I hereby declare that this thesis contains no material, which has been accepted for the award of any other degree or diploma in any university. To the best of my knowledge and belief, it contains no material previously written or published by another person, except where due reference is made.

Signed: ______________________

Khairool Azizul Bin Mohammad

Date: 19/7/13

Abstract

Paper sheets made from different ratio of recycled fibre (RCF) and TMP fibre were examined. Poly(amideamine)epichorohydrin (PAE) resins with different concentration were added to pulp mixture in order to see the effects on the physical properties of the paper. Handsheets with 60g/m^2 basis weight were evaluated for its wet strength, dry strength, compression strength, zero span tensile strength and bending stiffness.

The study has found that handsheet from a high fraction of recycled fibre produced a higher apparent density of the sheet. The recycled fibre sheet also showed better strength properties due to the better bonding between the fibres. The wet pressing seemed to have no significant improvement in the strength of the sheets. It was also proved that PAE resin significantly increased strength for handsheets made from all type of pulp. The optimum addition level was 5mg/g.

The study was consistent with the TMP fibres being thicker and less flexible which therefore produced lower density sheet with higher bending resistance.

Table of Contents

Chapter 1. Introduction

1.1 Project Objective

Each paper grade used in a field needs certain strength to satisfy not only the end uses but also the converting operations. Papermakers have been making efforts to produce papers with greater strength to meet the increasing requirements of modern life. Packaging products with lower density but maintaining high strength and bending stiffness are favoured by most businesses in the market to provide excellent product protection during transportation, and also easy carrying with cheap shipping cost.

The typical packaging paper and printing/writing paper are considered to be well bonded sheets. Refining was introduced in order to achieve the paper properties as required by manufacturers. Due to the high cost, which is major concern of all papermakers, this process is limited. Besides that, the refining is too harsh treatment for recycled fibres, because the fibres will get damaged and shortened. Therefore strength agent, which has significant cost, was used as strength additive to the paper production.

Today the reason for recycling includes reduction of solid waste, reduction of air and water pollution, and preservation of forest, energy, and other natural resources. Because of the importance of paper recycling, many researchers have tried to identify the effects of recycling on the paper fibres, and on the paper made from these fibres. Recycled fibre is lower cost than virgin fibre but generally has inferior properties.

1.2 Project Scope

The investigations on producing paper from mixture of recycled fibre and TMP pulp are very necessary as the mechanical fibre could potentially be used to provide higher strength to packaging materials. On top of that, the strength agent needs to be used in order to produce stronger packaging products that satisfy the market needs.

In this study, the investigation is focused on the paper properties of different ratios of recycled and TMP fibres. The reason for using the recycled fibres includes reduction of solid waste, reduction of air and water pollution, and preservation of forest, energy, and other natural resources.

In addition, the experiment uses different concentration of poly(amideamine)epichlorophydrin (PAE) as resin, which are able to improve the paper strength to meet higher requirement for structural materials. The reason for investigating on the addition of PAE is due to the fact that both TMP and recycled fibres have problems in poor mechanical properties. Results are evaluated and tested following Australian and New Zealand Standards.

Chapter 2. Literature Review

2.1 Mechanical Pulp

Mechanical pulp is produced from wood by mechanical defibration and no chemicals are used in the process. There are varieties of processes such as Stone Groundwood (SGW), Pressure Groundwood (PGW), Refiner Mechanical Pulp (RMP), and Thermomechanical Pulp (TMP). In general, the lignin is retained in the pulp and as a result it produces the highest yield of pulp from the wood. The total yield ranges from 90 to 98%. High yield, high bulk, low cost and high stiffness are the main characteristics of the mechanical pulp. In the mechanical pulping process, lignin is plasticized and remains in the pulp during mechanical defibration. This will result to higher light-scattering coefficient and opacity but lower strength properties compared to chemical pulp. Due to the preserving of the lignin, it leads to a poorer and less stable brightness level. Yellowing will take place if pulp is exposed to air and light. (Biermann, 1996; Herbert, 2006).

Mechanical pulps are generally used for the production of mechanical printing papers. The printing paper produced should have good opacity and printability at low basis weight, but only a limited strength and durability, and in addition should be reasonably cheap. Newsprint, uncoated (SC) and coated (LWC) magazine papers are the main grades of the mechanical printing paper. Other applications for mechanical pulps are various board grades, wallpaper, fine papers, soft tissue, and absorbent and molded products (Sundholm, 1999).

2.2 Thermomechanical pulp (TMP)

Thermomechanical pulp (TMP) has become the main source of fibres for the highest speed newsprint machines. It is made by heating the chips with steam and mechanically separating the fibres in a pressurized refiner. Figure 2-1 shows a typical flow diagram for a TMP plant.

