution ^{1}H NMR spectra were collected on a Bruker AMX 400. PEI-epi samples were added to deuterated dimethyl sulfoxide at 0.4% concentration. This was then placed in a 5-mm sample tube and scanned at room temperature. Collection of 126 scans was used for each sample.

8.2.7. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR experiments were recorded on a Nicolet Magna-IR 550. A KBr beam splitter was used with an Ever-glo source and an MCT-A detector. The number of scans for each spectrum was 64.

Reaction method of PEI-epi and Sodium Oleate for FTIR

For model conditions, PEI-epi was reacted with sodium oleate in solution at pH 7.0. A precipitate formed and was collected by vacuum filtration and dried on a drum dryer, held between filter paper, at 105-110^{O}C for 2 min. Initial scans were collected

of the material when: wet, air dried for one week and drum dried. The sample was then treated with pH adjusted water and aged for one week. The treated samples were again filtrated and aged for another week to allow for reaction. FTIR spectra were then collected of the reacted samples.

8.2.8. Gas Chromatography/Mass Spectroscopy (GC/MS) Measurements

A Hewlett-Packard 5890 II Gas Chromatograph equipped with Hewlett-Packard 5971A Mass Selective Detector was used for the GC/MS analysis and quantification. A SPB 30-M x 0.25-mm ID x 0.25-μm film column was employed for the separation. GC/MS was operated under the following conditions: initial temperature 45°C; initial time 4 min.; rate 12°C/min.; final temperature 265°C; inject temperature 250°C; solvent delay time 11 min.

Sample preparation for GC/MS impurity analysis

The liquid sample that was added with equal volume of saturated sodium chloride solution and was sealed in a 5-ml vial. A SPEM fiber that had been cleaned over 250 °C oven was inserted to the vial headspace. After three minutes, the SPEM fiber was inserted into the injection port of a Hewlett-Packard 5890 II Gas Chromatograph equipped with Hewlett-Packard 5971A Mass Selective Detector. A SPB 30 M x 0.251mm column was employed for the separation. GC/MS was operated under the

following conditions: initial temperature 45°C; initial time 3 min.; rate 12°C/min.; final temperature 260°C; inject temperature 250°C; solvent delay time 1 min.

Sample preparation for GC/MS rosin retention measurement

The content analysis of the rosin sizing agents in paper samples was conducted by saponification of resin acids in alkaline solution following by ether extraction and GC/MS quantification. In briefly, around 0.5-g (to the nearest of 0.0001-g) of paper sample was weighed into a 125-ml flask. After 50-ml of 0.5 M NaOH solution was added. The flask was heated-up on a hot plate. When the content in the flask begun to boil, the saponification was immediately timed and the process continued for two hours. After the flask was cooled down to room temperature, 1-ml internal standard (0.5mg/ml of heptadecanoic acid in methanol) was added. This was immediately followed by the filtering and washing, 3x50-ml deionized water, the content into a 200-ml beaker. The filtrate and paper residues were then acidified by using 6 N H_2SO_4 to a pH below 2.5. The acidic aqueous solution was transferred into an extraction funnel.

The extraction was carried out by using 50-ml ethyl ether that was first passed through the acidified paper residues. The process was repeated at least for three times. The solvent was combined and dried over sodium sulfate overnight. After the separation from the solid sodium sulfate, the solvent extracts were concentrated to a volume of 5-ml. From which 1-ml was taken to derivatize with TMAH

(trimethylphenylammonium hydroxide). 1-µl of derivatives was injected into GC/MS for the analysis and quantification.

9. Results and Discussion

9.1. Confirmation of Epi-chlorohydrin Modification of PEI

Proton NMR of the epi-chlorohydrin modification of PEI is consistent with the findings in the literature for the azetidinium ring hydroxyl.[68,75] A hydroxyl proton shows up at 8.1 ppm on the laboratory prepared samples using PEI as the polymer backbone, Figure 9.1. This is slightly less than the 8.3 ppm for the azetidinium hydroxyl reported by Devore and Fischer[68], Figure 9.2. This difference is not surprising given Devore and Fischer used PAE, which has a polyaminoamide backbone.

There is no amide peak at 7.7 ppm in PEI-epi samples. This again relates to the use of just a polyamine backbone of the PEI used. The polyamine backbone also produces fewer peaks below 2.0 ppm. Using a simple polyamine reduces the number of spectral peaks, making analysis easier. Further evidence that this is the same structure as seen in traditional PAE comes from the ability of these PEI-epi polymers to improve paper strength.

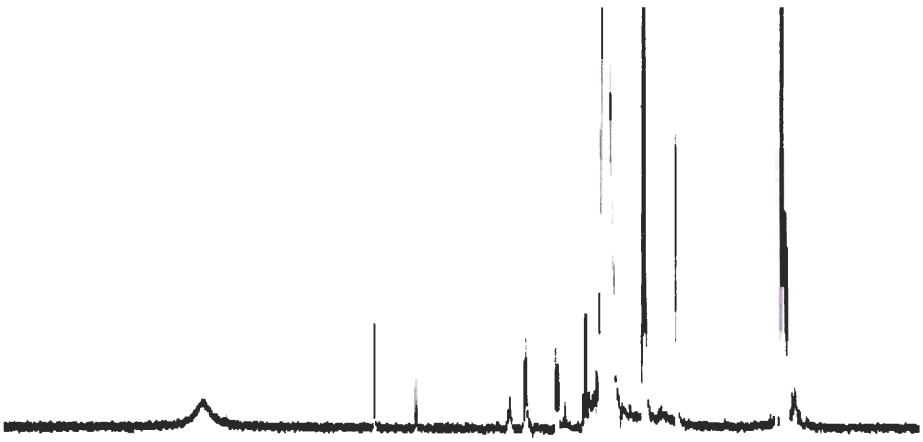


Figure 9.1 - Proton NMR spectra of laboratory prepared PEI-epi.

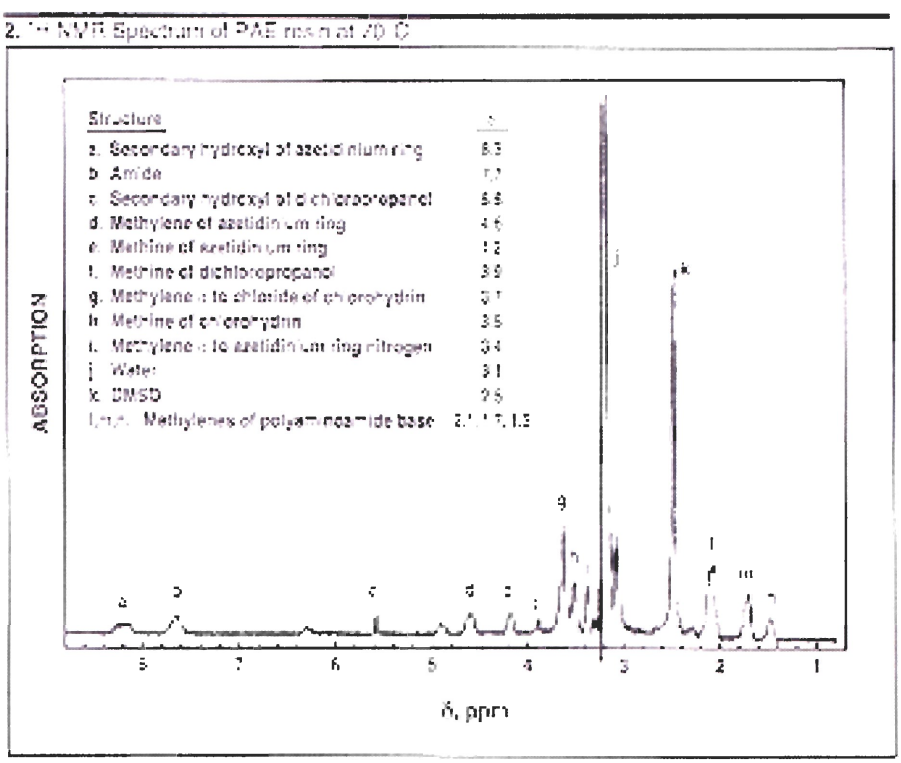


Figure 9.2 - Proton NMR spectra of PAE used by Devore and Fischer.[68]

Laboratory modification of the PEI retains charge density at higher pH, see Figure 9.3. The polymer characteristics of these samples are discussed later in Section 9.3.1, page 82. The azetidinium structure most likely provides the charge density of PEI-epi that is not impacted as much by pH. Unmodified PEI has a higher charge density than PEI-epi below pH 7.0.

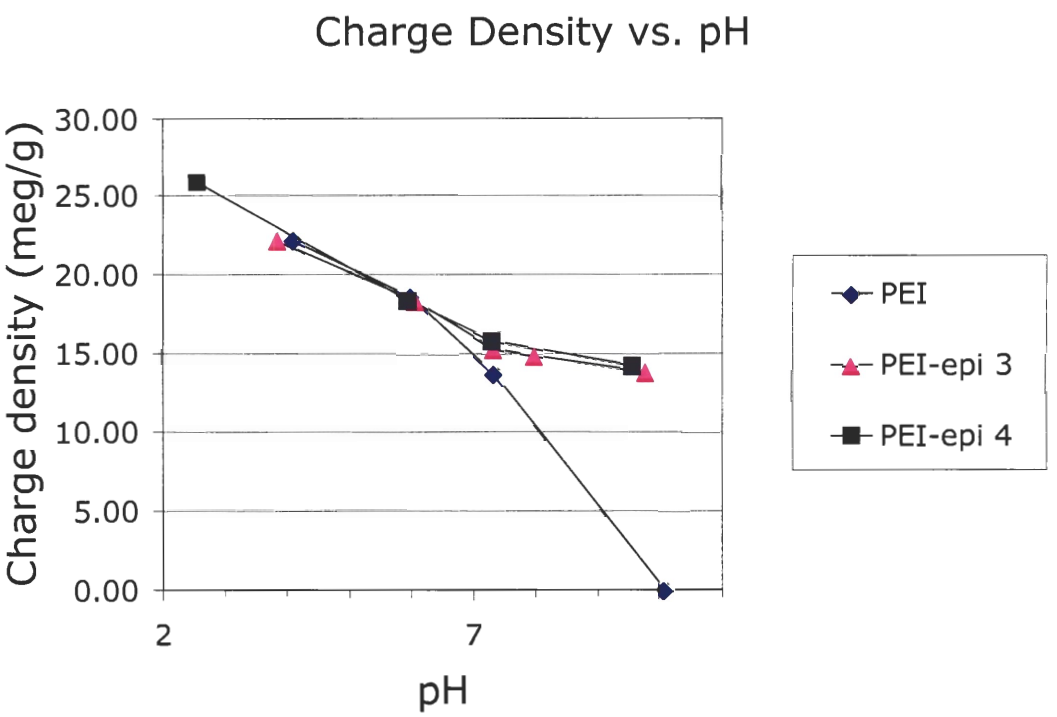


Figure 9.3 - Comparison of polymer charge density over pH.

The PEI-epi used in this study can also improve sheet strength as do PAE resins. Figure 9.4 and Figure 9.5 show examples of the impact on dry and wet strength, respectively, from PEI-epi dosages with and without the addition of rosin. The

amount of PEI-epi and rosin as weight percent of dry fiber are shown below each data point. Wet tensile samples were soaked for 48 hours to try and insure complete water penetration. These figures demonstrate that the PEI-epi synthesized acts like PAE and that rosin does interact with the PEI-epi during sheet formation.

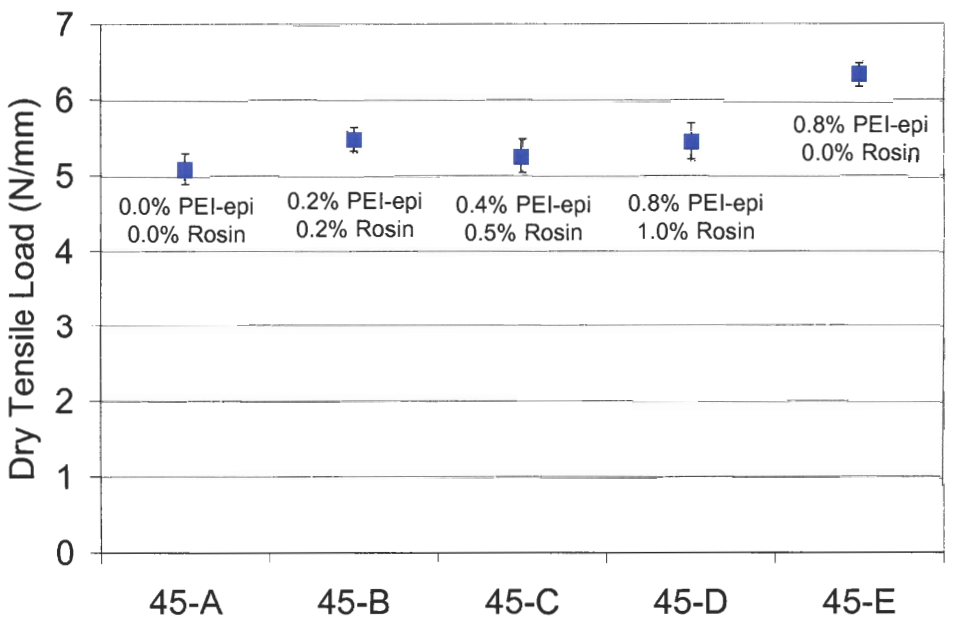


Figure 9.4 - Impact on Dry Tensile Strength on Handsheets from Laboratory Prepared PEI-epi.

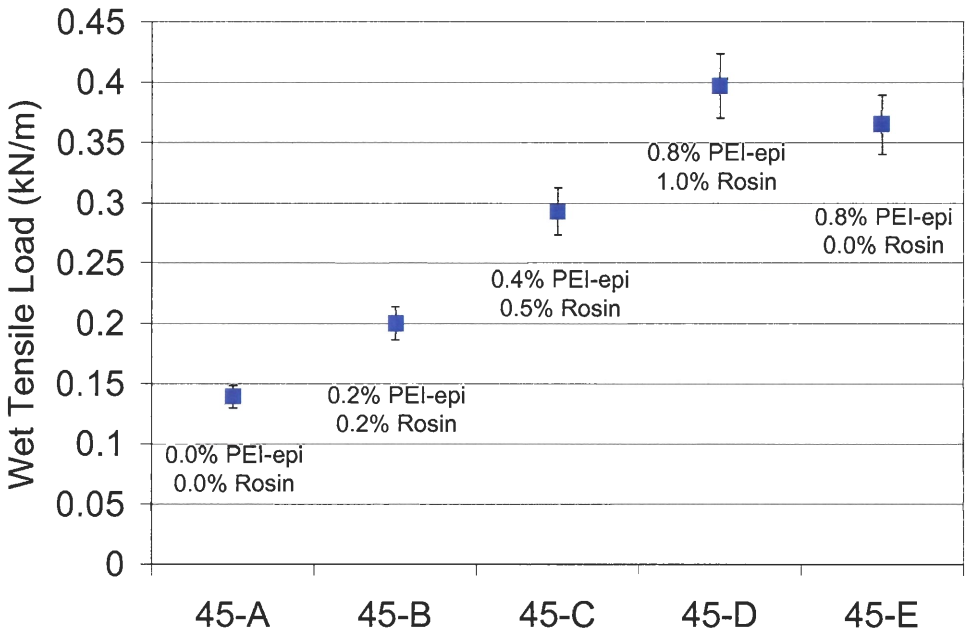


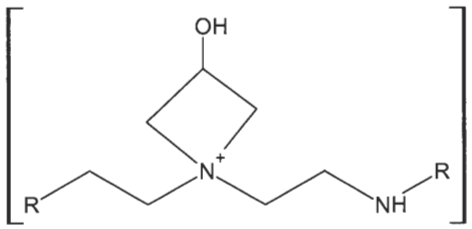
Figure 9.5 - Impact on wet tensile strength on handsheets from laboratory prepared PEI-epi.

Comparing the addition of PEI-epi without rosin, sample 45-E, to the control, sample 45-A, demonstrates that the prepared PEI-epi provides wet strength like PAE resins. Sample E provides a 25 percent dry strength and 169 percent wet strength increase over the control sample. Sample 45-E only retains 5.7% of its strength when saturated with water, Table 9.1. This is somewhat below the general rule of a minimum of 10 to 15 percent for "wet strengthened" paper. There are several reasons why the prepared PEI-epi does not achieve commercial levels of wet strength.

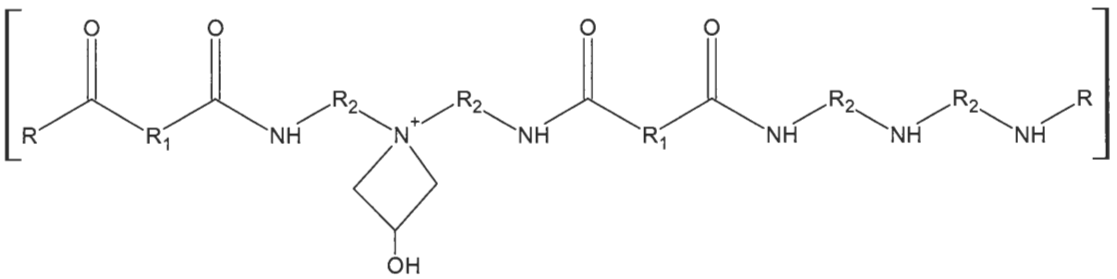
Table 9.1 - Rosin and PEI-epi dosages for laboratory strength testing.

Sample Number	wt. % Rosin on fiber	wt. % PEI-epi on fiber	% Wet/Dry Ratio	HST (s) (1% Formic Acid)
45-A	0.00	0.00	2.7%	
45-B	0.20	0.17	3.6%	
45-C	0.50	0.42	5.6%	
45-D	1.00	0.83	7.3%	504.7
45-E	0.00	0.83	5.7%	

The laboratory prepared PEI-epi has three major differences from commercial PAE. The first is that the PEI-epi used here has only a polyamine backbone while PAE typically has a polyaminoamide backbone, shown in Figure 9.6. The amides in PAE withdraw more electron density from secondary and tertiary amines than occurs with the PEI backbone. As pH is increases, secondary and tertiary amines in PAE will deprotonate sooner than the ones in PEI. The lower amount of protonated amines makes the polymer less soluble in water and will better retain it on the fiber surface. There are some circumstantial indications that the PEI-epi and rosin was flowing out of the sheet during pressing.



PEI backbone



Typical PAE backbone

R = continuation of chain

$R_1 = (CH_2)_4$

$R_2 = (CH_2)_2$

Figure 9.6 - Comparison of PEI and PAE polymer backbone structures.

The second difference is in how the PEI-epi was synthesized compared to commercial PAE. Commercial PAE is allowed to react further after removal of the epi-chlorohydrin. This reaction time causes the PAE to form significant amounts of crosslinks before application to the papermaking process. The PEI-epi used in this study was either not intentionally crosslinked or crosslinked for far less time than commercial PAE. This was done to increase the charge density on the PEI-epi to improve rosin retention and increase the number of potential reaction sites to rosin.

With less crosslinking than PAE, the laboratory PEI-epi may not have been as effective at bridging between fibers and thus protecting fiber to fiber bonds.

The final difference between the PEI-epi and commercial PAE is a lack of curing. Wet strength from PAE is not fully developed at the end of the paper machine.[76] Curing paper with PAE, either by aging or exposure to high temperatures, causes significant increases in wet strength. The PEI-epi samples shown in Figure 9.4 and Figure 9.5 were only aged for a couple days and were not exposed to high temperature conditions for only one minute during drying. Additional curing may have increased the wet strength results seen for this PEI-epi sample.

The samples with rosin added, samples 45-B, C, and D, provide some interesting information. It is likely that the wet strength gain is more from a sizing impact of rosin than true wet strength. There is only a small increase in dry strength on samples 45-B, C and D. The percent wet to dry is greater in sample 45-D than sample 45-E is unusual given they contain the same amount of PEI-epi. The most likely reason for the increased wet strength on samples 45-B, C, and D is that the sizing impact from rosin protected the fiber-fiber bonds from water during saturation. Interaction between rosin and PEI-epi is seen by the higher dry strength of sample 45-E over sample 45-D. The lower dry strength gain at constant PEI-epi dosage indicates that there is less PEI-epi-fiber interaction when rosin is present.

9.2. Comparison of PEI-epi Synthesis Methods

Two methods were examined for modifying PEI with epi-chlorohydrin. The first approach reacts epi-chlorohydrin with PEI all added to water. The second way was to add the epi-chlorohydrin in a water immiscible solvent, in this study octanol, and the PEI in water. The PEI modification occurs at the interface of the two solvents in the second method. The second method is claimed to reduce side reactions of epi-chlorohydrin with water.[74]

Table 9.2 compares the ion count from GC/MS of the relative amounts of the main by-product, 1,3-dichloro-2-propanol (DCP), formed in both methods. The ion counts from the single solvent method were adjusted to correct for the concentration differences between the samples. The GC/MS spectra provided the molecular weight and structural information of some other minor by-products. These other by-products were only detected in the single solvent method and are shown in Appendix I, page 140. Further, these other by-products are chlorinated propanols, closely related to DCP and epi-chlorohydrin.

Table 9.2 - GC/MS ion count of major by-product and unreacted Epi-chlorohydrin from dual and single solvent preparation techniques.