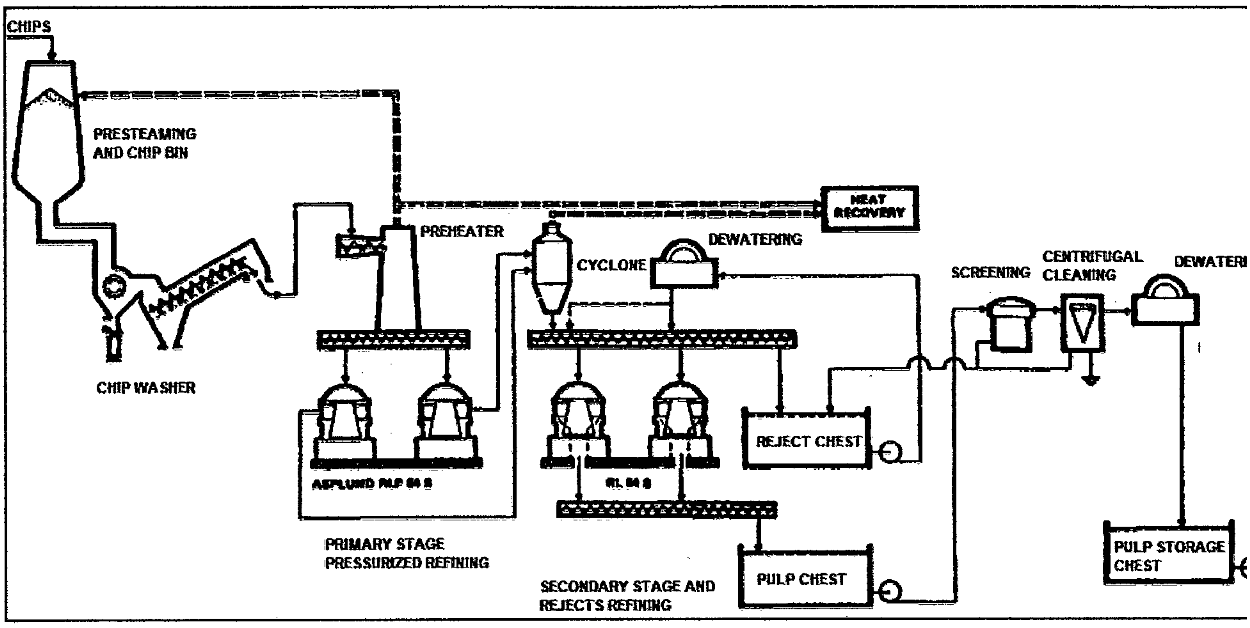

Figure 2-1. Representative layout of a newsprint TMP plant. (Biermann, 1996)

There are normally two stages of refining in thermomechanical pulping. In the first stage, the refiners are at higher temperature and pressure to support fibre liberation; in the second stage, the refiners are at ambient temperature to prepare the fibres for papermaking. The higher temperature during refining in the first step, 110-130°C, will make the fibres soft and will process the fibres with minimal cutting and fines compared to SGW or even RMP. In order to make sure the fibres separation is at the S-1 cell wall layer (Figure 2-2), the refining occurs just under the glass transition temperature of lignin, which is approximately 140°C.

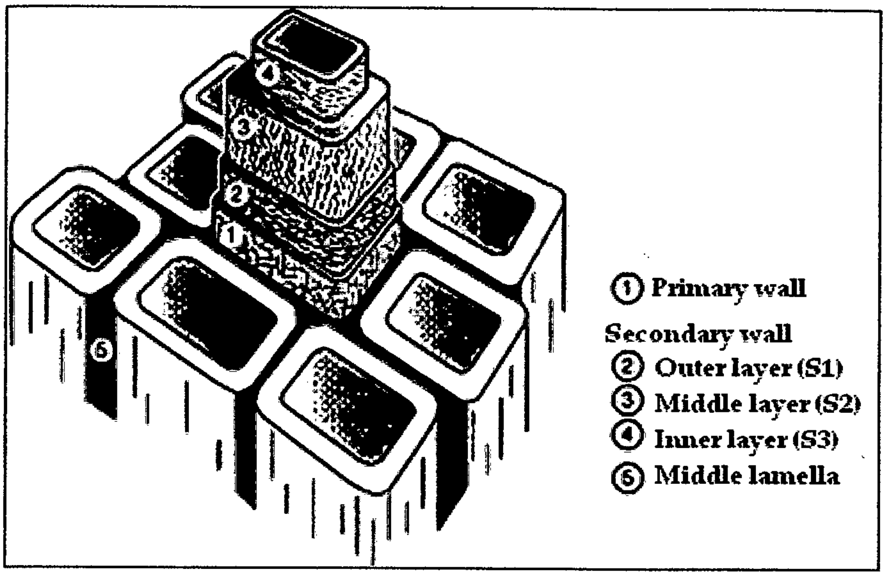

Figure 2-2. The anatomy of wood cell.