	Dual Solvent PEI-epi	Single Solvent PEI-epi
1,3-dichloro-2-propanol	4,085,301	49,375,407
Epi-chlorohydrin	66,636	685,224
Concentration (%)	2.64	adjusted to 2.64
MW (number avg.)	110,000	101,000
Charge Density (meq/g) (pH = 7.5)	15.28	12.65

As can be seen in, the dual solvent method produces less than ten percent of the amount of DCP seen in the single solvent method. This result further supports the claims of the patent on this process.[74] The dual solvent method also has less unreacted epi-chlorohydrin remaining. This indicates that more epi-chlorohydrin either added onto the polymer or remained in the water immiscible solvent.

These by-products have two main effects on PEI-epi-rosin sizing. The first effect of the by-products is a reduction in the degree of modification of PEI. DCP or unreacted epi-chlorohydrin represents epi-chlorohydrin that is not attached to PEI. This reduces the number of cationic azetidinium structures and charge density, see Table 9.2. Thus reducing both charge neutralization ability and the number of reactive sites.

The by-products also reduce the sizing efficiency of the PEI-epi-rosin sizing chemistry. Table 9.3 shows the loss in sizing from addition of DCP. Washing the PEI-epi samples with octanol improves the sizing, see Table 9.3. The washing procedure involved addition of octanol to the PEI-epi solution, mixing, and then separation of the octanol from the PEI-epi solution. The reason DCP reduced the sizing efficiency was not pursued. However, it is likely that the hydroxyl deprotonated in solution. This would create an anionic material that would interfere with the charge neutralization retention of a PEI-epi-rosin complex.

Table 9.3 - Impact of washing PEI-epi and addition of Epi-chlorohydrin by-product, 1,3-dichloro-2-propanol (DCP), on sizing efficiency of laboratory handsheets, 1.0% rosin (as wt. % of dry fiber).

	Molecular Weight	% PEI-epi (wt. % of dry fiber)	Initial PEI-epi HST (s)	Washed PEI-epi HST (s)	with DCP added HST (s)
Dual Solvent	110,000	0.40	139	213	85
Single Solvent	101,000	0.83	74	90	32

Overall the dual solvent method of epi-chlorohydrin modification produces a better sizing agent with fewer by-products. Table 9.3 shows the stark difference in degree of sizing between the two methods. Note the higher dosage of PEI-epi used in the water solvent method. Based on this better sizing ability and reduction in by-products, the dual solvent method was employed for the laboratory sizing and spectroscopy work.

9.3. Laboratory Data

9.3.1. Impact of Dosages and pH on Degree of Sizing

The impact of major variables was examined in the previous study.[77] Rosin dosage, pH, as well as the charge of the stock and fiber showed the greatest impact on degree of sizing. These variables also provide some insight into the sizing mechanism. The effects of rosin dosage, pH, and PEI-epi dosage on five PEI-epi formulations are shown in Figure 9.7 to Figure 9.9 respectively.

Table 9.4 shows the PEI-epi synthesis conditions and polymer characterizations. Sample 0 was made using the single solvent method. Samples 1 through sample 5 were made using the dual solvent method. Sample 6 is a commercial PEI-epi designed as a retention aid. All of the azetidinium groups in sample 6 were reacted in production to either form crosslinks or hydrolysis products. Light scattering was used to measure molecular weight and a Mutek charge analyzer to measure charge density. The PEI-epi numbers in the figures correspond to the sample numbers on Table 9.4.

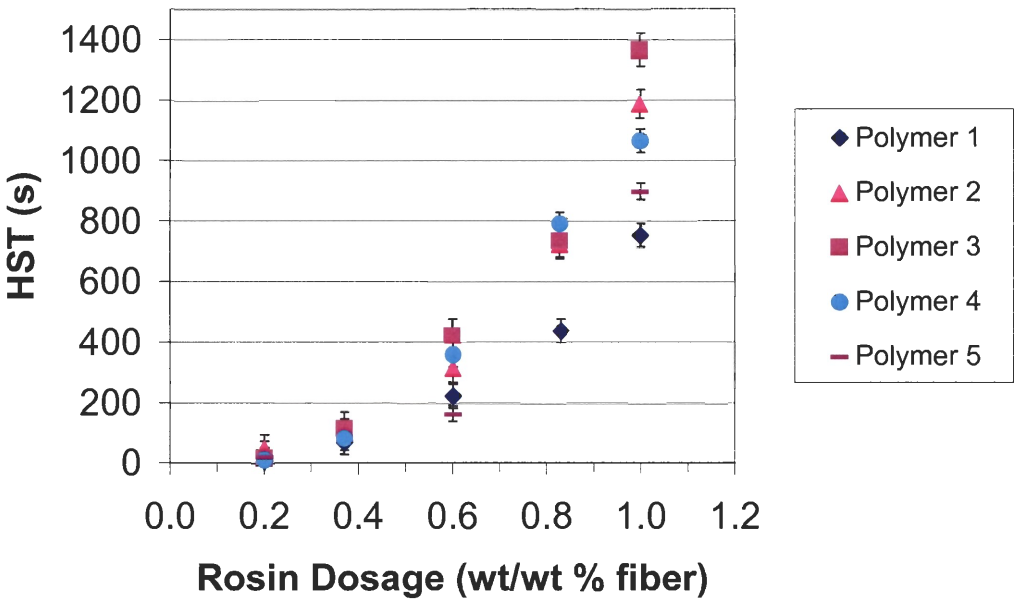


Figure 9.7 - Effect of rosin concentration on HST (Hercules Size Test) for different PEI-epi formulations. (7.0 pH, 0.4% PEI-epi, 1% formic acid)

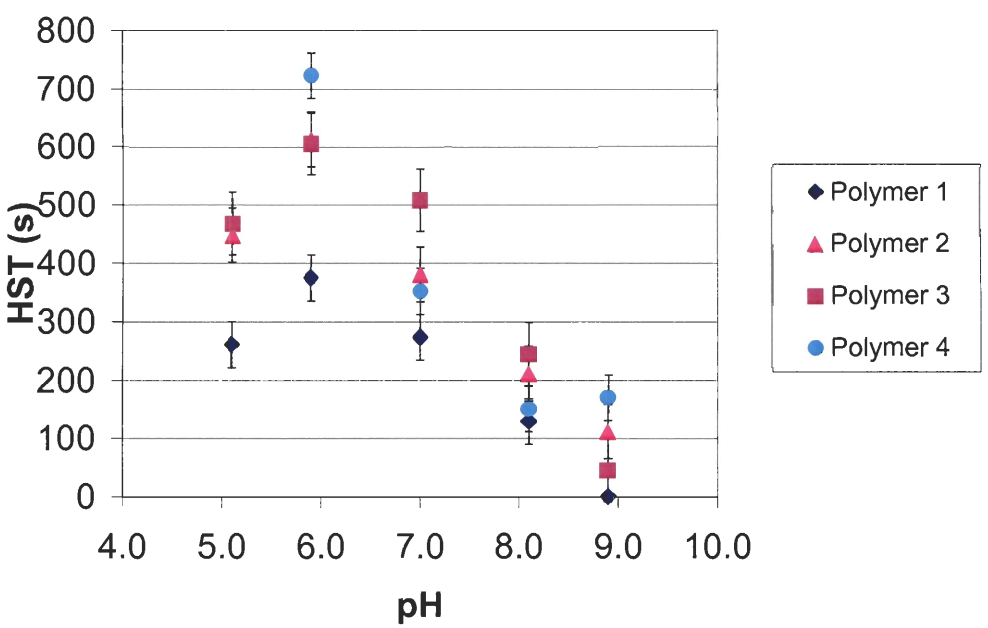


Figure 9.8 - Effect of pH on HST for different PEI-epi formulations. (0.6% rosin soap, 0.4% PEI-epi, 1% formic acid)

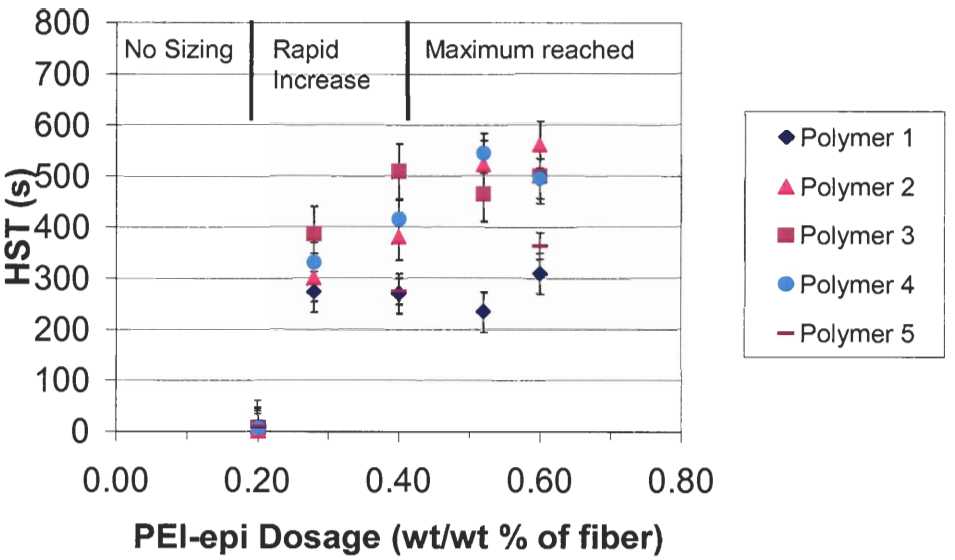


Figure 9.9 - Effect of PEI-epi concentration on HST for different PEI-epi formulations. (7.0 pH, 0.6% rosin soap, 1% formic acid)

Table 9.4 - Synthesis conditions and characterization of PEI-epi samples.

PEI-epi Number	Reaction Time (hr at 50°C)	Crosslink Time (hr at 70°C)	Number Avg. MW (g/mol)	Charge Density (meg/g) (pH = 7.5)
0	8.0 (ice bath)	---	101,000	12.65
1	0.5	0.0	111,000	15.28
2	3.0	0.0	157,000	15.41
3	4.5	0.0	209,000	15.54
4	3.0	3.0	326,000	13.91
5	3.0	6.0	411,000	12.80
6 (commercial sample)	---	---	1,200,000	7.50

Rosin dosage has the greatest impact on the degree of sizing achieved, as seen by Figure 9.7. This is expected since rosin is the source of hydrophobicity in this sizing chemistry. In addition to the presence of rosin, the hydrophilic portion of rosin must be properly orientated. Factors that impact retention and orientation of the rosin should also impact the degree of sizing.

The stock pH impacts the degree of sizing, seen in Figure 9.8. As the pH approaches 4.0 the rosin and fiber carboxyl groups become protonated, losing their anionic charge. Without an anionic charge on rosin and the fiber surface, the cationic PEI-epi can not effectively retain rosin on the sheet.

As the pH nears 8.0 the fiber hydroxyls begin to deprotonate making the fibers more anionic, which may cause more of the cationic PEI-epi to attach to the fiber, and leave less PEI-epi available for interaction with rosin. High pH may also lead to reactions between PEI-epi and hydroxyls in the water, reducing the charge and number of reactive sites on PEI-epi. In addition to rosin dosage and pH, PEI-epi dosage and structure has a significant impact on the sizing efficiency of this chemistry.

The impact of PEI-epi on the degree of sizing, shown in Figure 9.9, can be broken into three phases. At low dosages of PEI-epi, no sizing is achieved in the first phase. This is probably due to interference coming from dissolved anionic materials in the

stock. In the second phase, the sizing level rises. And then no significant change in the degree of sizing occurs in the third phase.

The lack of sizing in the first phase appears to be due to the presence of anionic material in the pulp. Dissolved materials in pulp are anionic and have a greater specific surface area than fibers and even fines. Due to this, additives such as PEI-epi will react with these dissolved materials before the fiber and fines. The presence of large quantities of dissolved materials can neutralize the PEI-epi-rosin complex. This will prevent the charge neutralization retention of a PEI-epi-rosin complex.

Neutralization of these anionic dissolved materials improves the sizing effect, see Figure 9.10. Shown in this figure are the sizing levels of a bleached and unbleached sample at 0.5 and 1.0 percent rosin addition. As can be seen in the figure, moving the pulp from an anionic to slightly cationic charge greatly improves the sizing effect. Pulps at higher anionic charge than shown in Figure 9.10 gave little to no sizing effect.

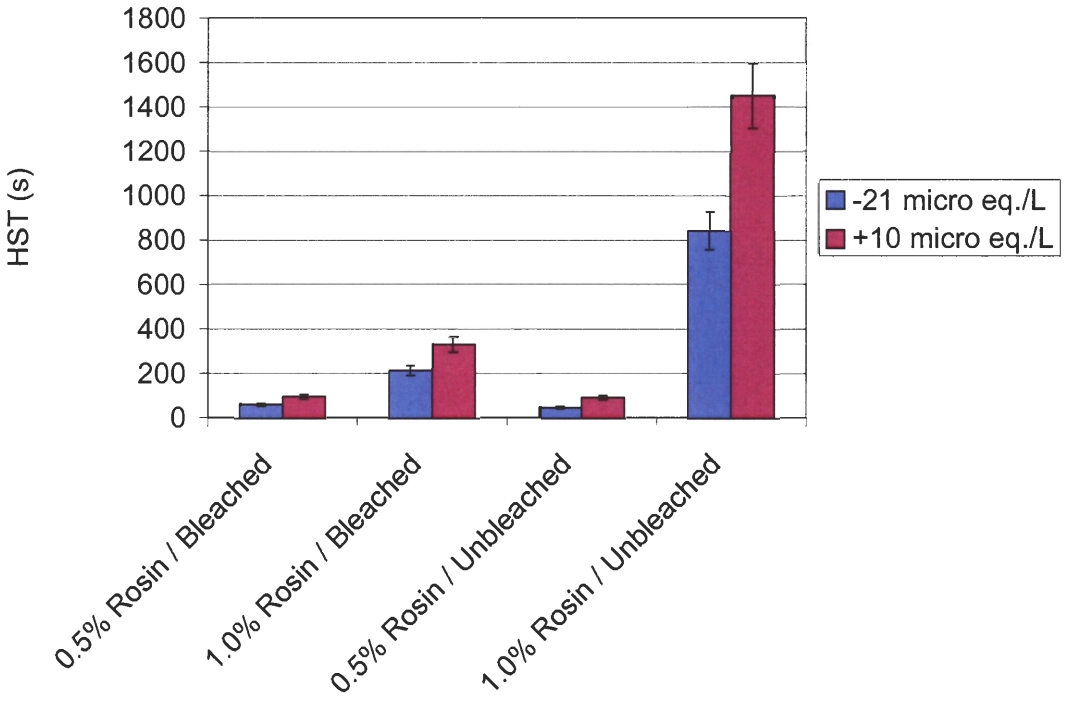


Figure 9.10 - Effect of neutralizing anionic material in bleached and unbleached pulp before addition of PEI-epi-rosin sizing chemistry on laboratory samples.

Commercially, a cheaper, low molecular weight high charge density polymer is used to neutralize anionic charge in the stock. No polymer of this type is present in this study in order to keep the system chemistry simple. Excess PEI-epi dosages provide neutralization of any anionic material present.

After the stock charge is balanced, retention of the sizing can be achieved. The PEI-epi quickly reaches a maximum effect, phase 2. Higher doses provide no improvement in sizing, phase 3. The leveling off is not surprising because PEI-epi is hydrophilic and it can not directly contribute to sizing. When all of the rosin present is retained, more PEI-epi does nothing to improve sizing. At extremely high dosages, at

or above 0.9% with these samples, PEI-epi can cause a decrease in sizing. Possibly this decrease is a result of excess PEI-epi forming salts with deprotonated carboxyl groups on both the fiber surface and rosin. At high PEI-epi concentrations this will make both the fiber surface and PEI-epi- rosin complexes positively charged and repulsive to each other.

9.3.2. Impact of PEI-epi Structure on Degree of Sizing

The formulation of PEI-epi impacts the number of azetidinium structures, which impacts the polymer charge and number of reactive structures. The charge density and HST (Hercules Size Test) values for the samples in Table 9.4 are shown on Figure 9.11. Significant differences are seen from the various reaction conditions.

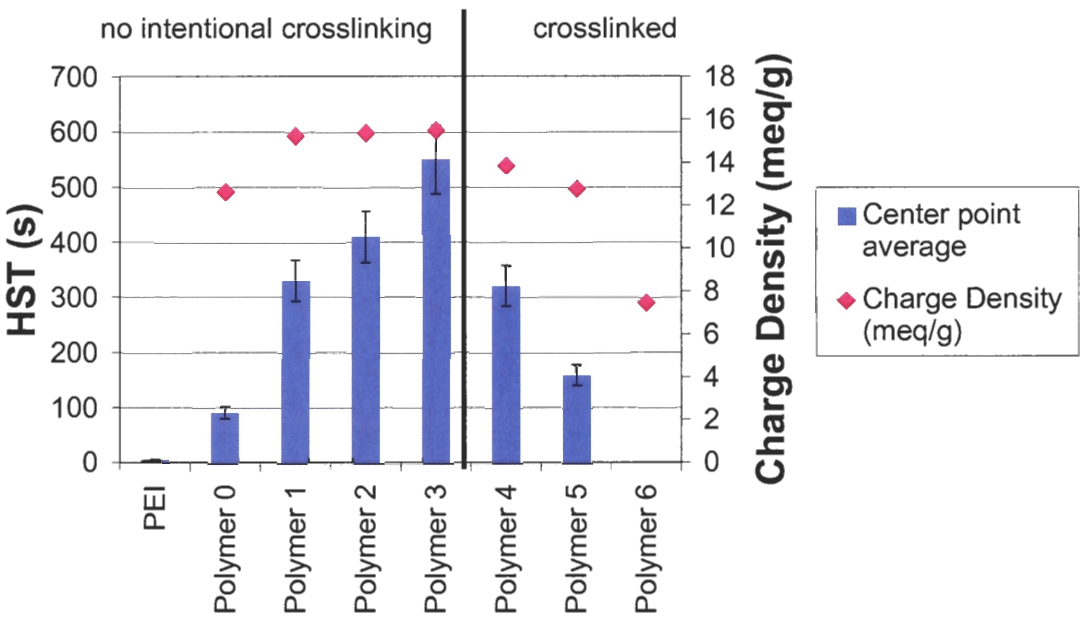


Figure 9.11 - Comparison of charge density and increasing molecular weight of PEI-epi to HST time. (7.0 pH, 0.6% rosin soap, 0.4% PEI-epi or 1.0 % PEI, 1% formic acid)

PEI-epi synthesized using the Hercules' method[74] improved HST values by 100-300 percent, using the same rosin soap, concentrations, and fiber stock. A comparison of the earlier method, sample 0, to the Hercules' method, samples 1-5, is seen in Figure 9.11. Clearly this method makes a better epichlorohydrin modified polymer for rosin sizing. Increased charge density and molecular weight appear to be related to this improved sizing.

A comparison of several different degrees of modifications of PEI is shown in Figure 9.11. Figure 9.11 compares HST of polymers with different charge densities and

molecular weights. The molecular weight is increasing going from left to right. As molecular weight is increased, see Table I, there is an increase at first and then a decrease in HST time. This increase in sizing efficiency correlates to an increase in charge density and molecular weight of the polymers.

The decrease in HST occurs when crosslinking is introduced, which also corresponds to a decrease in charge density and number of azetidinium structures. By comparing samples of different molecular weight but similar charge density, it can be seen that molecular weight is also an important factor. Sample 4 has a lower charge density but higher HST than sample 1, see Figure 9.12. It can also be seen that while samples 0 and 5 have similar charge densities, sample 5 with a higher molecular weight achieves a higher degree of sizing, shown in Figure 9.13. Apparently a minimum size of the PEI-epi- rosin complex is needed in addition to high charge density.

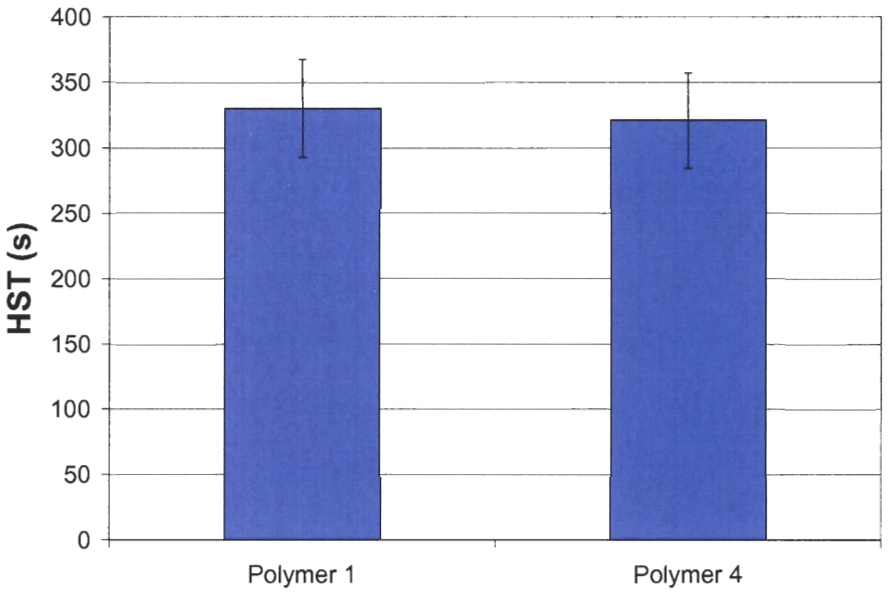


Figure 9.12 - Comparison of sample 1 to sample 4, lower charge density with higher molecular weight.

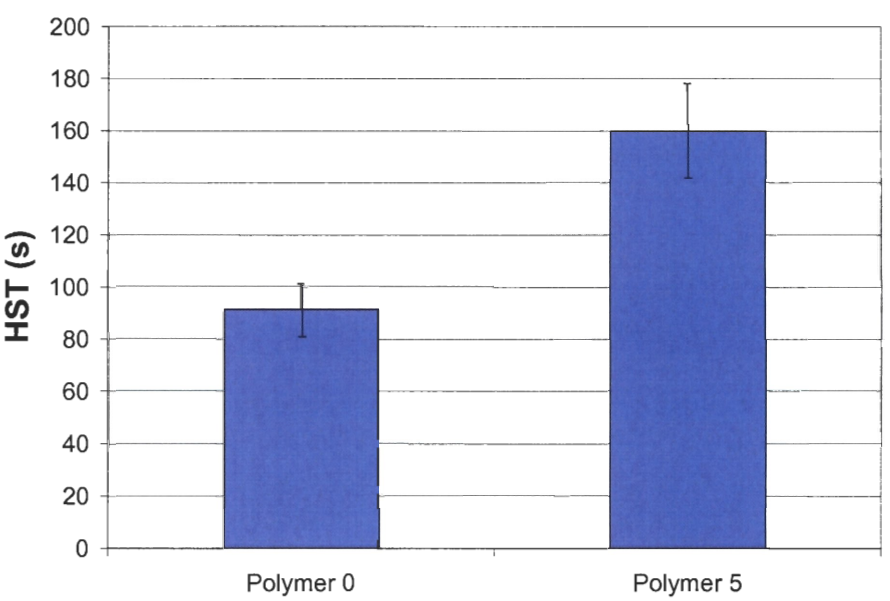


Figure 9.13 - Comparison of sample 0 to sample 5, impact of higher molecular weight at constant charge density.

Comparing at constant molecular weight shows that charge density is also important. Samples 0 and 1 have approximately the same molecular weight, see Table 9.4. Sample 1 has a higher charge density and higher HST value, shown in Figure 9.14. Unfortunately, low rosin retention levels in the sheet, less than fifteen percent, prevented the collection of usable rosin content data. It is therefore unclear if the higher charge density contributed to higher sizing by increased retention or just a higher content of azetidinium groups.

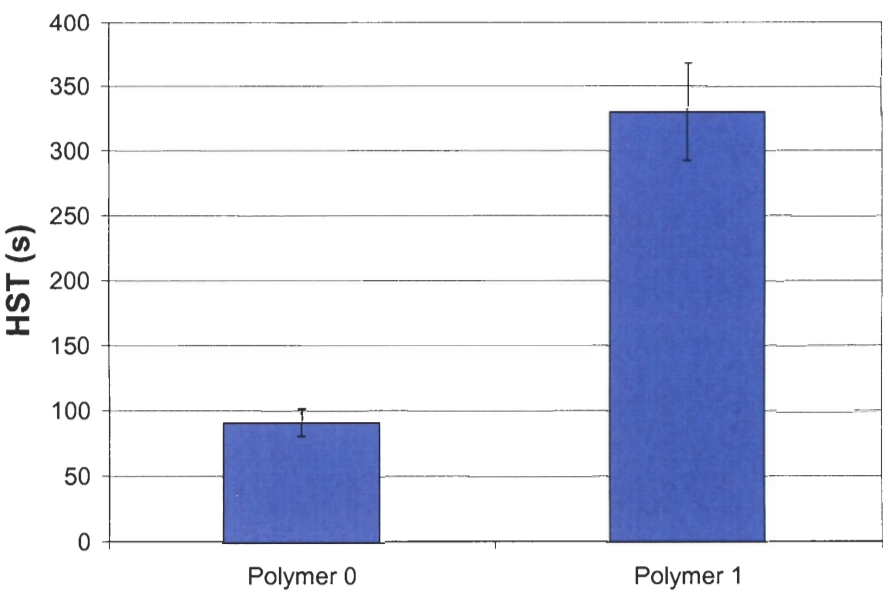


Figure 9.14 - Comparison of sample 0 to sample 1, impact of higher charge density at constant molecular weight.

PEI-epi sample 6 achieves no sizing. This product was stored at a pH of 9.5 for over two weeks before use. Under this condition all azetidinium structures have reacted either to form hydrolysis or crosslinked products. Sample 6 shows the extreme case of

a pre-reacted PEI-epi and gives further evidence that the azetidinium structure is important to sizing.

Further sample 6 acts as a control showing that it is not interaction with the crosslinked epi-chlorohydrin polymer or simple retention of the rosin that provides sizing. This product is manufactured for use as a retention aid and not as a rosin sizing agent. For sizing, epi-chlorohydrin modified polymers appear to perform best when they have little crosslinking. It is expected that in addition to differences seen by polymer formulation, the presence of acid or base in the handsheet would break the ester bond between PEI-epi and rosin.

9.4. Source of Reversion

Reversion was seen in some samples, but not all. Samples made at low pH, less than 5.5, reverted within days after initial drying. Within a week, these samples retained less than twenty percent of the original level of sizing. Sheets made at or near neutral pH showed no reversion. Some samples saw an increase in the degree of sizing with time, a common effect that is attributed to molecular movement of the rosin.

Measurement of the handsheet pH was done using the TAPPI Standard Procedure T509 OM-02. This method extracts and measures hydronium content in paper at room temperature. The pH measurements show that acid is present in the handsheets that

lost their sizing. Figure 9.15 shows the handsheet pH, the stock pH, the initial HST and the HST over time of handsheets made at various stock pH values.

With the stock pH within the range of 6.0 to 8.0, no reversion is seen, even after six months of storage. At lower handsheet pH, a loss of HST value occurs over time. The presence of acid in the handsheet is believed to be the only difference between these samples and therefore appears to be the cause of this reversion. To further test this finding, handsheets sized at a neutral pH were modified with acid and base.

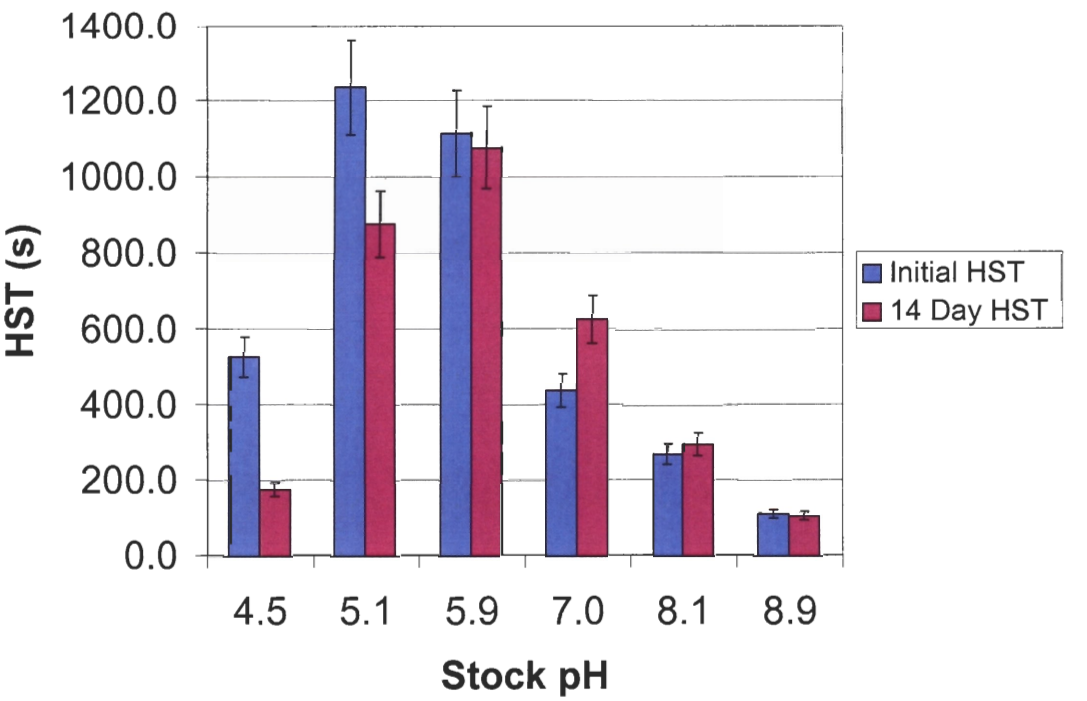


Figure 9.15 - Impact of stock pH on HST over time and sheet pH. (0.6% rosin soap, 0.4% PEI-epi, 1% formic acid)

In order to prove the above proposed mechanism of sizing reversion at different pH levels, the handsheets initially sized at neutral pH were treated with acidic, neutral or basic solution. The results of these treatments are shown in Figure 9.16. In all cases, after the pressing treatment, the degree of sizing decreases. Apparently, the pressing itself disrupts some of the size barrier as seen in the neutral/control sample. However, the neutral case shows far less sizing loss than the acid or base treated samples.

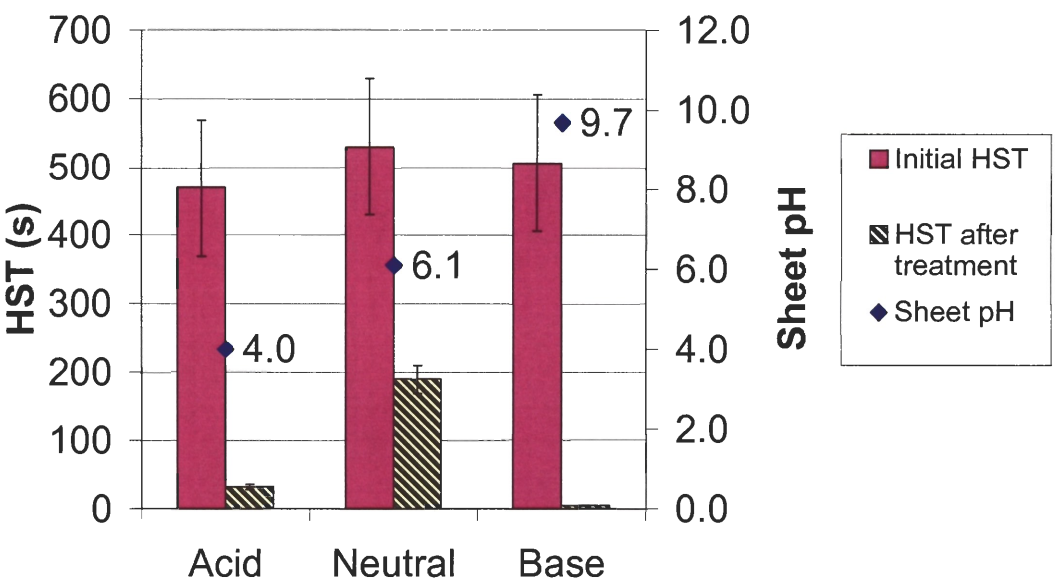


Figure 9.16 - HST loss due to penetration of HCl and NaOH. (0.6% rosin soap, 0.4% PEI-epi, 7.0 pH, 1% formic acid)

The proposed mechanism involves an ester bond between PEI-epi and the rosin carboxyl groups.[78] It is well known that acid and base can catalytically cleave an ester bond. This may explain the greater loss of sizing for the acid and base cases in Figure

9.16 and the reversion seen in Figure 9.15. If an ester bond between PEI-epi and rosin anchors and orients rosin to produce sizing, then the cleavage of that bond by residual acid or base explains the reversion effect seen.

9.5. Herty Pilot Trial Data

The Herty pilot trial conditions were established based on the laboratory findings. The dosages used for each condition of the pilot trial are shown in. Addition points are shown in Figure 8.3. Condition 1 is a control used to show that no residual sizing agent was carried over in the recycled stock. Conditions 2-5 tested the PEI-epi-rosin sizing chemistry without any PCC, using high and low dosages of each chemical. Conditions 7-9 tested various dosages of a one-micron PCC, Albacor HO, at the high dosage of the sizing chemistry. Likewise, conditions 10-12 examined different dosages of a three-micron PCC, eXtend, with the same sizing chemistry dosages. A condition 6 was intended to be used as a replicate of condition 4, but was cut due to loss of stock and chemicals during preparation.

Table 9.5 - Herty pilot trial dosage levels.

Condition	Rosin (%)	PEI-epi (%)	PCC
1	0.0	0.00	Control
2	0.5	0.09	None
3	0.5	0.18	None
4	0.9	0.18	None
5	0.9	0.09	None
7	0.9	0.18	5%PCC (1μm)
8	0.9	0.18	10% PCC (1μm)
9	0.9	0.18	20% PCC (1μm)
10	0.9	0.18	5%PCC (3μm)
11	0.9	0.18	10% PCC (3μm)
12	0.9	0.18	20% PCC (3μm)

Some of the sheet properties are shown in Table 9.6. Throughout the trial, the basis weight ran high. Strength data is normalized to the target basis weight to reduce any effect from basis weight variation. The pH drops for condition 2-5. This is likely due to the acid used to store the PEI-epi.

Table 9.6 - Basis weight, caliper, and sheet pH from Herty pilot trial.

Condition	Basis Weight (lb/1000ft^2)	Caliper (0.001 in.)	Sheet pH
Target Values	42.0	none	6.0-8.0
1	47.4	14.1	8.17
2	48.7	14.7	6.57
3	47.5	14.6	7.00
4	43.7	14.8	6.72
5	44.2	12.9	7.09
7	45.8	13.8	9.57
8	45.5	13.7	9.56
9	44.2	13.1	9.56
10	43.8	13.7	9.52
11	43.4	13.6	9.67
12	47.4	14.3	9.84

The conditions with PCC show a jump in pH, probably from carbonate. There was no acid available during the trial with which to lower the pH. A pH of 9.5 and higher was initially not expected. However, Colasurdo and Thorn[32] report on commercial sheets sized with AKD that the extracted pH results for PCC filled sheets were between 9.5 and 10. In their samples, the PCC slurry had a pH of only 8.5 and the white waters had a pH of 7.0 to 7.5. For GCC samples, they report an extracted pH in the range of

7.0 to 8.0. Colasurdo and Thorn conclude that the higher extraction pH of PCC filled sheets is from either a concentration or release of alkali during drying. That GCC does not have the same effect indicates that the geometry of the calcium carbonate filler plays a role in the increased pH.

Ash content gives evidence of PCC retention in conditions 7-12. Table 9.7 shows the calculated amount of PCC retained in the sheet. TAPPI Standard Method T211 OM-93 was used to measure ash retention. The amount of ash measured for the base sheet condition with no calcium carbonate addition is subtracted from the ash percentages of conditions 7-12 to account for any ash present that is part of the incoming stock.

Table 9.7 - Ash content of PCC conditions from Herty pilot trial.

Condition	PCC added (wt/wt %)	Particle Size (μm)	PCC in Sheet (wt/wt %)	PCC Retention (%)
7	5.0	1	4.3	86.0
8	10.0	1	9.3	93.0
9	20.0	1	17.5	87.5
10	5.0	3	6.0	120.0
11	10.0	3	11.5	115.0
12	20.0	3	23.8	119.0

The results reflect good retention for both particle sizes of PCC. The three-micron PCC shows better retention in the sheet, which is expected due to better entrapment of its larger particle size. There is more PCC measured in the sheet for the three-micron conditions than was intended to be added during the trial. Possible reasons for this are computational error in make down concentration or pumping problems. The retained PCC also increased sheet brightness.

Sheet brightness for all of the conditions is shown in Figure 9.17. A Technodyne Technobrite TB-1C instrument was used to measure brightness. Conditions 1-5 have a brightness of 13.5, with no PCC present. The addition of the PCC increases the brightness significantly. As is expected, the one micron PCC provides as much brightness as the three micron PCC at lower retention levels.

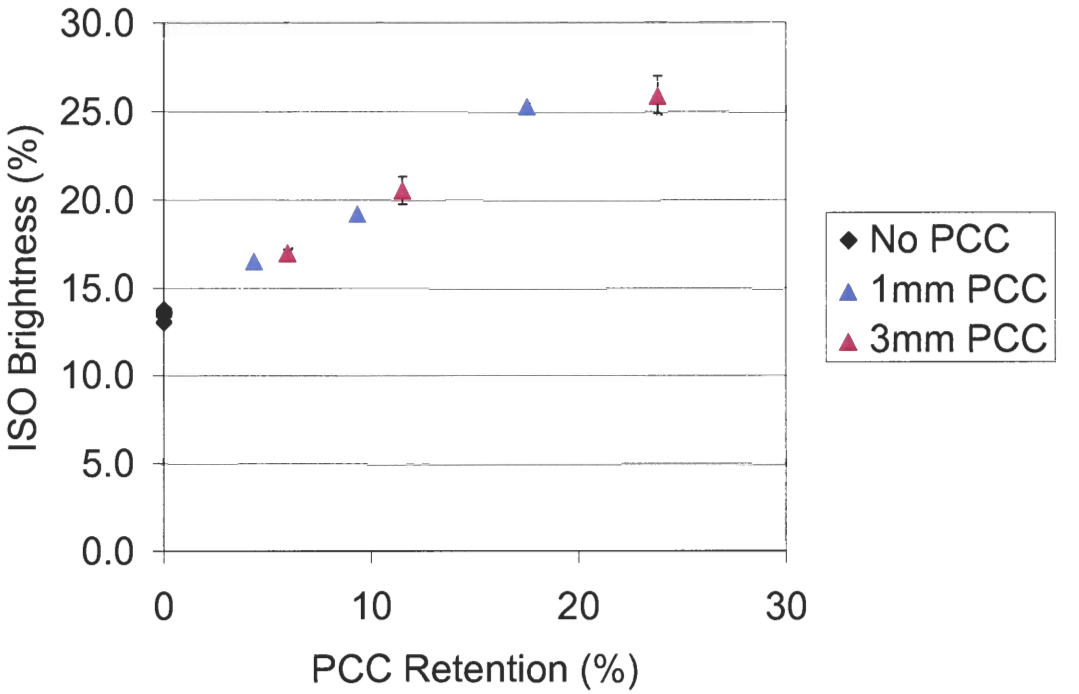


Figure 9.17 - Percent ISO brightness of PCC conditions from Herty pilot trial.

9.5.1. Sizing Results of the Herty Pilot Trial

Sizing measurements were taken off machine, after conditioning, and after aging for 90 days. Rosin content was also measured. These tests give indications on how to size with PCC and the stability of the sizing chemistry.

During production, a two-minute Cobb test was performed to determine the off machine sizing impact. The Cobb test measures the amount of water absorbed into the sheet in a given amount of time, two minutes for these tests. Test time is adjusted depending on the expected rate of absorption of the grade. The amount of water retained per sample area is reported as the Cobb value. The Cobb test was used during

production because it is easier to transport the needed equipment and no hazardous chemicals are used. A comparison of the Cobb test to the one-day HST values is shown in Figure 9.18. HST was used in the laboratory because it more clearly shows differences in the level of sizing between samples.

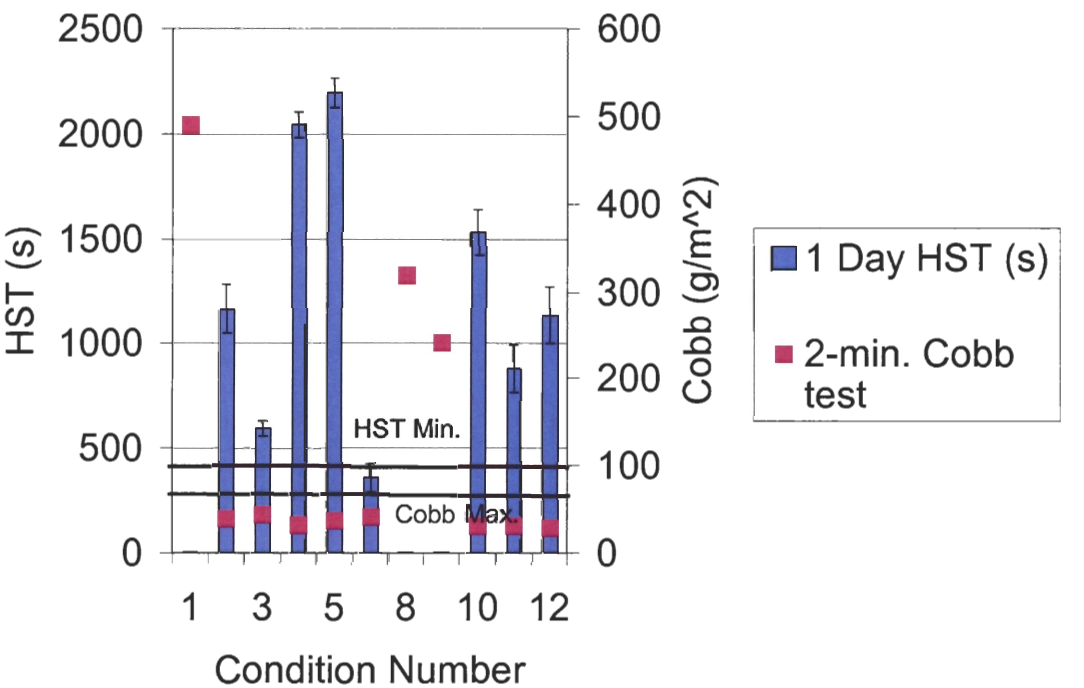


Figure 9.18 - Off machine Cobb (Two-minute) and one-day HST (10% Formic Acid) from the Herty pilot trial.