The most important character of this pulp compared to the other mechanical pulps is the relative higher strength (Biermann, 1996).

In mechanical pulping, softwoods are the major fibre source used because of their capability to fibrillate on refining. Hardwoods do not to fibrillate well and break down easily to short rigid debris (Fengel & Wegener, 1984). Mechanical pulp fibre is very similar to natural wood fibre. The hemicellulose in this type of pulp is not chemically altered. Because the hemicellulose is hydrophilic, the TMP fibres can swell easily. The high concentration of lignin remaining in the fibre does to some extent limit its swelling capability. This is generally compensated for by refining which introduces both internal and external fibrillation to the cell wall. Internal fibrillation creates pores which allow water to penetrate the cell wall structure, debonding and separating microfibrils (Laine, Hynynen, & Stenius, 1997).

2.3 Recycled Fibre

2.3.1 Introduction

Recycled paper product means any paper or paperboard product that contains wastepaper. Wastepaper can be pre-consumer and post-consumer waste materials. Pre-consumer waste is the waste from manufacturing, forest residues and other production activities including dry paper and paperboard waste generated after completion of the paper making process. Post-consumer waste is any waste material that has passed through its intended end usage including paper, paperboard and fibrous wastes from retail stores, office buildings, homes and other places (Jolley, 1990).

Traditionally, recycling was practiced because of advantage of the relatively low cost of recycled fibres. Today the reason for recycling includes reduction of solid waste, reduction of air and water pollution, and preservation of forest, energy, and other natural resources. Because of the importance of paper recycling, many researchers have tried to identify the effects of recycling on the paper fibres, and on the paper made from these fibres.

Pulp selection, degree of refining, wet-pressing pressures, and drying conditions of the previous papermaking cycle as well as those of the present cycle are parameters which can affect the mechanical properties of the recycled sheet. Changing of these parameters could also affect sheet properties (Wuu, 1993).

It has been generally observed that the use of recycled fibres in papermaking results in lower mechanical properties. This apparent deficiency of recycled fibre can be overcome by refining or the addition of a few chemicals to the papermaking process (Ellis and Sedlachek 1993).

2.3.2 Recycling Process

The nature of the operation for recycling paper varies from mill to mill and depends on the product being produced and the material source. The recycling process can either be brown grade recycle plants or deinking plants. In deinking, flotation deinking process and probably a bleaching operation are added. A recycle or deinking plant is, basically, a pulping process followed by several separation operations. Figure 2-3 below shows the basic steps in recycling process. Various contaminants such as baling wire, tape, plastic film, beer cans, pieces of glass, metal objects, sand, Styrofoam, wood chunks in the flow are removed via separation processes(Hutten, 1996).

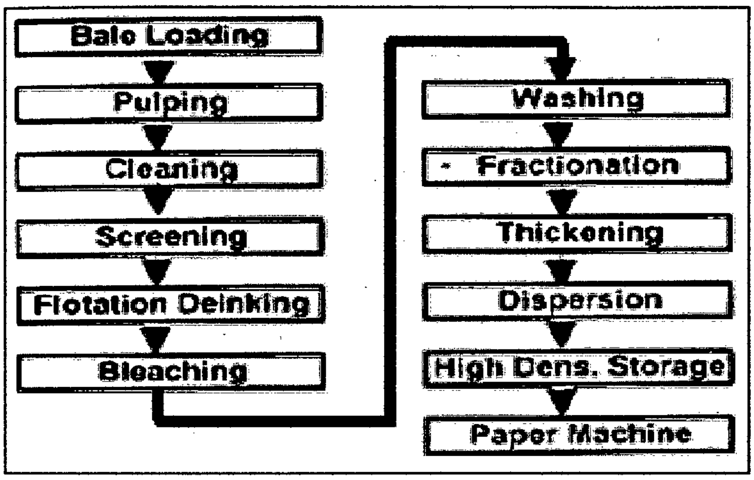

Figure 2-3. The operations in a deinking/recycle process. Picture from (Hutten, 1996)

The recycled papers are turned to pulp in a pulper, which contains water and chemicals. The pulp is screened in order to remove small contaminants such as bits of plastic and globs of glue. Heavy contaminants like staples are removed in cleaning process using large cone-shaped cylinders.

Deinking process is necessary to get rid of printing ink and stickies. In this operation, small particles of ink are rinsed from the pulp with water in washing process and larger particles and stickies are removed with air bubbles in another process called flotation.

The pulp is beaten in refining process to increase the fibre contact area, increase fibre flexibility through delamination and swelling, promotes interfibre bonding, therefore, increases bond strength (Vainio & Paulapuro, 2007). Sometimes refining will be included in the recycling process but many times it will not be as fibres are too fragile. This has been a trend recently as each fibre has been recycled more times on average. The pulp will go through a bleaching process if white recycled paper is being produced; otherwise for the production of brown recycled paper such as that used for packaging, the bleaching process is not necessary.

The clean pulp is then converted into paper in paper machine. The recycled fibre can be used alone, or blended with virgin fibre to give an extra strength or smoothness(TAPPI, 2001).

2.3.3 Main Problems With Recycled Fibre

There are two major problem faced by the paper and paperboard recycling industry since 1970. The main problem is the loss of the strength due to a reduced fibre bonding. Hornification and the loss of the swelling ability of recycled fibres are the factors of this weaken bonding. The other problem is that shortened fibres and excess fines can reduce drainage rate, decreasing the water removal ability. In the forming, wet pressing and drying sections, water removal ability is reduced due to accumulation of fines in the white water. This will lead to a low runnability on the paper machine (Zhang, Peterson, & Qi, 2000).

2.3.4 Influence of Recovered Fibre on Handsheet Strength Properties

Two main factors that contribute to the tensile strength of paper are interfibre bonding ability and intrinsic fibre strength (Cao, Tschirner, & Ramaswamy, 1999). Lower bulk increases the bonded area between fibre and leads to a higher strength sheet (Bown, 1985; Minor & Atalla, 1993). Accordingly, one would expect that increasing recovered fibre content would result in a stronger paper because of the increasing compaction of the sheet. Also it is known that the bonding strength decreases with recycling.

However, it is also well known that lower intrinsic fibre strength will lead to a decrease in paper strength (Cao, et al., 1999). The damage to the fibres may well be responsible for the lower tensile index with increased recovered fibre content.

Recycled fibre can reduce the bulk of the paper due to long fibre fraction. The decreased bulk and increased compactness of the sheet with higher recovered fibre concentration can in this situation be attributed to the higher ash content and the abundance of collapsed and vertically split fibres present in the recovered fibre (Chatterjee, Roy, & Whiting, 1992).

Ash affects the strength of the paper in two ways. First, as ash increases, it will substitute for fibre and thus less fibre is available to carry the tensile load. Secondly, the ash interrupts the fibre-to-fibre bonding, which leads to the reduction of relative bond area in the paper (Bown 1985). Figure 2-4 shows the relationship between ash content and tensile index of sheets from recycled fibre.

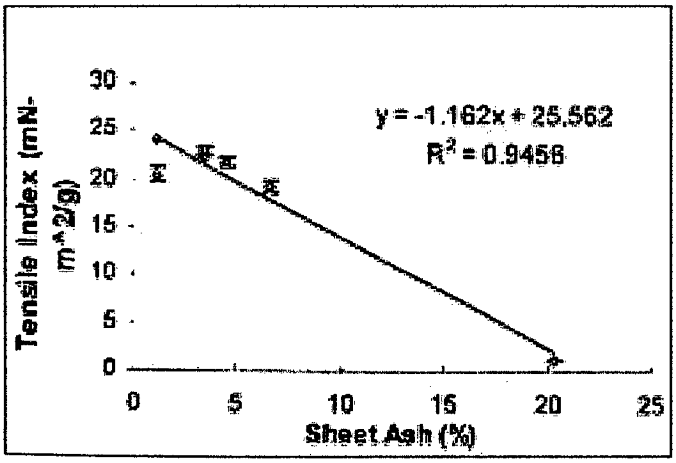

Figure 2-4. Strong relationship between the tensile index of the handsheets and the amount of ash they contain. Taken from (Krigstin & Sain, 2006).

The decrease in tensile strength can also caused by high curl of the recovered fibre. This is due to the fibres basically being curled out of the plane in which the tensile test is taking place. High curl decreases the effective fibre length and therefore more stresses react on the interfibre bonds which opposed to the fibre. On the other hand, curl has a positive outcome for tear strength (Page, Seth et al. 1985).

Another important paper characteristic is tear strength which is affected by fibre length and fibre strength (Minor and Atalla 1993). The recovered fibre offers the benefit of a longer average fibre length (over the TMP fibre), resulting in the higher tear strength.

Some workers have suggested that wet zero-span tensile strength is more truly indicative of fibre strength than dry zero-span strength since fibre bonding effects are eliminated (W. Cowan, 1990). As can be seen in Figure 2-5, the zero-span tensile strength of handsheets made from the unbeaten fibres was gradually increased continuously by the recycling treatment. This is due to reorientation and alignment of the microfibrils and therefore, once-dried fibres with their tightly packed cell walls could be stiffer and more brittle, even in water, than never-dried ones (Khantayanuwong, 2002).