From Figure 9.18 it can be seen that most conditions are sized. Typical Cobb values for linerboard range from 30-60 g/m^2 for 42-pound linerboard. Common HST values for 42-pound linerboard are greater than 400s testing with 10% formic acid. A bar for the Cobb maximum value and the HST minimum value are shown in Figure 9.18. The higher bar corresponds to the HST minimum. Conditions 1, 8, and 9 show no sizing

effect, by either the Cobb or HST tests. The first condition has no rosin or PEI-epi added and no sizing is expected. In conditions 8 and 9, the lack of sizing is probably due to interference from the one-micron PCC. However, the three-micron PCC appears to have less of an impact on sizing.

Figure 9.19 shows the one-day HST and rosin retention values for the conditions with no PCC. Rosin was solvent extracted and then quantified by GC/MS. The procedure used to measure rosin retention is described in Section 8.2.8, page 68. Rosin dosage and retention appears to be the main controlling factor on the degree of size.

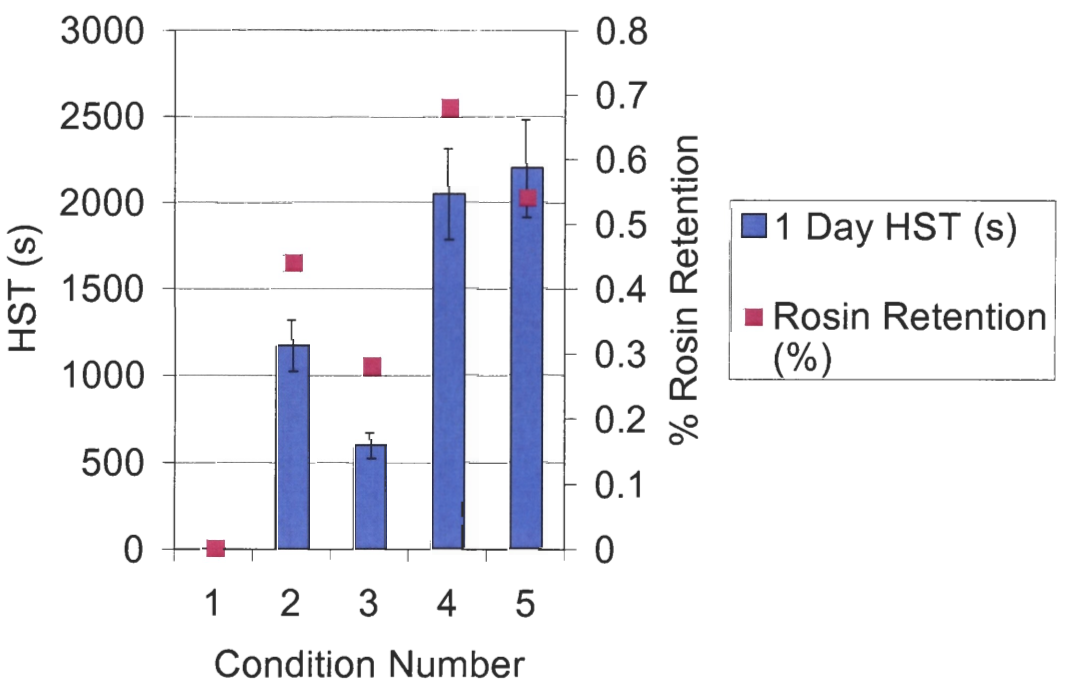


Figure 9.19 - One-day HST (10% Formic Acid) and rosin retention for conditions with no PCC from Herty pilot trial.

Condition 3 had the same amount of rosin and more PEI-epi added, why less rosin was retained is unclear. Most likely the stock charge became more anionic or the higher pH hindered rosin retention, see Table 9.6. Despite higher rosin content, condition 4 shows the same level of sizing as condition 5. All sized conditions with no PCC exceed the degree of sizing expected in typical linerboard grades.

A comparison of the Herty pilot trial (linerboard) to the laboratory prepared handsheets (fine paper) is shown in Table 9.8. The linerboard has an apparent density that is about twice that of the laboratory handsheets, which contributes significantly to the increased degree of sizing seen. Higher and more uniform tension on the pilot machine probably contributes some to the higher sizing as well. The linerboard had a greater content retention of rosin, 30-70 percent as compared to less than 15 percent for the laboratory fine paper. The sizing difference shown between the two sample sets in Table 9.8 is commonly known to occur.[79]

Table 9.8 - Comparison of Herty pilot trial (linerboard) to laboratory prepared handsheets (fine paper).

Sample	Grade	PEI-epi	Rosin Soap	10% Formic Acid HST (s)	1% Formic Acid HST (s)
Herty - 2	Linerboard	0.09	0.50	1167	>2000
Herty - 3	Linerboard	0.18	0.50	595	>2000
Herty - 4	Linerboard	0.18	0.90	2045	>2000
Herty - 5	Linerboard	0.09	0.90	2195	>2000
Lab 108-25	Fine paper	0.52	0.83	28	897
Lab 108-10	Fine paper	0.28	0.83	38	1109
Lab 108-19	Fine paper	0.28	0.83	58	1125

Figure 9.20 shows the one-day HST and rosin retention values for the conditions with PCC added. Only the five-percent addition level shows any sizing for the one-micron PCC conditions. All addition levels of the three-micron PCC exceed the needed degree of sizing for linerboard. The sizing failure of the one-micron PCC is likely due to its higher specific surface area and/or greater number of particles per pound of PCC.

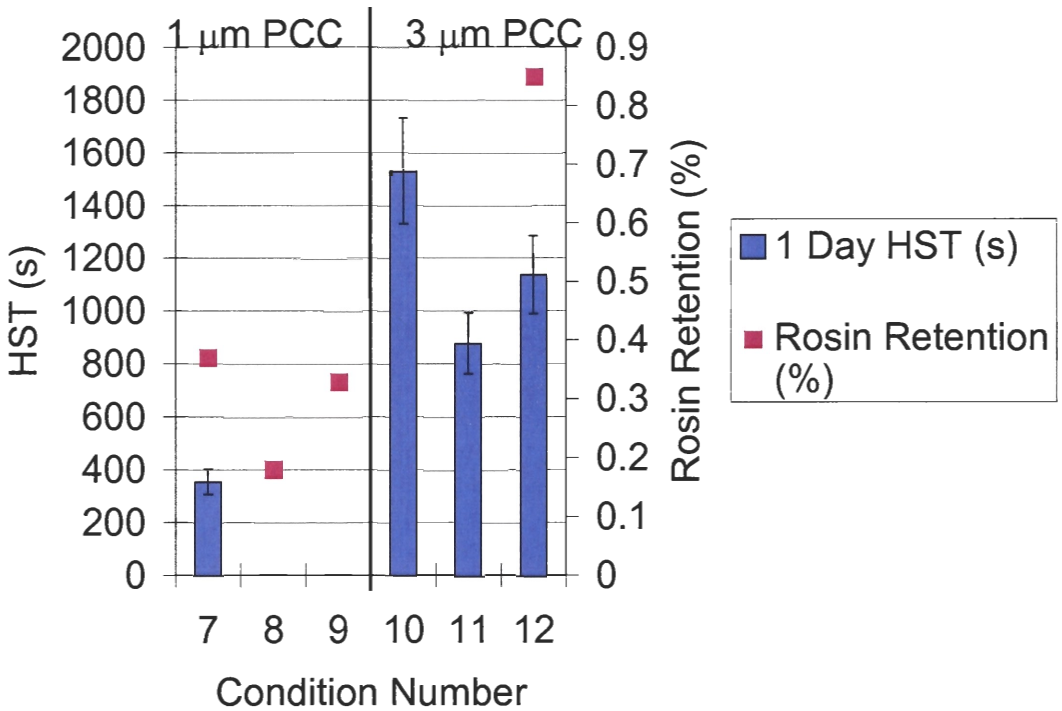


Figure 9.20 - One-day HST (10% Formic Acid) and rosin retention for conditions with PCC from Herty pilot trial.

Since the specific surface area of PCC filler particles is much larger than that of fibers and fiber fines, it is likely that some of the rosin size will adsorb onto the filler. Further, since PCC has a cationic surface, there will be competition in solution between PEI-epi and PCC. The rosin and PEI-epi were added together late at the fan pump to minimize rosin-PCC interactions.

At a constant dosage, the one-micron PCC will have a greater number of particles than the three-micron PCC. The PCC was added earlier than the sizing chemicals and may have neutralized anionic sites on the fiber, preventing PEI-epi-rosin complexes from being retained. This would explain why the one-micron PCC conditions show a

lower rosin retention and lower degree of sizing than the three-micron PCC conditions.

Condition 12 shows by far the highest percent retention of rosin, but not the highest degree of sizing. Further, conditions 8 and 9 show rosin retention but no sizing. Sizing of PCC with rosin can be done, but requires greater amounts of rosin to cover the greater surface area of PCC.[80] The greater surface area of the one-micron PCC is probably why condition 7 had little sizing and conditions 8 and 9 gave no sizing effect, despite retention of rosin. It is also likely that high surface area is why condition 12 has a lower HST value than conditions 4 and 5, despite a higher amount of rosin retention.

No reversion occurred during the Herty pilot trial, see Figure 9.21. The pH stayed between 6.5 and 7.5 for the sized conditions with no PCC. That no reversion happened in this pH range is consistent with findings discussed in section 9.4, page 93. There was no reversion for sized conditions that used PCC. The sheet pH of these conditions is greater than 9.5. That no reversion occurs differs from the results discussed in section 9.4. A major difference that may explain the different results is that on the linerboard the alkali source is carbonate and for the handsheets in section 9.4 the alkali source is hydroxide. Clearly, the PEI-epi-rosin sizing chemistry provides a stable sizing that is sufficient for linerboard needs.

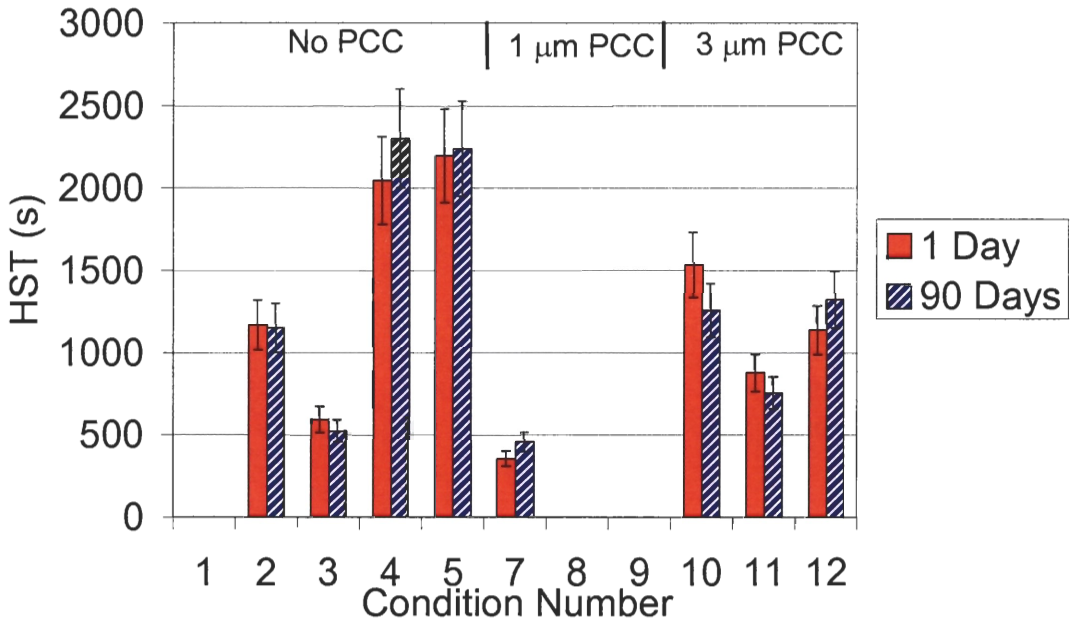


Figure 9.21 - Reversion testing at 90 days on Herty pilot trial.

9.5.2. Strength Results of the Herty Pilot Trial

Strength measurements were also taken of the linerboard from the Herty pilot trial. Tensile, tear resistance, burst, and compression tests were conducted. The results from conditions 2-5, with no PCC present, show little to no impact in strength. Significant drops in strength are seen in conditions 7-12 as the PCC content increases. Both findings are expected results. The PEI-epi-rosin sizing chemistry does not appear to have any significant impact on sheet strength.

The measured sheet strength is shown for conditions without any PCC in Figure 9.22 through Figure 9.26. There is a slight decrease in strength at the 0.9 percent rosin

dosage level, see Figure 9.24 - Figure 9.26. This small drop in strength probably comes from reduced fiber-fiber bonding caused by interference from adsorbed PEI-epi-rosin complexes. Less than 0.5 percent rosin dosages will be required to meet the sizing needs of linerboard. At this dosage, the PEI-epi-rosin sizing chemistry should have no noticeable impact on sheet strength.

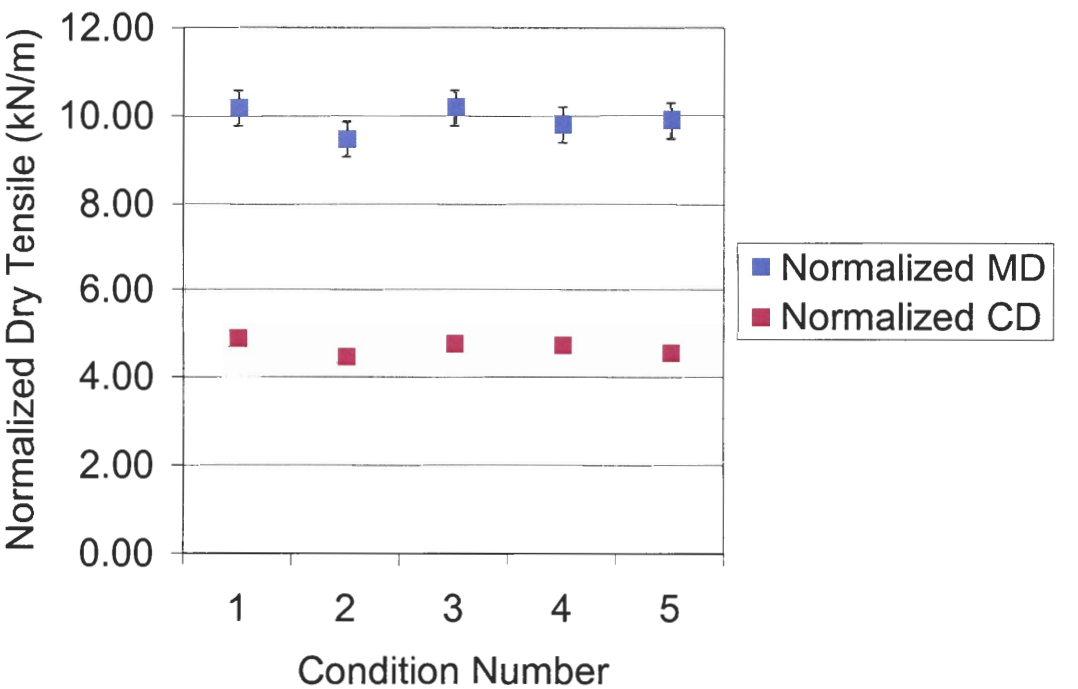


Figure 9.22 - Normalized dry tensile of no PCC conditions from the Herty pilot trial.

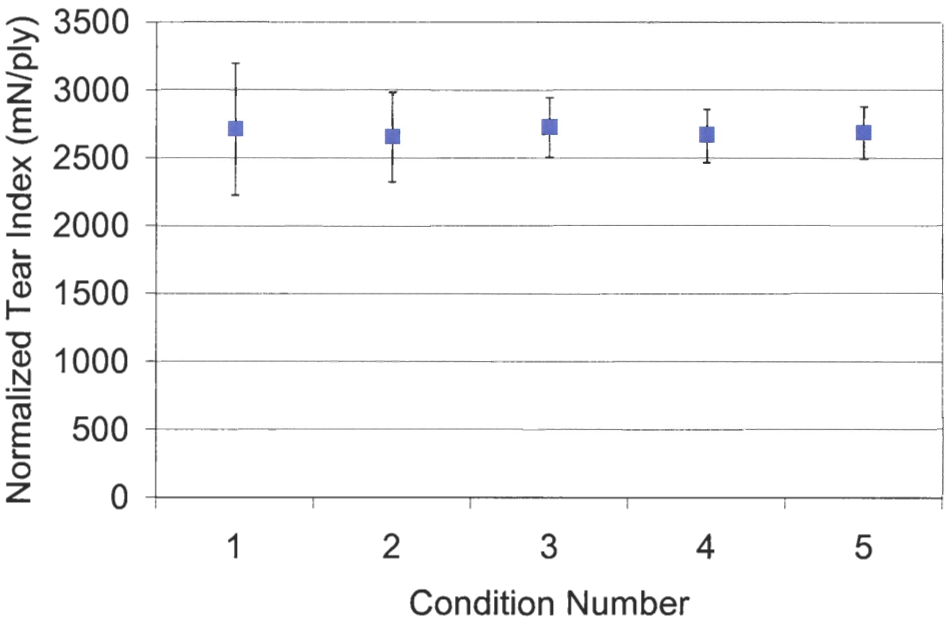


Figure 9.23 - Normalized MD Tear Resistance of No PCC Conditions from the Herty Pilot Trial.

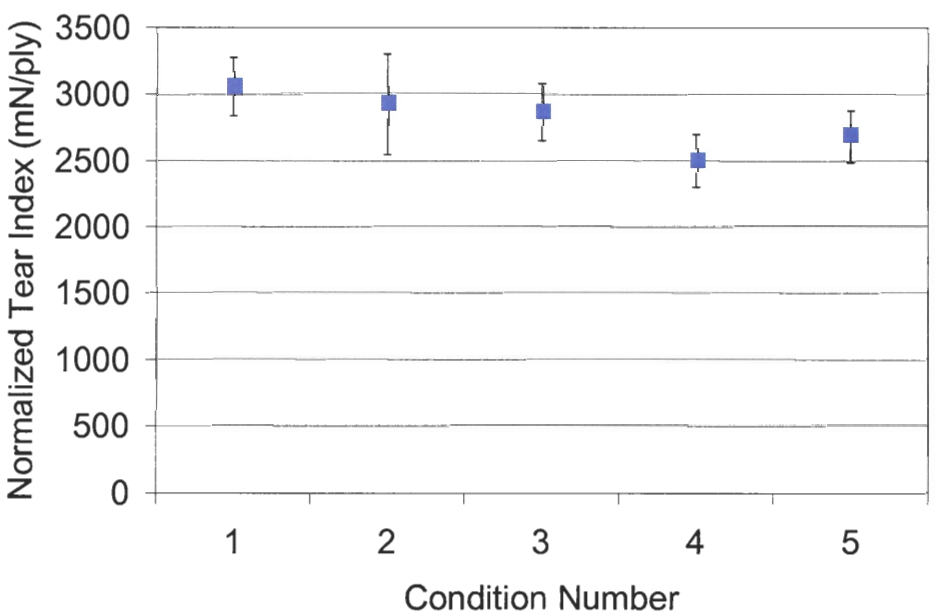


Figure 9.24 - Normalized CD tear resistance of no PCC conditions from the Herty pilot trial.

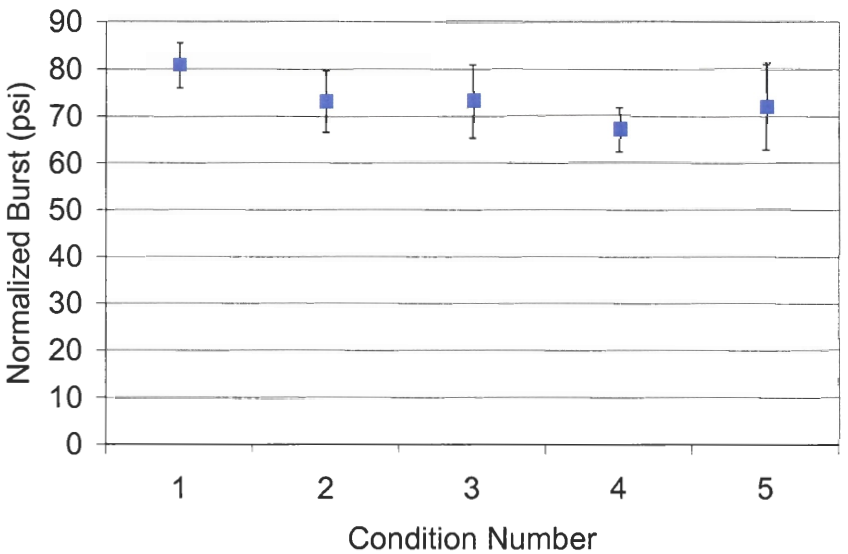


Figure 9.25 - Normalized burst strength of no PCC conditions from the Herty pilot trial.