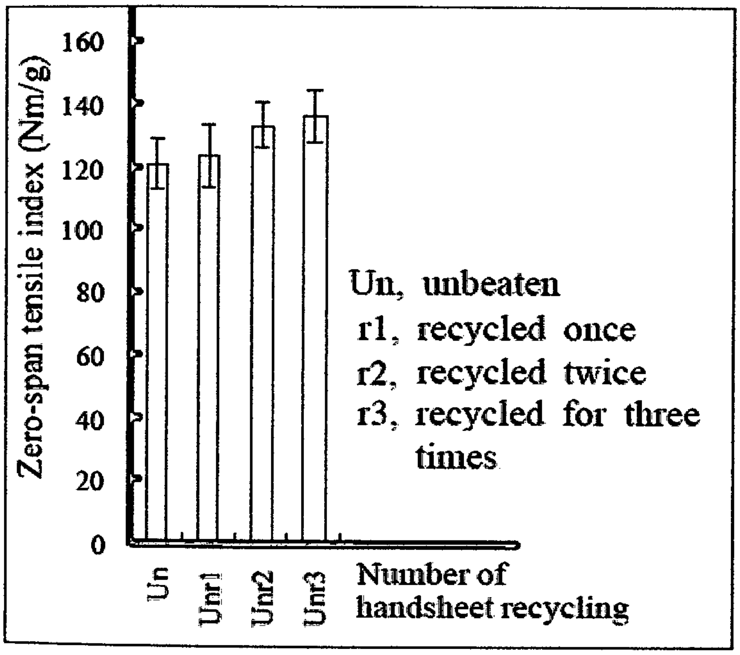

Figure 2-5. Changes in dry zero-span tensile indices of handsheets by recycling treatment. Fibre is from a virgin hardwood bleached kraft pulp (HBKP).Taken from (Khantayanuwong, 2002)

The recycling process increases the strength of mechanical pulps. For all type of mechanical pulp, recycling increases tensile strength and density of sheets. This is due to an increased level of bonding in these recycled handsheets. The increased bonding is because the fibres are flattening and becoming progressively more flexible during successive sheetmaking, pressing and drying cycles (Howard & Bichard, 1992).

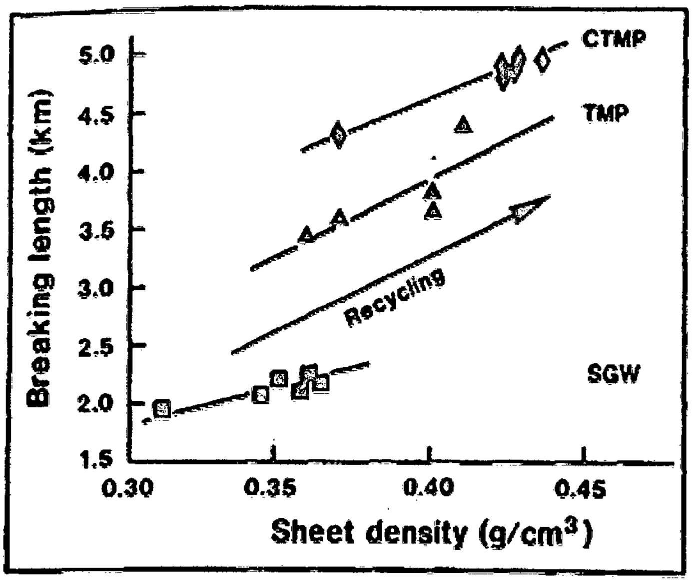

Figure 2-6. The relationship between sheet density and tensile strength during the recycling of mechanical pulps. Arrow indicates increasing number of cycles. Taken from (Howard & Bichard, 1992).The breaking length in meters is numerically equal to 102 times tensile index in newton meters per gram (Tappi Method *T 494 om-01*)

2.3.5 Recover the lost property potential of recycled pulps

There are many ways to restore the properties lost (fibre strength) when pulps are recycled. Amongst them are(Howard, 1990);

a. Beating or refining

b. Chemical treatment

c. Blending with virgin pulp

d. Fractionation

High shear field refining (HSR) and or alkali treatment are the two techniques to increase the strength of recycled fibre (Bhat, Heitmann, & Joyce, 1991). From that research, a combination of alkali treatment followed by HSR was found to be most effective to such an extent that the performance of the secondary fibre was comparable to the virgin pulp.

Other researchers investigated the use of acetylation to reverse the effects of recycling. It was found that acetylation resulted in swelling and strength properties being comparable with those obtained using a never dried pulp (Ehrnrooth, Htun, & de Ruvo, 1977).

Conclusion here is that HSR and acetylation are not in commercial use. The four methods from Howard are used to some degree.

2.4 The Development Of Paper Strength With Polyamideamine-Epichlorohydrin (PAE)

Wet strength becomes the most essential property of paper for structural applications and many specific end-uses such as tissue paper, paper towel, and paperboard for packaging and similar grades. The chemistry, mechanisms of action, and applications of commercial wet strength resins have been extensively reviewed by many researchers (Roberts, 1996; Scott, 1996).