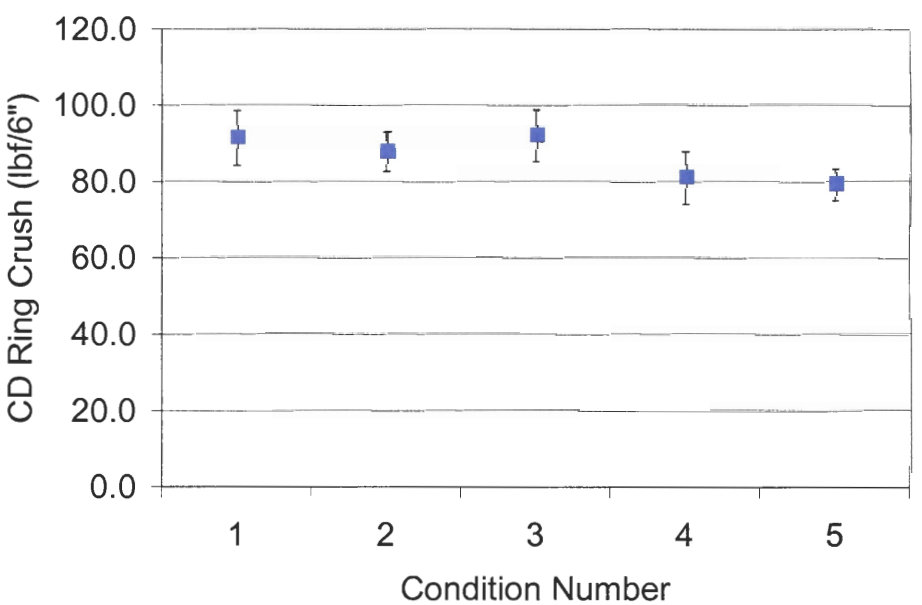


Figure 9.26 - Normalized ring crush of no PCC conditions from the Herty pilot trial.

Addition of PCC drops the sheet strength, shown in Figure 9.27 to Figure 9.32. The lowering of strength from increased PCC addition is expected due to blocking of fiber to fiber bonding by the PCC. There is little if any difference seen between the one-micron and three-micron PCC. Strength gains from making under alkaline conditions will be needed to offset this loss. These gains could come either from chemical strength agents or the increase strength seen in alkaline papermaking over acidic papermaking.

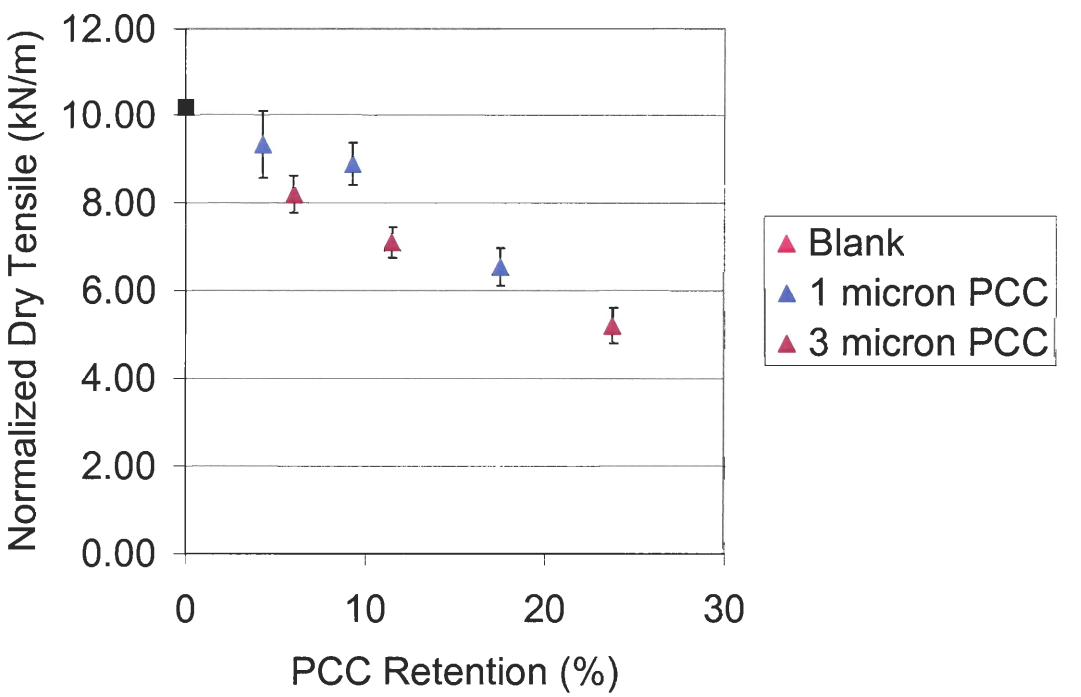


Figure 9.27 - Normalized MD tensile strength of PCC conditions from the Herty pilot trial.

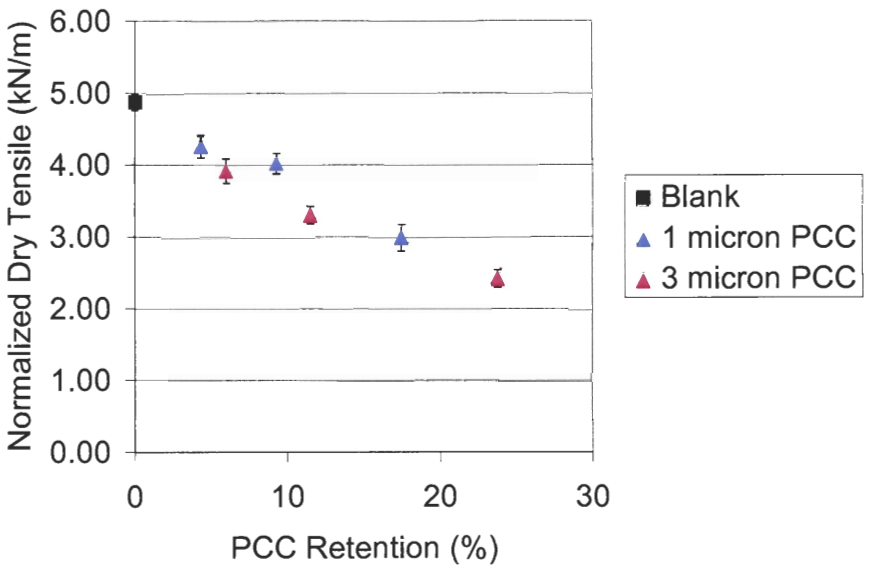


Figure 9.28 - Normalized CD tensile strength of PCC conditions from the Herty pilot trial.

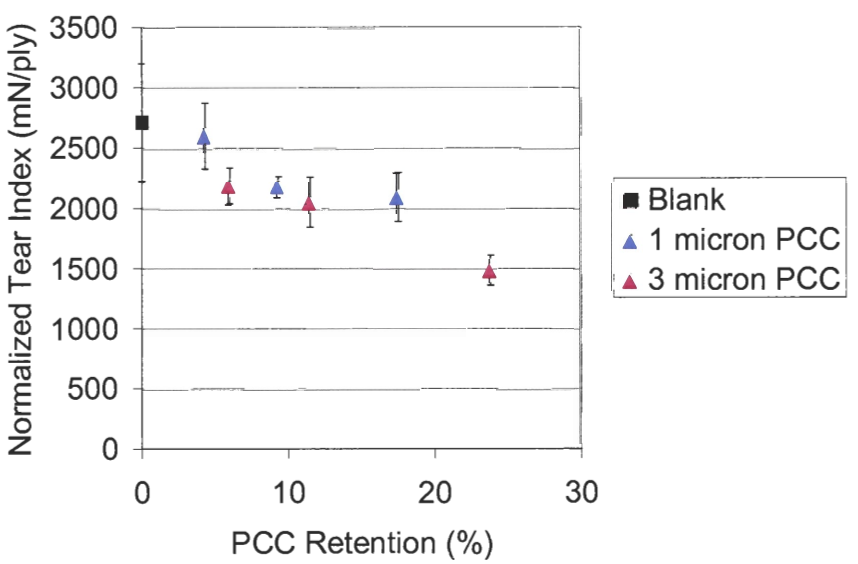


Figure 9.29 - Normalized MD tear resistance of PCC conditions from the Herty pilot trial.

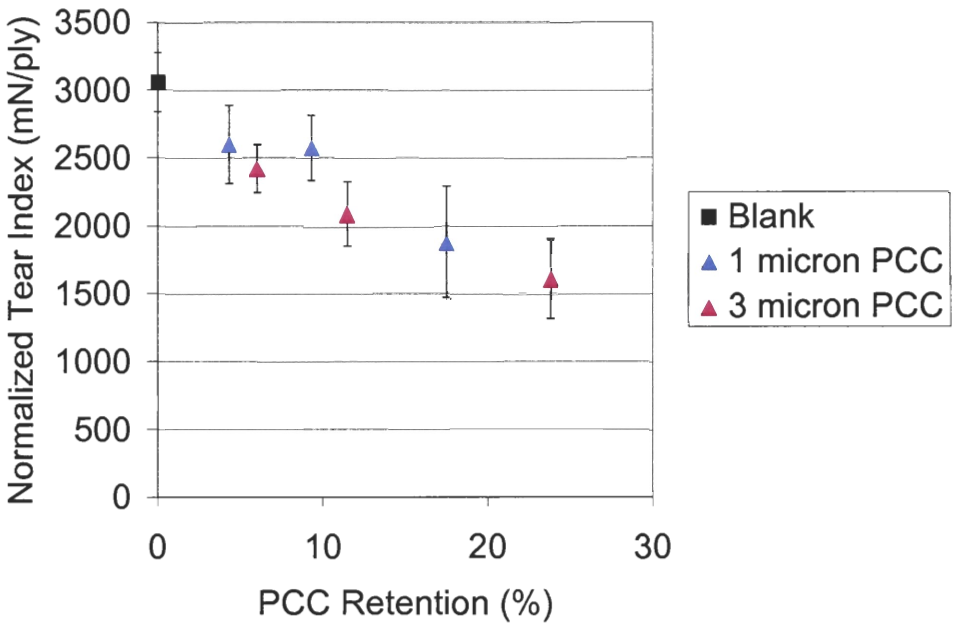


Figure 9.30 - Normalized CD tear resistance of PCC conditions from the Herty pilot trial.

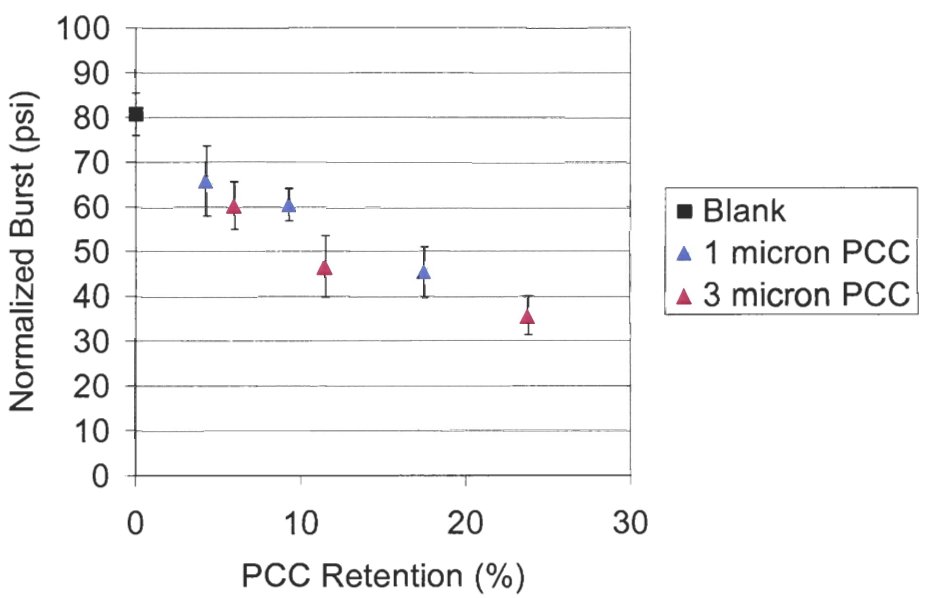


Figure 9.31 - Normalized burst strength of PCC conditions from the Herty pilot trial.

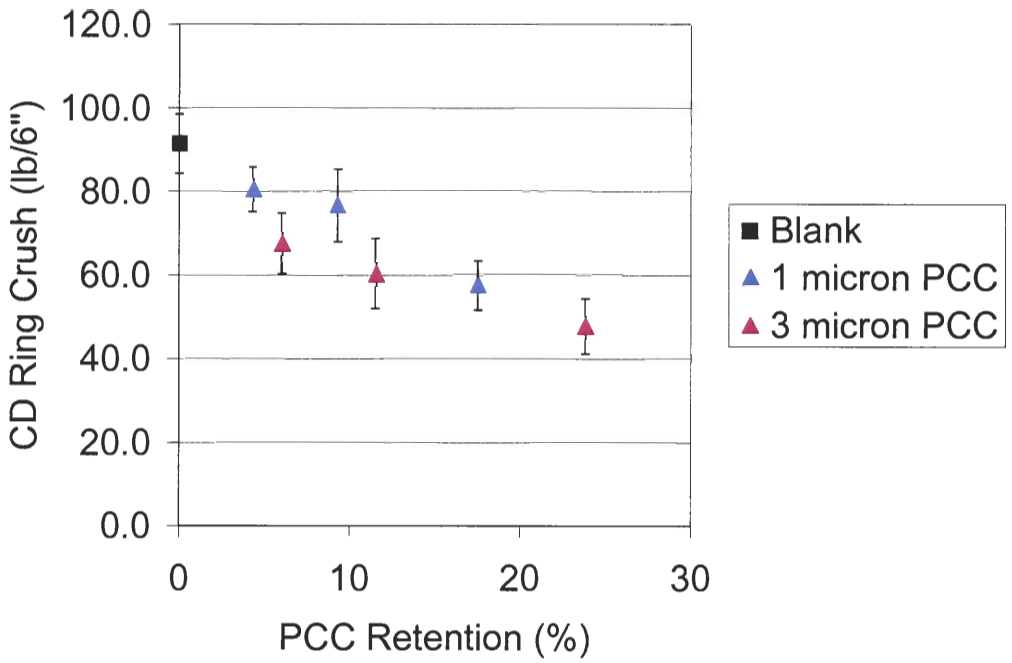


Figure 9.32 - Normalized ring crush of PCC conditions from the Herty pilot trial.

9.6. Evidence of and Contribution to Sizing from Ester Bonds

9.6.1. FTIR Evidence of Ester Bonds

As seen previously[72,77], carboxyl groups can react with epichlorohydrin modified polymers to form ester bonds. Figure 9.33 shows the FTIR spectra of sodium oleate, PEI-epi, and the reaction of these two chemicals at pH 7.0 cured at various times and temperatures. The spectra of reacted samples in Figure 9.33 are of the initial product

with no aging, after aging at room temperature for one week and the initial product after drying at 105^{O}C for two minutes with no aging time and aging for one week, respectively.

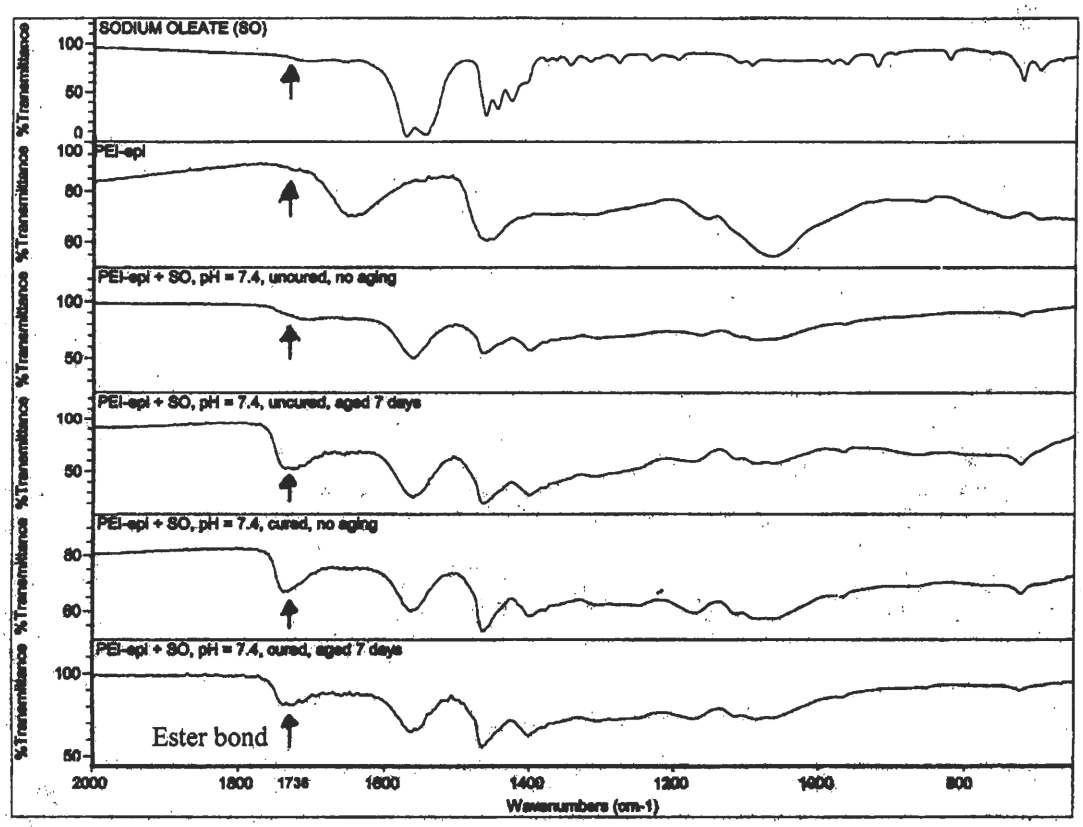


Figure 9.33 - FTIR spectra of sodium oleate (SO), PEI-epi, and varied drying temperatures and aging times.

The full spectra of each sample are shown in Appendix II, page 142. Sodium oleate is used instead of rosin because sodium oleate has a less complex FTIR spectrum. Sodium oleate has a carboxyl group that is similar to that of rosin. If there is an ester bond formed, the sodium oleate carboxyl group should have the same functionality as

those on rosin. In addition, experimental results indicate that sodium oleate combined with PEI-epi can also size handsheets.

Reaction conditions used here are milder than in previous work[77] to address concerns of an inaccurate representation of the papermaking environment. The higher azetidinium content of the dual solvent PEI-epi increased the polymer charge and probably increased the number of ester bonds formed, compare sample 0 to sample 1 in Table 9.4. This allows for use of a lower dosage of PEI-epi than before. Crosslinked PAE resins used for wet strength have less azetidinium structures and therefore can not form as many ester bonds. The ester bonds may be present in other studies, but undetected due to the reduced quantity. In any event, ester bonds are seen to form between PEI-epi and sodium oleate under moderate conditions, similar to those seen in papermaking.

As seen in Figure 9.33, there is no ester, 1736 cm^{-1}, present in the raw materials or after initial reaction of PEI-epi and sodium oleate. However, an ester bond forms at room temperature with aging or immediately with heating. The presence of the peak at 1736 cm^{-1} supports the other evidence that an ester bond is present. The drying time used for the FTIR study is longer than for the handsheet study to allow for heat transfer through the filter paper used to keep the sample from direct contact with the dryer surface. If these ester bonds are important to the sizing seen in the handsheets, then the cleavage of the ester bond by addition of an acid or base is expected.

The reacted PEI-epi-sodium oleate sample shows a decrease in the number of ester bonds present when subjected to acidic or basic conditions. Figure 9.34 shows the peak area of 1736 cm^{-1} normalized by the peak area of the C-H stretch at 2950 cm^{-1} of the same sample treated at various pH conditions. The full spectra of these samples are shown in Appendix III, page 149. All samples are taken from the same material used in Figure 9.33 after initial curing.

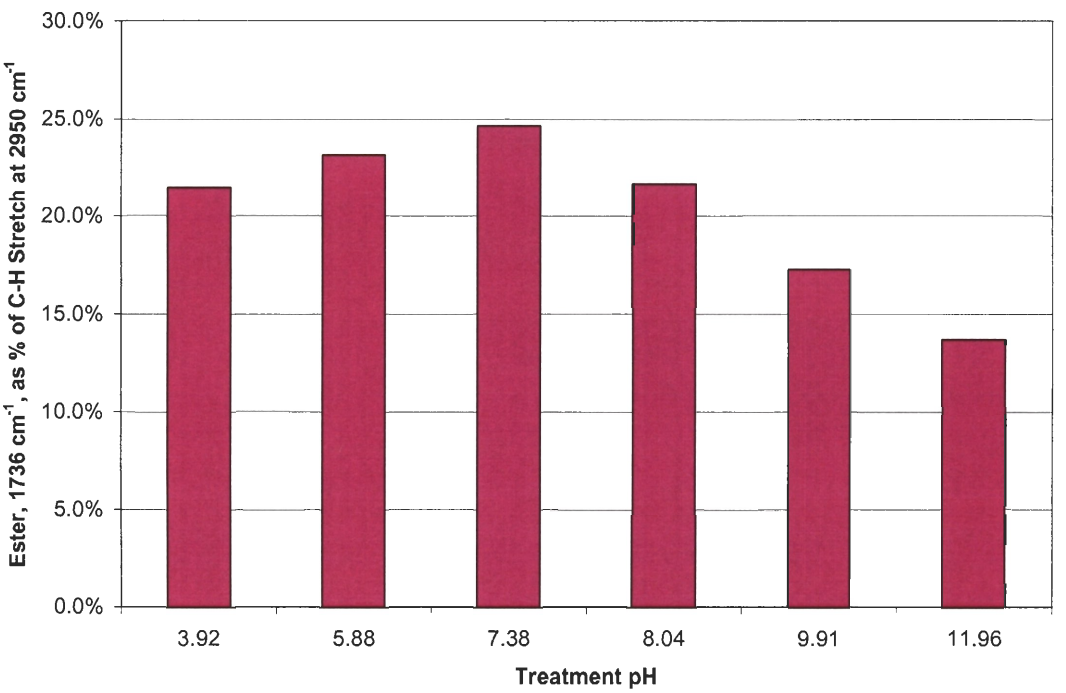


Figure 9.34 - Ratio of FTIR peaks showing effect of pH on number of ester bonds present.

Exposing the PEI-epi-sodium oleate mixture to acidic or basic environments causes a decrease in the number of ester peaks present. Based on the evidence of ester bond formation, Figure 9.33, and cleavage of ester bonds, Figure 9.34, it seems reasonable to conclude that an ester bond forms under sizing conditions and cleavage of the ester

bond occurs when the sheet is made with acid or base retained in the sheet. The presence of this ester bond and its cleavage under these conditions is comparable to the handsheet study using rosin, see Figure 9.16.

9.6.2. SS NMR Correlation of Ester Bonds to Sizing Effect

Difficulties in accurately reproducing sheet formation conditions often present questions about the relevance of model studies. It can be argued that the conditions of this FTIR model study are different from those of the handsheet formation. Therefore a direct measure of the ester bonds in handsheets was done. The use of labeled 1-^{13}C oleic acid shows that in a handsheet, ester bonds form when sizing is established and is greatly diminished when reversion occurs.

As mentioned before, Isogai[57] attempted to use solid state NMR with PAE and fatty acid anhydrides. He was unable to get a signal without dissolving away some of the carbohydrates by a cellulase treatment. Two things are done differently in this study in order to overcome the NMR signal problem and avoid using the cellulase treatment. The epichlorohydrin-modified polymer is not crosslinked and therefore has a greater content of azetidinium structures. This increases the potential number of ester bonds and NMR sensitivity. Also, the addition dosage of fatty acid is three percent, about ten times the amount used by Isogai. While this level of addition is not likely to be seen commercially, it provides useful information about reactions with PEI-epi under comparable sheet making conditions.

Figure 9.35 shows the ^{13}C solid state NMR spectra for handsheets made with sodium oleate and several different polymers or polymer conditions. Full spectra of each sample as well as an untreated handhsheet sample are shown in Appendix IV, page 156. The region shown, 140-200 ppm covers where carboxylic acids and salts as well as esters appear. A spinning side band from the cellulose carbon 1 is seen near 157 ppm. Some secondary spinning side bands may be present around 170-175 ppm, as marked on Figure 9.35c. If the signal marked is a secondary spinning side band, the intensity is small and does not compare in magnitude to the ester or carboxyl peaks seen.

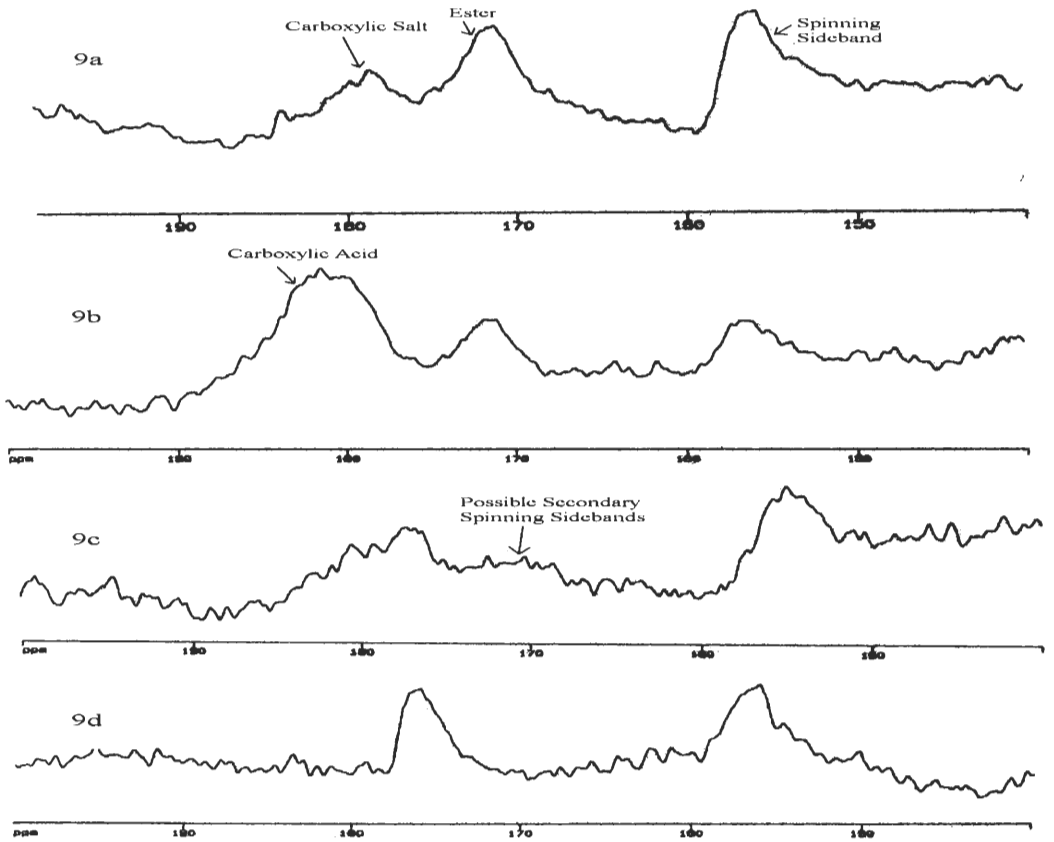


Figure 9.35 - Solid state NMR spectra of handsheets sized with 1-^{13}C sodium oleate and various polymers.

Figure 9.35b is a portion of the same handsheet shown in Figure 9.35 after being treated with sodium hydroxide using the same procedure as done in the handsheet study. It is assumed that the peaks between 170 and 185 ppm in Figure 9.35 are from the sodium oleate labeled ^{13}C interacting with the added polymer.

Ester bonds are only seen with the non-crosslinked PEI-epi. The initial PEI-epi sample, 9a, shows mostly ester bonds, 171 ppm, with some carboxylic salt formation, 177 ppm. When this sample is treated with sodium hydroxide, the ester peak becomes

smaller while the peak at 177 ppm shifts to 182 ppm and increases in intensity relative to the ester. This shift is indicative of a change from carboxylic salt to a carboxylic acid. Such a change is expected from an ester cleavage reaction with hydroxide only with an acid wash treatment.

No acid wash treatment was done on sample 9b. So how a carboxylic acid formed is unclear. Normal base catalyzed cleavage of an ester bond follows the first mechanism shown in Figure 9.36. Without the acid wash, step 4, the reaction would be expected to stop between steps 3 and 4, giving a carboxylic salt and an alcohol. This was the expected result for sample 9b. One possible explanation for carboxylic acid in sample 9b is shown in the second reaction in Figure 9.36. Here a neighboring hydroxyl from PEI-epi donates or even shares its proton, preventing the abstraction of the proton off of the carboxylic acid. The oxygen may have alternatively pulled a hydrogen atom from a protonated amine on the polymer. Another possibility is that the peak at 182 ppm on sample 9b is actually a carboxylic salt, just shifted higher during the base treatment process.

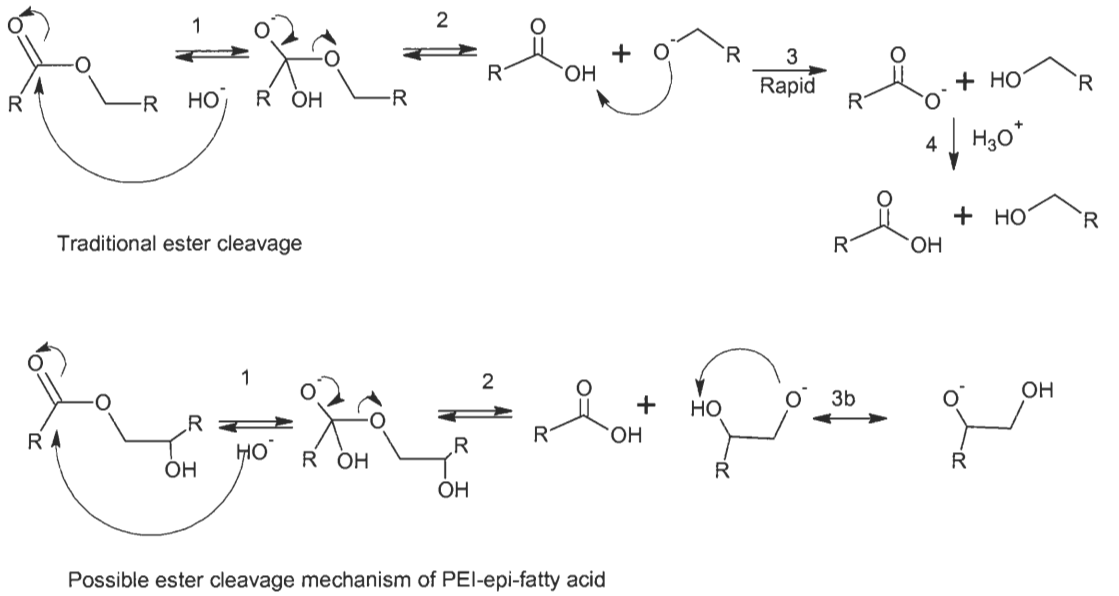


Figure 9.36 – Traditional base catalyzed ester cleavage and possible alternative mechanism for base catalyzed cleavage of PEI-epi-fatty acid ester bond.

The c-PAM and crosslinked PEI-epi show only carboxylic salts under the same conditions. Only the initial non-crosslinked PEI-epi sample gives a sizing effect, see Table 9.9. Retention of a fatty acid alone does not appear to give any sizing effect, 9c and 9d HST values. No sizing is achieved with a c-PAM, crosslinked PEI-epi or after sodium hydroxide treatment of PEI-epi even though similar amounts of fatty acid are retained. Treating non-crosslinked PEI-epi with sodium hydroxide completely destroys the sizing effect achieved.

Table 9.9 - HST and NMR peak values for solid state NMR study.

Sample number	Sizing Chemistry	HST (s) [1% Formic Acid]	Ester bond (ppm)	Carboxylic group (ppm)
9a	Non-crosslinked PEI-epi 3	2031	171	177
9b	NaOH treated PEI-epi 3	4	171	182
9c	c-PAM	1	---	178
9d	Crosslinked PEI-epi	1	---	177

As reported previously, a c-PAM improves fatty acid retention but provides no sizing effect.[47] The carboxylic salt peak in figure 9c confirms the retention of fatty acid by addition of c-PAM. The ability of crosslinked PEI-epi to retain fatty acid but provide no sizing supports the claim of Ehrhardt and Evans[55] that crosslinked PAE wet strength resins alone do not provide rosin sizing. The presence of a significant amount of fatty acid as a carboxylic salt or acid does not appear to be enough alone to create a sizing effect.

10. Industrial Implications of the Research

The results of this testing demonstrate that PEI-epi, and most likely any epi-chlorohydrin modified polyamine or polyamine amide, can size paper with rosin at neutral to alkaline pH. These findings open up the possibility of using rosin sizing on grades that had to switch to synthetic sizes, but could benefit greatly from the control and lower coefficient of friction that rosin provides. Grades that fall into this category include: coated basesheet, newsprint, fine paper for aqueous printing applications, and potentially all printing grade because of the reduced slipping. The Herty pilot trial demonstrates that this chemistry is viable for shifting linerboard from acid to alkaline pH.

This study also provides evidence supporting the formation of an ester bond between epi-chlorohydrin modified polymers and carboxylic acids. The carboxylic acids on the fatty acids used in this study are similar to those on fibers. In conjunction with other work [71, 72,77], this gives strong evidence that the azetidinium structure is key to the wet strength provided by PAE type resins. This knowledge will help steer future research for a better strength agent or rosin mordant.

11. Conclusions of the Research

The sizing mechanism of PEI-epi-rosin sizing is connected to charge neutralization retention and an ester bond formed during drying or with aging. While the amount of rosin retained controls the degree of sizing, retention alone is not enough to give sizing. The most effective pH for this sizing chemistry is near neutral. At low pH rosin and fiber carboxylic acids become protonated, preventing retention. A drop in sizing at high pH may be related to the drop in charge on PEI-epi and/or the increased anionic charge on fibers due to hydroxyl deprotonation. The presence of anionic material or epi-chlorohydrin by-products decreases the sizing efficiency. Sizing efficiency increases then decreases with the degree of modification of PEI-epi. This appears to be a combination of need for a high charge density on PEI-epi and a critical molecular weight to maximize sizing efficiency.

Results from the Herty pilot trial shows that PEI-epi-rosin can size linerboard even with some calcium carbonate filler present. PEI-epi-rosin is able to exceed the needed level of sizing for linerboard with moderate dosage levels. Sizing is achievable with high dosages of three-micron PCC filler. However, sizing with a one-micron PCC filler only sizes at low dosages. This is most likely due either to adsorption of rosin on the greater surface area of the one-micron PCC or neutralization of more anionic sites on the fiber surface from the greater number of particles in the one-micron PCC. With or without PCC, no reversion of size is seen, even after ninety days. Sheet strength is

not noticeably impacted by PEI-epi-rosin dosages at levels needed to achieve the level of sizing used in linerboard. As is expected, strength drops steadily as more PCC filler is added, regardless of particle size.

FTIR and solid state NMR shows that an epichlorohydrin modified polyamine can form ester bonds with fatty acids in handsheets under conditions comparable to papermaking. The presence of residual acid or base in handsheets destroys the sizing effect achieved, consistent with catalytic ester cleavage. Solid state NMR shows that the destruction of the sizing by addition of sodium hydroxide parallels the cleavage of many of the ester bonds present. PEI-epi functions as a mordant for rosin by creating an ester bond to anchor and help properly orient the hydrophobic portion of rosin.

12. Suggestions for Future Research

There are several areas of this study that further analysis would benefit. These include:

- More analysis of factors that impact rosin retention and correlation of sizing to rosin retention. The factors of main interest are PEI-epi dosage, different base polymers for epi-chlorohydrin modification, rosin dosage, pH, and possibly examining different sheet formers.
- Further solid state analysis of ^{13}C labeled sodium oleate at varied pH, PEI-epi dosage, rosin dosage, and fiber type. Also, optimization of delay time may improve signal intensity.
- Analysis of peak shift in NaOH treated solid state NMR sample, from carboxylic salt to acid. Without an acid wash, this is unexpected. Further testing could help to confirm and explain this result.
- A correlation of the degree of sizing to both polymer particle size and polymer-rosin complex size may help provide knowledge on the best polymer modifications to optimize the sizing.
- A study of the kinetics of the polymer modification and rate of decay in storage would provide a better understanding of how to adjust the manufacturing of the polymer and quantify shelf life.

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- Hercules (Chemicals) - Susan Ehrhardt and George Joncas
- Eka Chemical (Chemicals) - R. Danny Haynes and Richard Urbantas
- Kemira (Chemicals) Daniel Wise and William Garrett
- Specialty Minerals Inc. (PCC) - Bob Gill and Elizabeth Ingram

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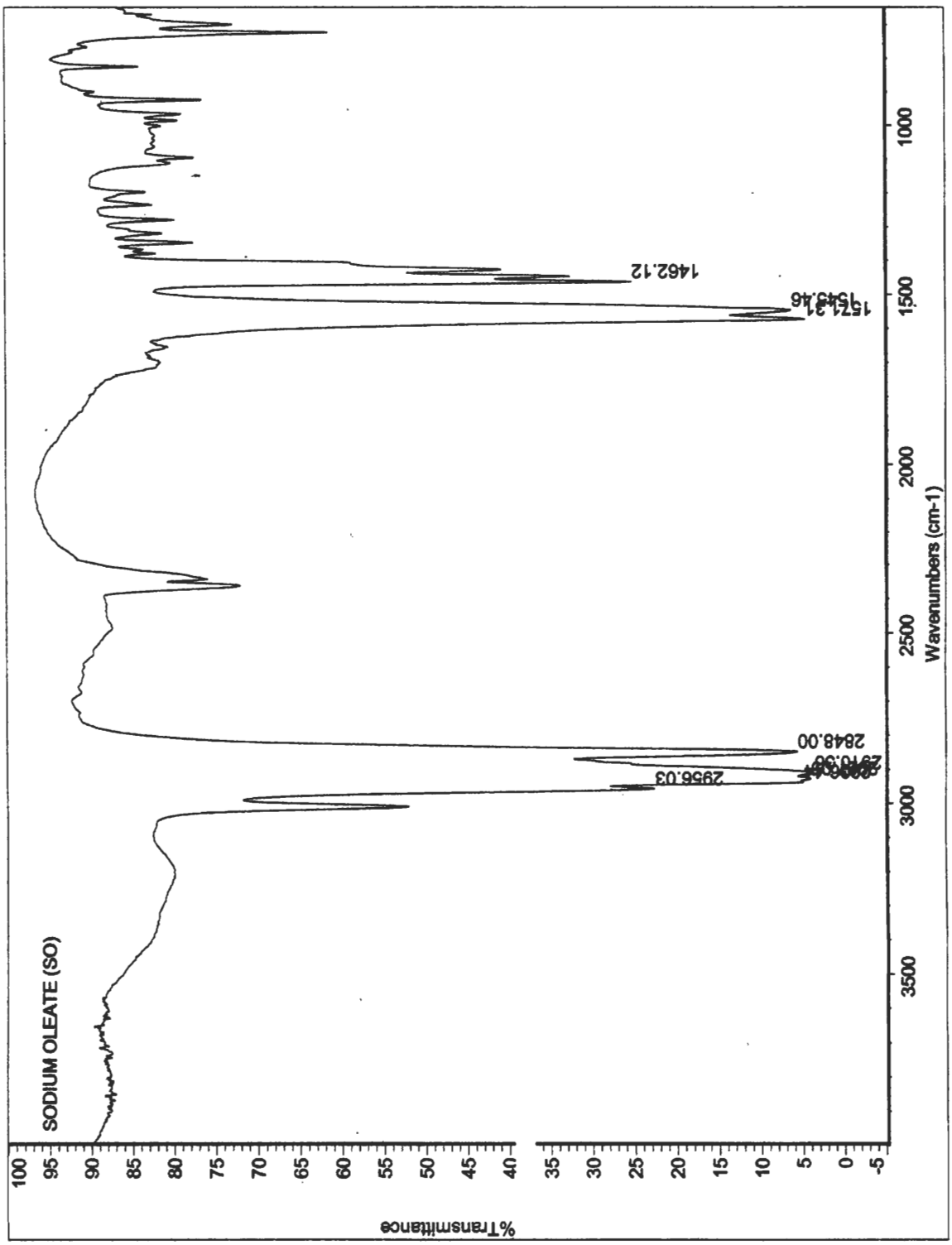
15. Appendix

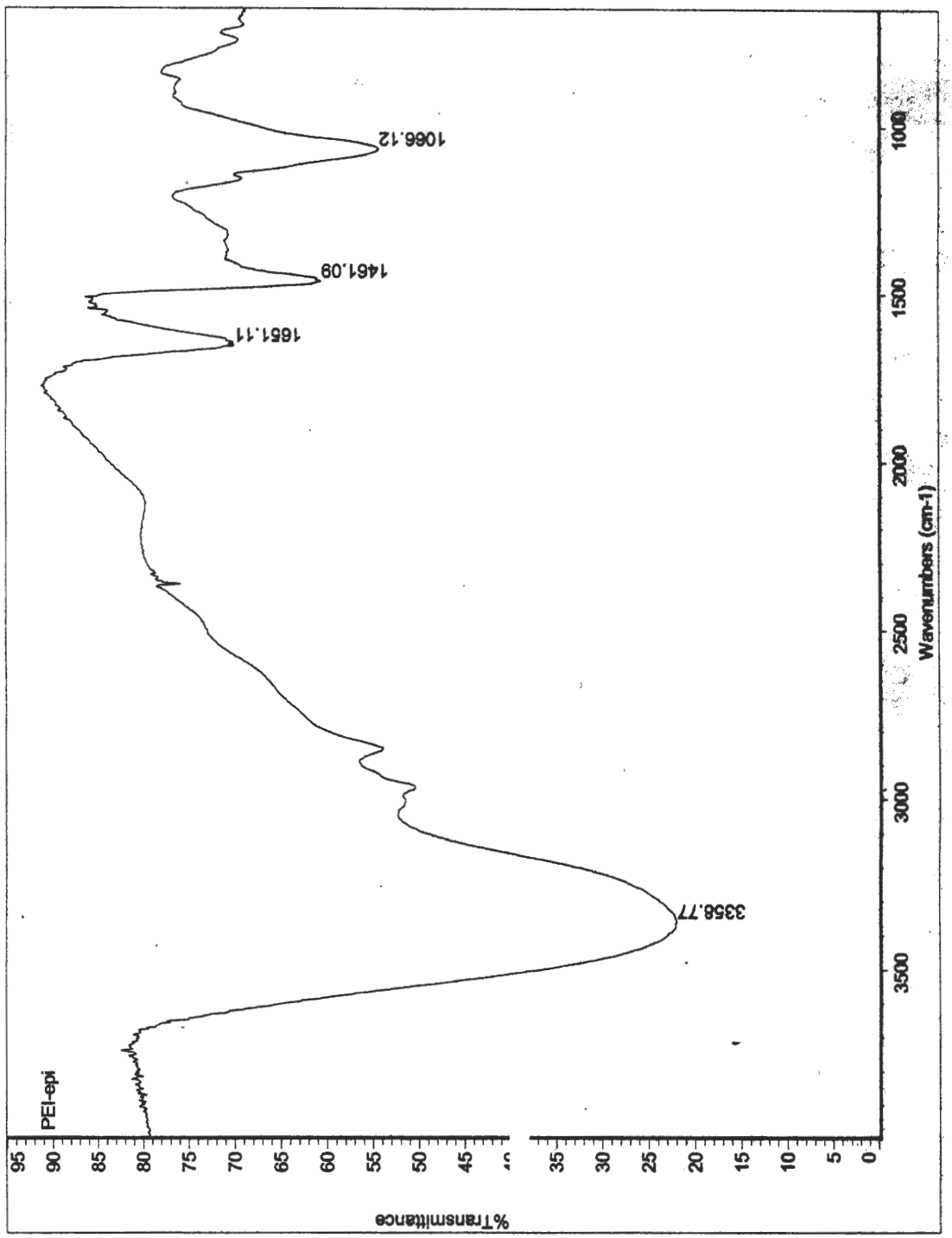
15.1. Appendix I – GC/MS Full By-product List