Polyamideamineepichlorohydrin (PAE) resin, developed in the 1950s, has been used widely and regarded as one of the most commercially important wet-strength chemicals. PAE is formaldehyde-free and can work in a neutral pH papermaking environment. It also provides higher level of wet strength than the early technology using ureaformaldehyde and melamine-formaldehyde resins. Importantly, PAE polymers can provide both homo-crosslink with itself and hetero-crosslink with cellulose to enhance the wet strength of paper (Crisp &Riehle, 2009).

The primary mechanism of PAE is the self-crosslinking of the resin (Xu, 2001). Some researchers suggested that azetidinium (defined below) of the resins can react with carboxylate groups of hemicellulose, though not with hydroxyl groups of cellulose (Dulany, 1989).

PAE establishes chemical bonds at fibre-fibre contacts in two steps: retention of the polymer and development of bonds. The efficiency of reaction of PAE is based on azetidinium concentration, the type of fibres, and the drying conditions (Obokata & Isogai, 2004; Saito & Isogai, 2005). The retention of PAE resin increases with increasing carboxylate content of the fibre. Pulping and bleaching process will decide the level of carboxlyate content in the fibre. Generally the pulps that contain the highest carboxylate levels and are the most responsive to PAE resins are unbleached Kraft pulps (UBK) followed by bleached hardwood Kraft pulps, bleached softwood pulps, recycled secondary fibre and then sulphite pulps (Crisp & Riehle, 2009).

After PAE adhesion to cellulosic fibres, this resin network restricts the re-hydration and swelling of the fibres. The network also acts to protect the hydrogen bonds in the fibre-to-fibre contact area. The curing process facilitates the formation of bonds between fibres. These chemical bonds will remain even after the water has disrupted all the naturally occurring hydrogen bonds (Devore & Fischer, 1993).

The mechanism of action of the PAE resin is classified into two categories:

(1) the preservation mechanism, in which the self-cross-linking of the resin within the cellulose or surrounding the fibre-fibre contacts, reducing cellulose fibre swelling and holding the fibres with hydrogen-bonding distance; and

(2) the reinforcement mechanism, in which the covalent linking of cellulose to cellulose is achieved through a resin molecule or the resin network (Espy & Rave, 1988)].

The two mechanisms are shown in figure 2-7 and 2-8 below.

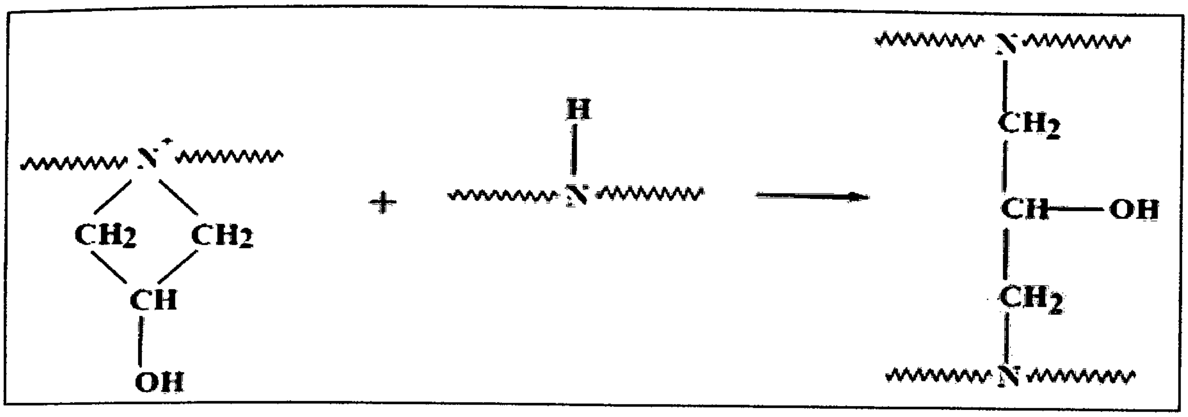

Figure 2-7. The azetidinium group in the wet strength resin reacts with residual amines to form cross links and increase the resin's molecular weight. Taken from (Liu, 2004)