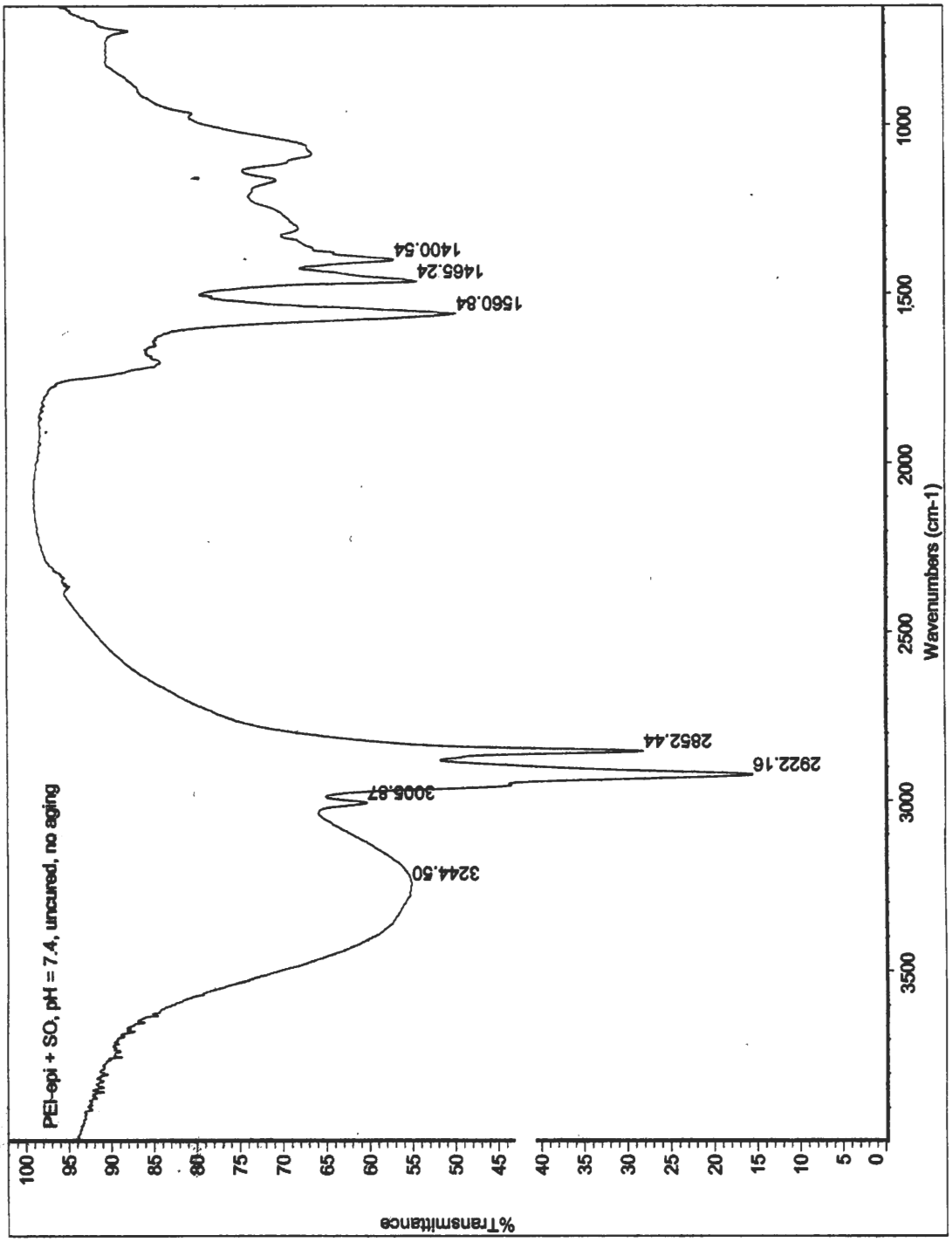
Decomposition Products	129-B	129-A adjusted
1,3-dichloro-2-propanol	**4,085,301**	**49,375,407**
Epi-chlorohydrin	**66,636**	**685,224**
1,2,2-Trichloropropane	N/d*	14,657
1,1,2-Trichloropropane	N/d	73,367
1,1,3-Trichloropropane	N/d	20,442
1,1,3-Trichloro-1-propene	N/d	112,352
1,3-dichloro-1-propene	N/d	251,359
2,3-dichloro-1-propene	N/d	11,112
Concentration (%)	2.64	adjusted to 2.64
MW	110,000	101,000
Charge Density (pH = 7.5)	15.28	12.65

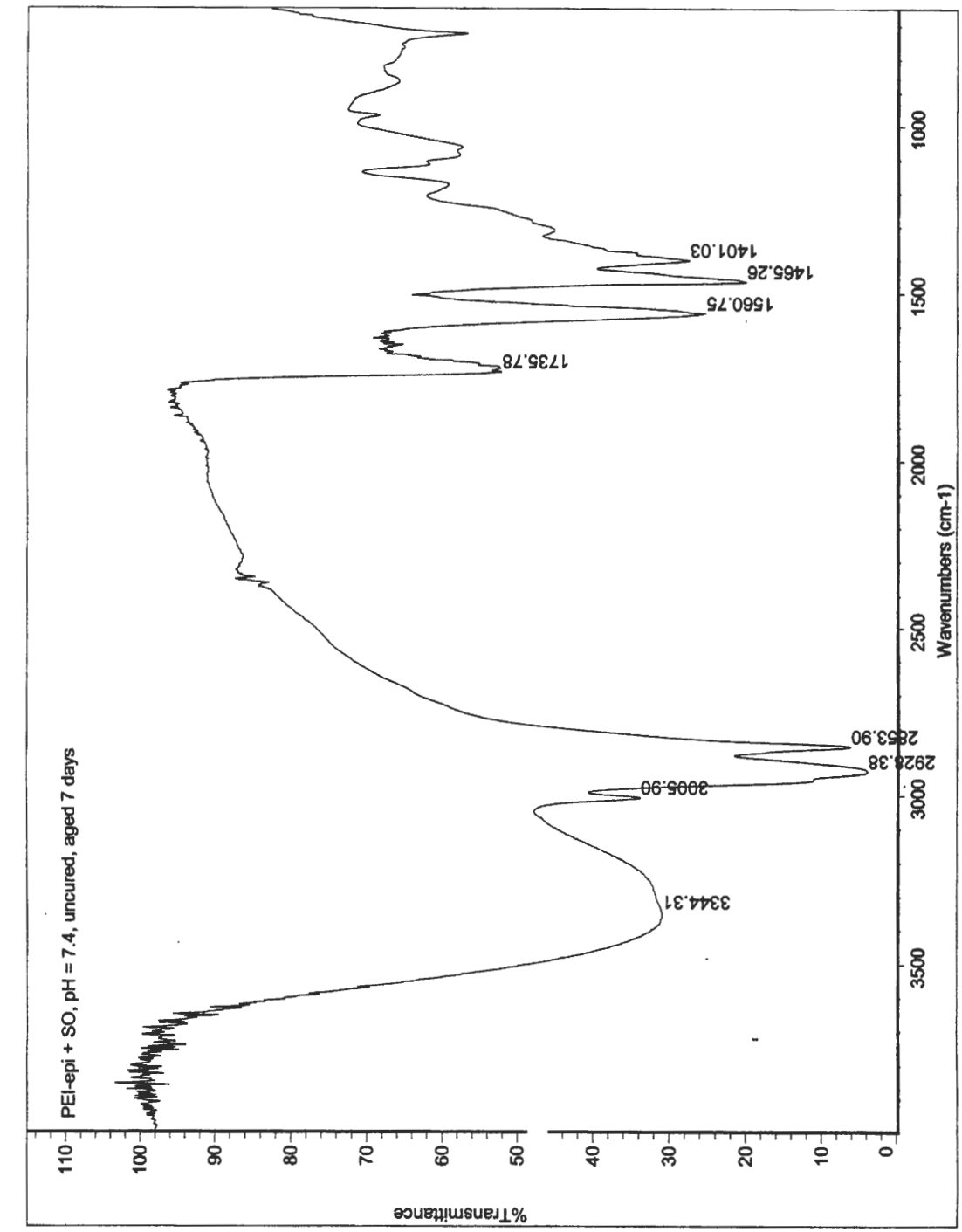
* not detectable

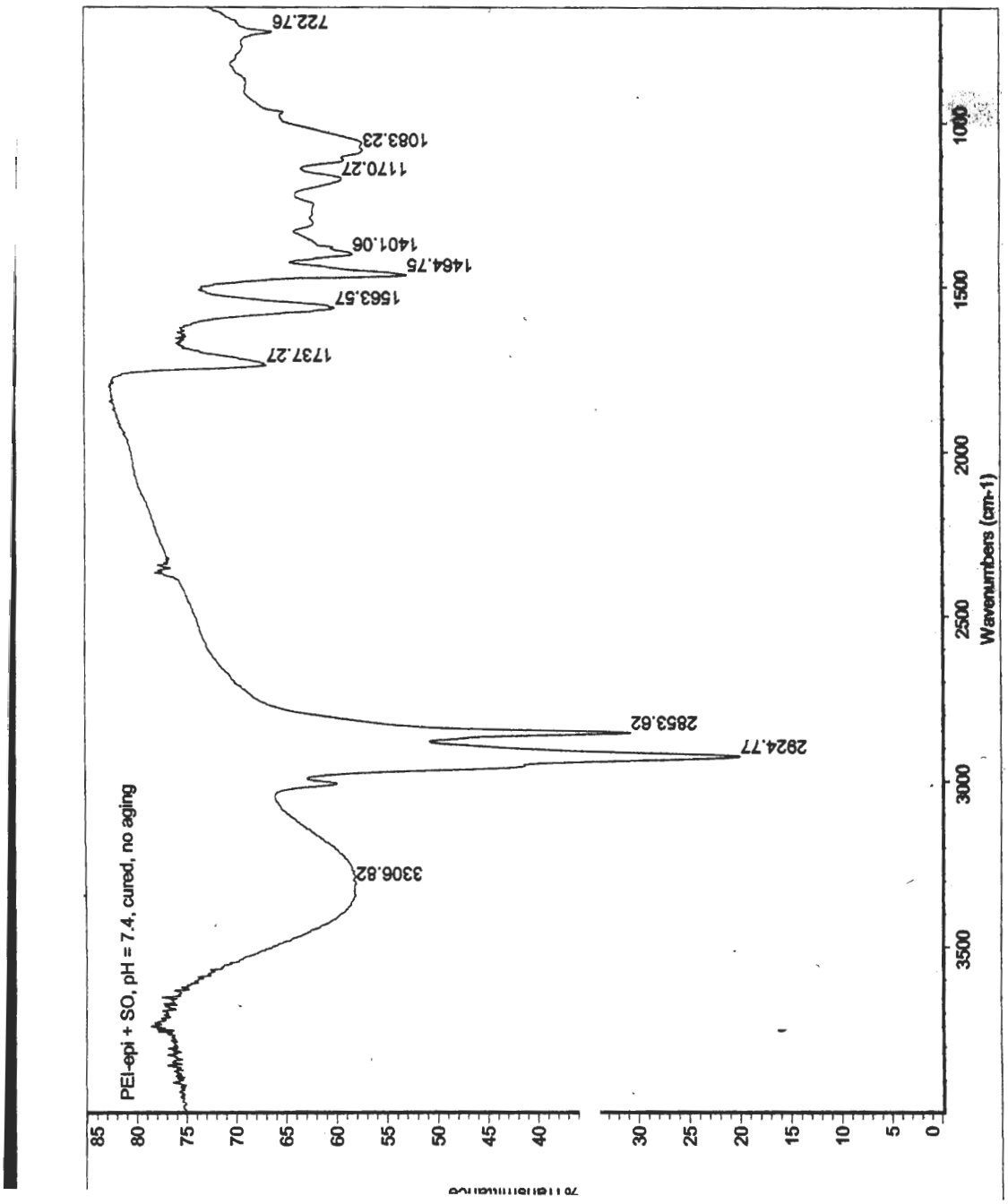
15.2. Appendix II – Full FTIR Spectra of Aging Study


SODIUM OLEATE (SO)
%Transmittance
Wavenumbers (cm-1)
2956.03
2848.00
1462.12
1543.46


PEI-epi
%Transmittance
Wavenumbers (cm-1)
3358.77
1651.11
1461.09
1066.12

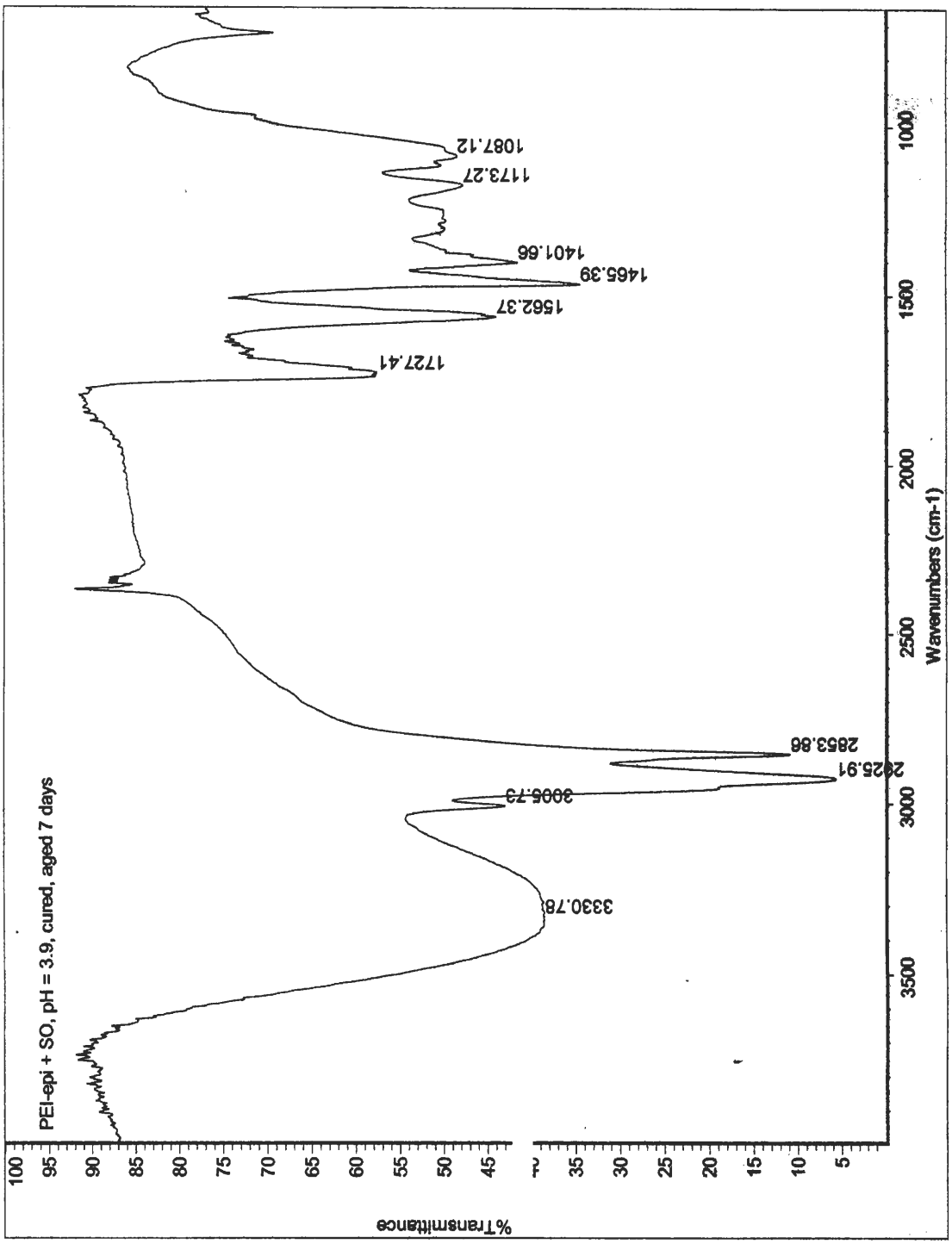

PEI-epi + SO, pH = 7.4, uncured, no aging
%Transmittance
Wavenumbers (cm-1)
3244.50
3006.87
2922.16
2852.44
1560.84
1465.24
1400.54

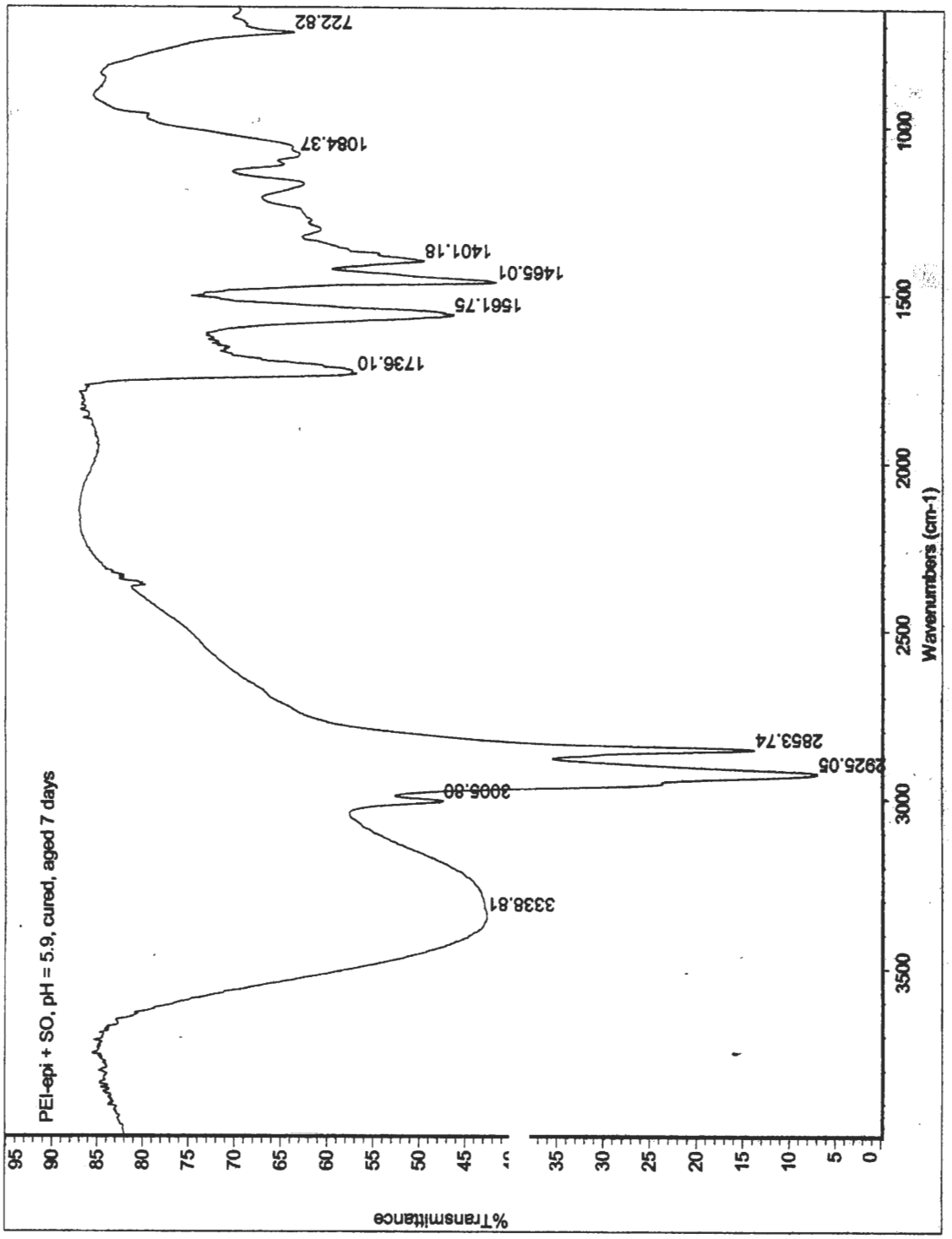

PEI-epi + SO, pH = 7.4, uncured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3344.31
3005.90
2928.38
2853.90
1735.78
1560.75
1465.26
1401.03