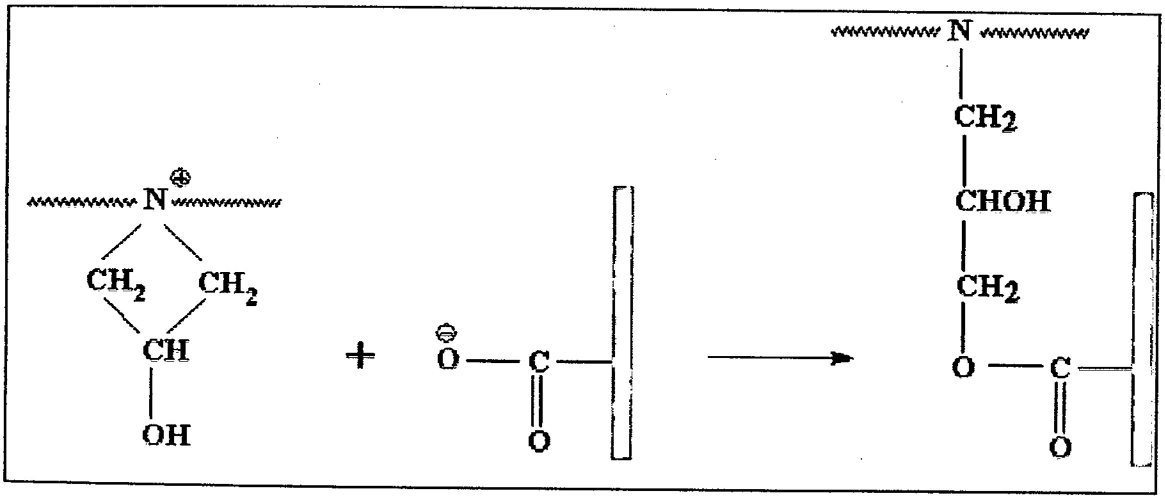

Figure 2-8. Wet strength resin molecule reacts with the carboxyl group of cellulose surface. Taken from (Liu, 2004).

PAE is used to boost the strength of paper sheets. In order to give a high bending resistance of paper, the sheets should have a lower density. But a low density sheets result in low strength. Therefore perhaps by addition of PAE can increase the strength of paper.

Chapter 3. Experimental

3.1 Materials

1) Pulp/Paper.

Two types of pulps are used in this study. One is reject radiata pine TMP pulp (21.7 % solids and 2.09% shive content) taken from the feed stream to the reject refiners. It contains mainly (70%) long fibres, intermediates (20%) and a small amount of fines (10%). The product typically consists of large, coarse and open fibres. This pulp is known as the whole TMP pulp in this study.

The second type of pulp is recycled pulp from VISY, which was in roll form and stored dry. This pulp is believed to have no chemical additive and no starch on it.

2) PAE

The cationic Nopcobond 1213 (33.5%) wet strength agent under the class of PAE resins was used. 5 addition level of PAE resin in pulp slurries are used: 0 mg/g, 2mg/g, 5 mg/g, 10 mg/g, and 20 mg/g (Sample calculation is shown in Appendix section).

3)Water

Deionised water was used in sheets preparation.

3.2 Pulp Preparation

Recycled paper from VISY was cut into small pieces and soaked in water overnight. The wet pieces were then disintegrated using standard pulp disintegrator for 30,000 revolutions in order to turn it into pulp fibre.

TMP pulp, which stored in refrigerator, was disintegrated at 30,000 revolutions to produce pulp slurry with uniform consistency (about 7%). Consistency is the term used to describe solid content of pulp during pulp processing. For pulp and paper maker this is the most important process parameters. The method to calculate pulp consistency is shown in Appendix 1.

Pulps were prepared in several different ratios between TMP pulp and recycled pulp. Before mixing, the moisture content of each slurry (i.e recycled fibre and TMP) was measured in order to get the right ratio of mixture. Four different ratios of recycled fibre (RCF) to TMP were prepared; (100:0), (60:40), (20:80) and (0:100).

3.3 Making Handsheets

Round handsheets 15.9cm (6.25 in.) in diameter are made according to TAPPI Standard T 205. This handsheet former is called a *British sheet mold.* Pulp with 0.2% consistency was prepared and 1.21g of dry weight pulp was used for each handsheet in order to achieve a grammage of 60 g/m^2. Prior to sheet making, PAE solutions were prepared at five addition levels, 0 mg/g, 2mg/g, 5 mg/g, 10 mg/g, and 20 mg/g. New PAE was prepared for each batch so that there was no time delay in PAE preparation. After PAE was added to 0.2% consistency pulp and thoroughly stirred, solution was poured into the handsheet former. The designated stirrer was used to mix the suspension before water was drained. Blotting paper (200 g/m^2) was laid on the formed sheet and rolled by couch roller. Handsheet was removed from the mesh and then pressed with the blotting paper for 5 minutes in first press and another 2 minutes in the second. Three pressing pressures were used: 0 bar (unpressed), 3.75 bar and 5.6 bar. For combination of furnish, pressing pressure and PAE addition rate, eight handsheets were made. All handsheets were cured once in Semmar auto drum dryer at 95 °C for about 5 minutes each, then placed in handsheet holders and stored in the conditioned room (23°C ±0.15°C and relative humidity of 50% ±2%) ready for testing.