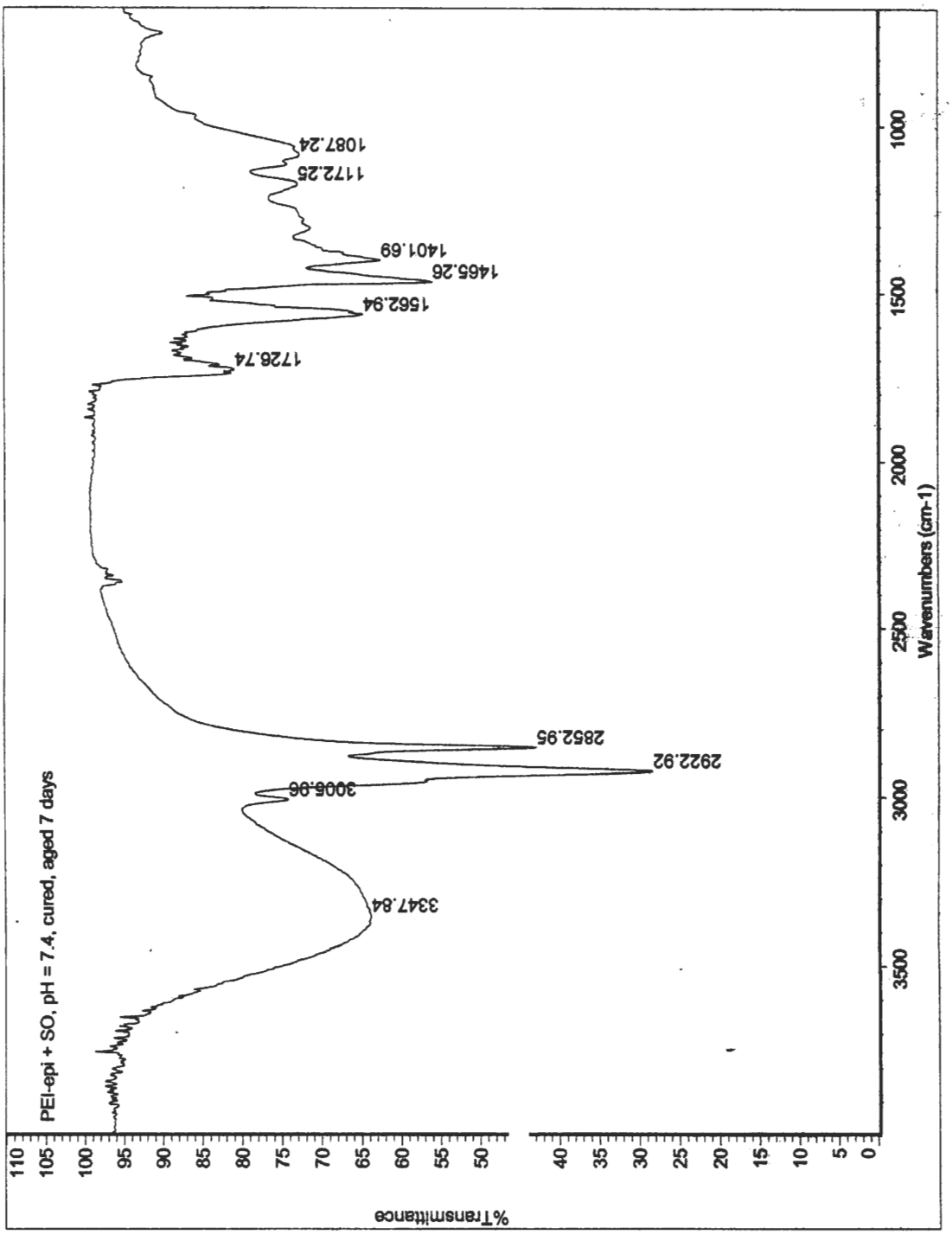

PEI-epi + SO, pH = 7.4, cured, no aging
3306.82
2924.77
2853.82
1737.27
1563.57
1464.75
1401.06
1170.27
1083.23
722.76
Wavenumbers (cm-1)

PEI-epi + SO, pH = 7.4, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3347.84
3006.96
2922.92
2852.95
1726.74
1562.94
1465.26
1401.69
1172.25
1087.24

15.3. Appendix III – Full FTIR Spectra of pH Study


PEI-epi + SO, pH = 3.9, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3330.78
3006.73
2925.91
2853.86
1727.41
1562.37
1465.39
1401.66
1173.27
1087.12


PEI-epi + SO, pH = 5.9, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3338.81
3005.80
2925.05
2853.74
1736.10
1561.75
1465.01
1401.18
1084.37
722.82

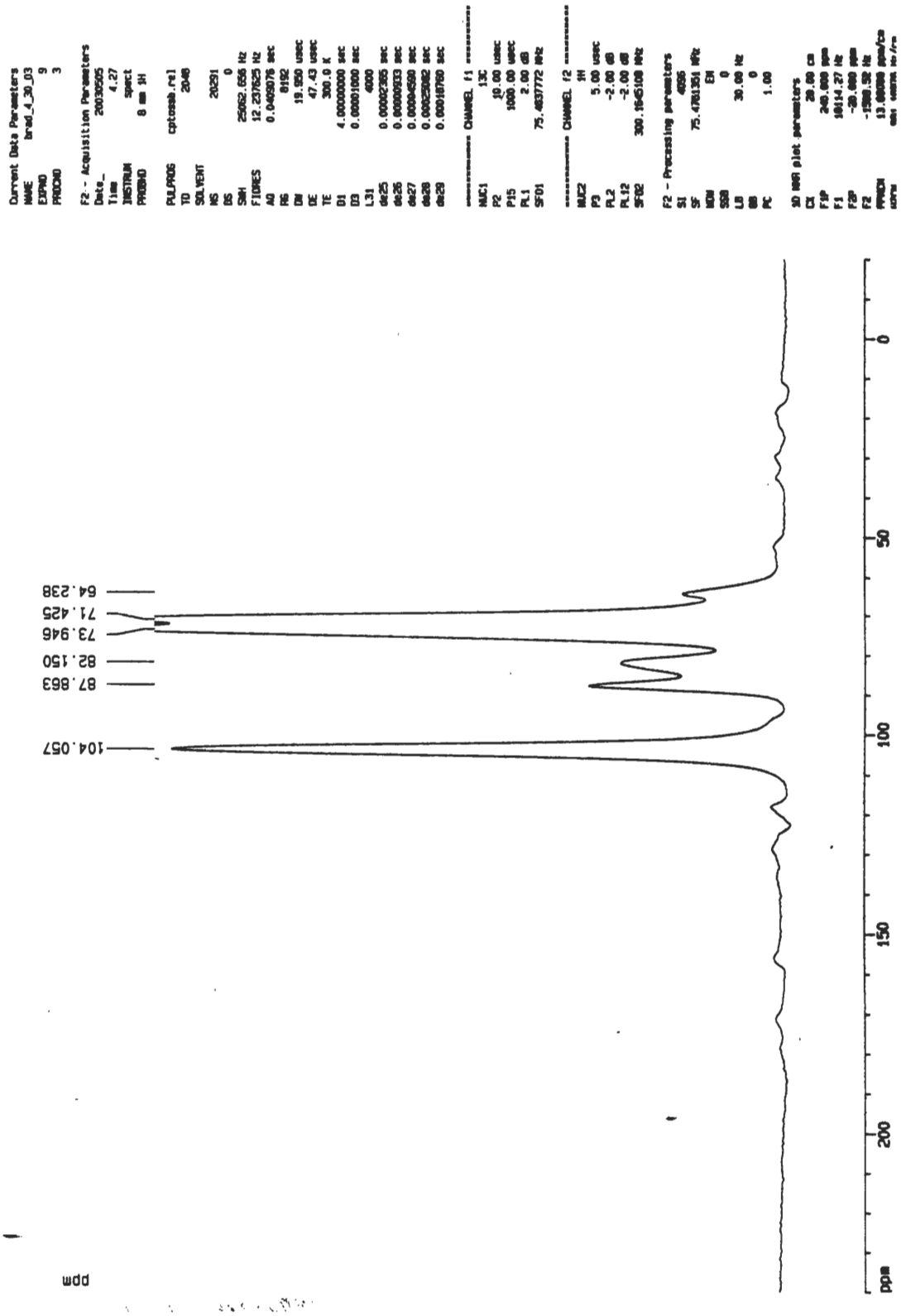

PEI-epi + SO, pH = 7.4, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3347.84
3005.96
2922.92
2852.95
1728.74
1562.94
1465.26
1401.69
1172.25
1087.24

PEI-epi + SO, pH = 8.0, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3281.92
3006.87
2925.02
2853.70
1735.76
1561.24
1465.15
1400.91
1085.79
722.21

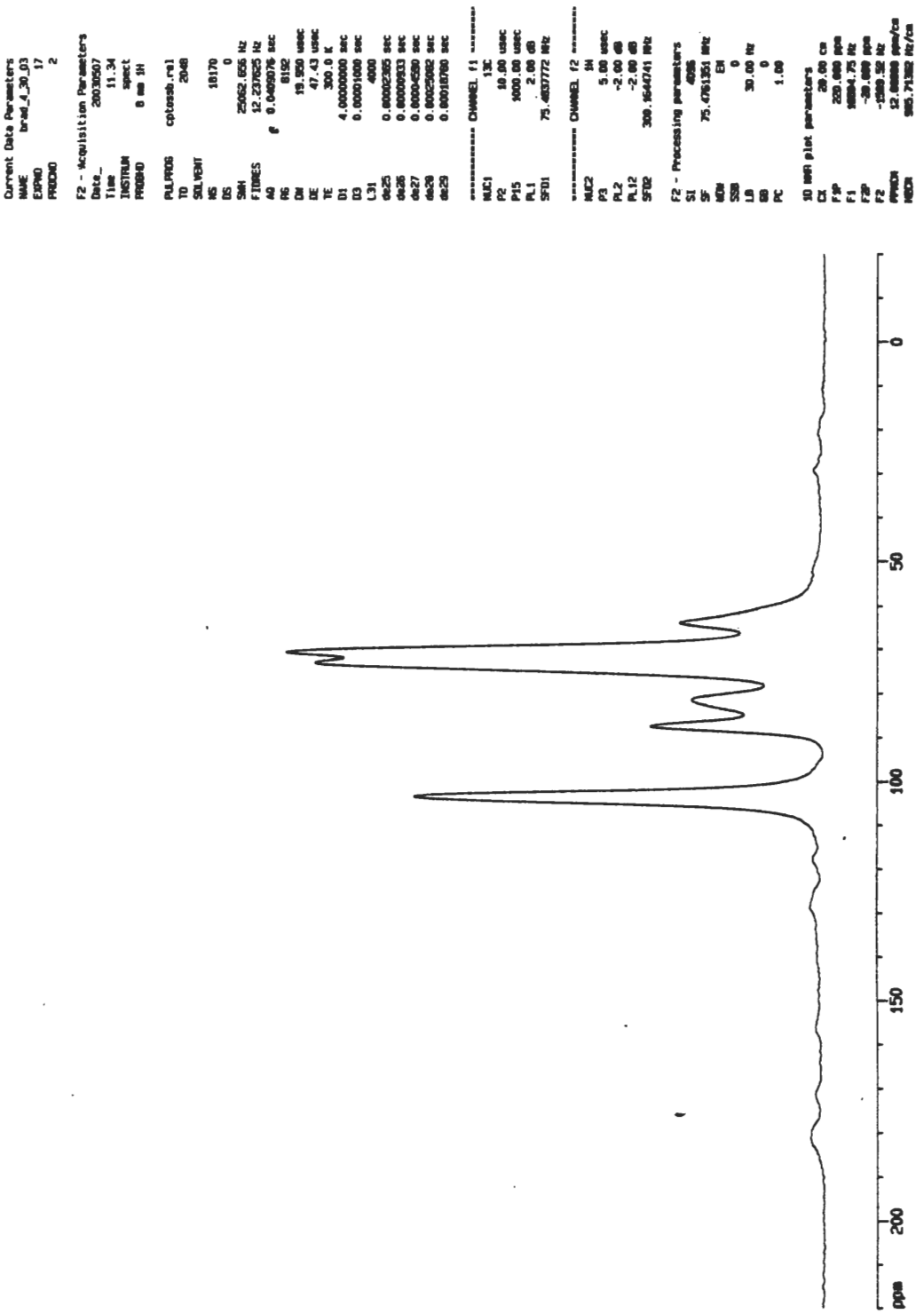
PEI-epi + SO, pH = 9.9, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
722.38
1400.87
1464.93
1560.96
1736.13
2853.94
2925.83
3005.87
3347.87

PEI-epi + SO, pH = 12.0, cured, aged 7 days
%Transmittance
Wavenumbers (cm-1)
3279.35
3005.83
2925.25
2853.76
1736.27
1561.01
1464.71
1400.44
1084.52
722.71

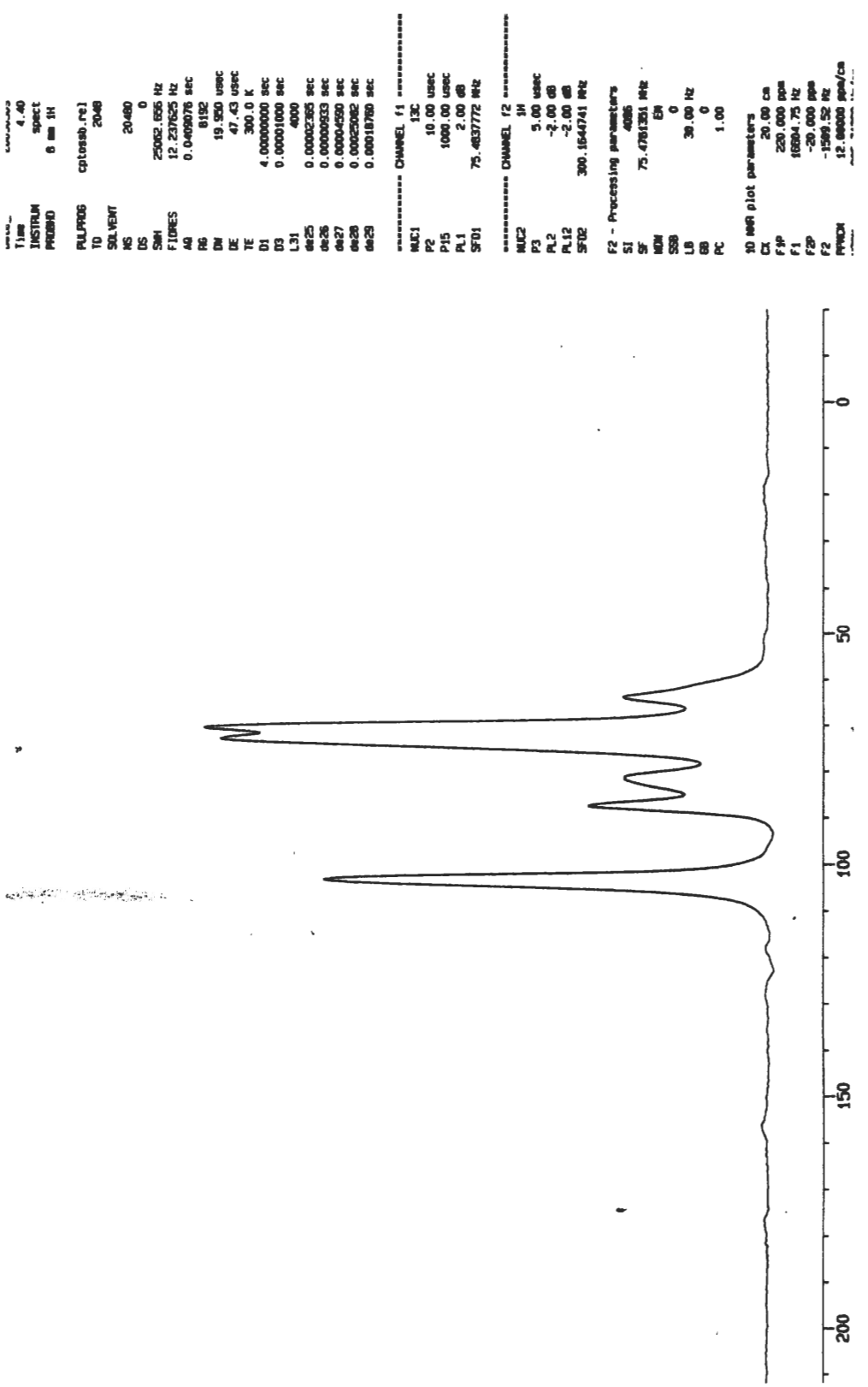
15.4. Appendix IV – Full Solid State NMR Spectra of Handsheet Study



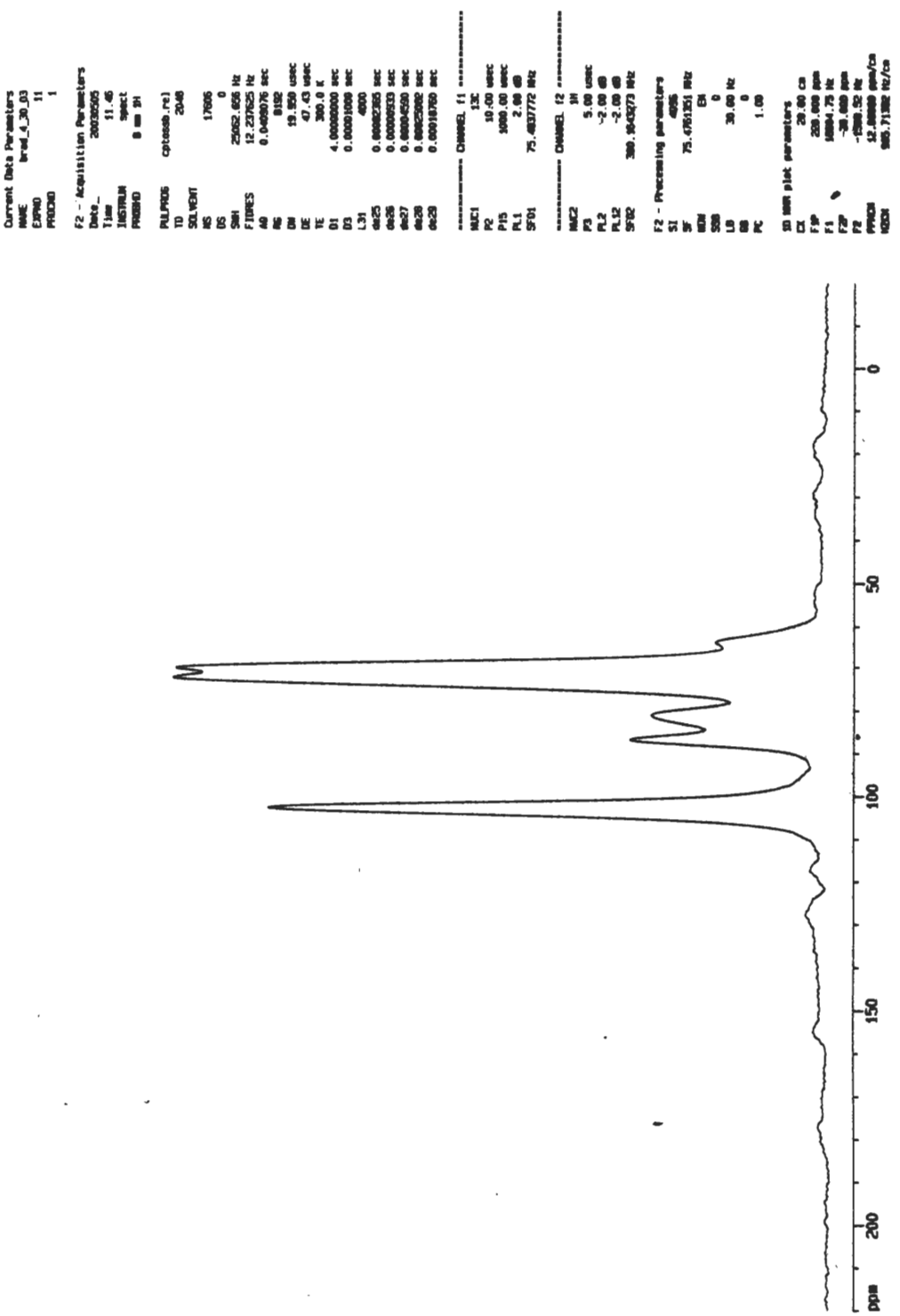
Sample 9a – PEI-epi 3 and Sodium Oleate



Sample 9b – PEI-epi 3 and Sodium Oleate after NaOH treatment



Sample 9c – cationic polyacrylamide (c-PAM) and Sodium Oleate



Sample 9d – PEI-epi 6 (crosslinked) and Sodium Oleate

Blank handsheet with no chemicals added