3.4 Experimental Methods

All testing were conducted following AS/NZ 1301.415S:2008, Standard atmosphere for testing paper and procedure for monitoring the atmosphere.

3.4.1 Conditioned Grammage

The tested handsheets were prepared and conditioned in accordance with AS/NZS 1301.203s and AS/NZS 1301.415s as to obtain accurate and reproducible results. The conditioned grammage, in g/m^2, of the selected handsheets was also used for the calculation of each tensile strength and tensile index.

Each test piece was made at total area of 201 cm^2 and weighed using an analytical laboratory balance. All results were obtained to the nearest 0.001 g. By following AS/NS1301.208s, the conditioned grammage for each test piece was calculated from the relationship:

$$G_c = \frac{10000\,m}{A}$$

Where

G_c = the conditioned grammage in g/m^2

m = the total mass of the conditioned test pieces in g

A = the total area of the test pieces in cm^2

3.4.2 Single Sheet Thickness and Apparent Sheet Density

Under AS/NZS 1301.426s, the thickness testing for each tested handsheet was conducted using a micrometer. The micrometer was from Messmer, model 171 with serial no. 33004. All tests were done in the standard atmospheric conditions at which the samples were conditioned. The instrument reading was adjusted to zero before each series of experiments.

The micrometer reading for each tested sample was recorded after the value become steady within 2s to 5s, before any compaction of the paper can occur. Any manual stress on the test piece or micrometer while a reading is being made was avoided. Five measurements at five different places of the sheet were conducted on each test piece and the value was averaged.

The apparent sheet density in grams per cubic centimetre was calculated from the formula: $\frac{g}{\delta_2}$.

Where,

g = the grammage of the paper, in g/m^{2}and

δ_2 = the mean single sheet thickness of the paper, in μm.

3.4.3 Bending Stiffness

A Lorentzen & Wettre Tester was used for bending stiffness test. All test pieces were cut to 14 mm in length and 15mm wide and were used later for the tensile test. The test sample was placed in the two clamps on the tester and closed once the test started. The right-hand clamp is a pulling clamp, and at the beginning of the test, it was in its home position that is determined by the approximate stiffness of the test piece. The left-hand clamp is the oscillating clamp, it holds the test piece fairly loosely and oscillates it with a frequency of 25 Hz (Standard). PF1 function was selected to set up specification for test strip, such as grammage, strip width, length, thickness and number of test piece. Once the test started, the amplitude meter recorded the resonance of the test piece by an inside light-emitting diode and a position-sensitive photodetector. The build-in microcomputer simultaneously recorded the amplitude and the length of the strip that had been pulled. Then the free length of the test piece at resonance was calculated. The bending stiffness (Sb in mNm) of the test piece was calculated from the equation below and shown in the display. The following results were recorded:

$Sb = 2 \times 10^3 \times w \times l^4$

Where w= grammage (g/m^2)

l = resonance length (m)

3.4.4 Tensile Strength

Tests were done according to AS/NZS 1301.448s standard. Tests were done by following the standard conditioning of paper for testing and standard atmosphere for testing paper and procedure for monitoring the atmosphere, AS/NZS 1301.414s AND AS/NZS 1301.415s.

For each sample, two different tests were conducted; dry tensile test and wet tensile test. For wet tensile test, the strip was soaked in water for a few seconds until it completely wet.

An Instron tester with 100 ± 0.1 mm distance between the clamping lines was used. To prepare the samples, test piece cutter with guillotine-knives which is capable of cutting test pieces 15 ± 0.1 mm in width and 210 ± 0.1 mm in length was used. For each tested handsheet, eight test pieces were cut. The averaged results were used in the tensile strength calculation. The test was conducted at a constant elongation rate of 10mm/min. Any test pieces that broke within 5 mm of a clamping line was discarded, and results were excluded. The maximum tensile load developed for each test piece was recorded

The tensile strength in kN/m was calculated from:

$$\text{tensile strength} = \frac{a}{w}$$

where

a = *mean maximum tensile force in* N

w = the width of the test piece in mm

The tensile index can be calculated from the following equation in Nm/g

$$\text{tensile index} = \frac{\text{mean tensile strength (N/m)}}{\text{conditioned grammage } (\frac{g}{m^2})}$$

3.4.5 Ring Crush Test

The ring crush or compression test was conducted according to TAPPI standard test method T818 om-97. The Instron tester with a compression platen has upper and lower platens. The two platens are smooth and flat surface. Specimen holder was placed on the centre of the lower platen of the compression machine. Specimen holder is a circular block, which has an annular square cut groove of 6.4 mm deep and 49.2 mm outside diameter. For each condition, eight samples were tested and average results were used in data analysis.

A test strip of 12.7 mm wide and 152.4 mm long was cut and placed in the specimen holder. A pressure was applied to the specimen by driving the upper platen