A New Technique to Measure Shear Bond Strength

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Declaration

"All statements of fact in this report are true and correct and I have made claims of acquired competencies in good faith. The report is my own work and is a true representation of my personal competence in written English. I confirm that I understand that members of the engineering team in Australia are required to display a commitment to exercising professional and ethical responsibility in all aspects of their work"

NAME: KAUSTUBH VIVEK JOSHI

SIGNATURE: ______________________________

DATE: ____________________________________

Dedication

There are powers beyond man's senses which govern the world. Not meaning to be overtly religious, but just reminding myself that even man doesn't know everything and has to look at some higher entity for guidance and help-the entity we call God!

I dedicate this thesis to Shri. Kasaba Ganpati, Shri Narasimhalaxmi (Sangameshwar), Shri Ram (Tulshibaug), Shri Yogeshwari (Ambajogai), Shri Dattatreya (Gangapur), Shri Balaji (Tirupati), Bhagwan Parshuram (Chiplun) and to all the saints and sages from all world religions who have guided men by serving as a direct link between them and God. I ask their blessings and guidance to help me stay on the path of righteousness and make this world a better place.

I dedicate this thesis to my parents Mr.Vivek Joshi and Mrs.Pratibha Joshi who have cared and loved me, even putting themselves through hardship at times to make my life better. If God walks this earth, I know where to find him.

There are many people I miss today; people who have made a difference to my life and influenced me to an extent. Foremost amongst them are my grandparents, Late.Dr.Laxman Joshi, Late.Mrs.Kusum Joshi and Late.Mr.Anant Kokil. I also miss my uncles Late.Dr.Ashok Joshi and Late.Dr.Vasant Joshi. I dedicate this thesis to their memories.

I dedicate this thesis to humanity and hope we continue building a world which our children and their children can enjoy.

Sincerely,

Kaustubh Vivek Joshi.

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Summary

A new method to measure the shear bond strength of paper has been established. The bond strength accounts for paper as a network instead of single fibre measurements. Single fibre measurements have been found not to represent the entire paper network and hence have not been considered appropriate for the experiments. The new measurement procedure is also much quicker than previously published procedures.

Isotropic handsheets with proper grammages and thickness control have been prepared using a specialized sheet former (moving belt sheet former). Acid (HCl) exposure has been used to weaken the fibres in the sheet of paper to such an extent that the fibre strength equals the bond strength of a single fibre-fibre bond. This is at the point where all the fibres are broken across the fracture line (except the ones that are bonded on one side of the fracture line only). The lowest exposure time where this occurs is called the optimum point in this thesis. A new rig has been designed for proper acid exposure of paper sheets. Sheets need to be exposed to acid vapours uniformly and there also needs to be an arrangement to rapidly remove the acid vapours from the vicinity of the sheet to stop the reaction between the acid and the paper. These factors were taken into account and verified with the newly designed rig. The rig, here, is a two plastic chamber assembly joined by a plastic pipe with a valve. Acid is kept in small beakers in one of the chambers and the paper is kept in the other chamber. The valve controls the passage of acid vapours from one chamber into the other. Rapid de-aeration is provided with the help of a metal pipe from one of the chambers connected to a vacuum apparatus. Optimum exposure has been determined by observing the tensile test fracture line with the help of confocal laser scanning microscopy after different levels of acid exposure. Zero span tensile strengths have been used to determine the fibre strength. Fibre width has been measured using the confocal microscopy and image analysis software.

Values for Shear bond strength have been calculated for sheets made from never dried (29.6 ± 3.3 MPa), once dried (24.7 ± 2.8 MPa) and high temperature dried (19.7 ± 2.2 MPa) Radiata pine pulp, 60% yield. The following formula was derived to calculate the shear bond strength:

$$\sigma_s = \frac{\frac{8}{3} \times \mathbf{Z_i} \times \rho \times \mathbf{C_s}}{\frac{\mathbf{D_w^2}}{\cos\theta_{\mathbf{avg}}}}$$

Bond strength values show that fibres tend to lose shear bond strength after drying and the loss of shear bond strength is much more if the fibres are undergoing a heat treatment for drying. This may be due to the Hornification. Further investigations are needed to determine the cause of shear bond strength loss and the mechanisms by which it would be possible to reverse the strength loss. This thesis is a part of the ongoing studies in the field of paper science and could be used as an input in developing the complete model describing paper mechanical properties.

Chapter 1: Introduction

The word paper comes from the Greek term for the ancient Egyptian writing material called papyrus, which was formed from beaten strips of papyrus plants. Paper is produced by the amalgamation of fibres, typically plant fibres composed of cellulose, which are subsequently held together by hydrogen bonding. While the fibres used are usually natural in origin, a wide variety of synthetic fibres, such as polypropylene and polyethylene, may be incorporated into paper as a way of imparting desirable physical properties. The most common source fibres used in papermaking is wood pulp from pulpwood trees, largely softwoods and hardwoods, such as spruce, pine etc. Other plant fibre materials including those of cotton, hemp, linen, and rice have also been used. Wood or plant cell walls are composed of fibres bound together. During pulping, these fibres are separated from each other and carbohydrate surfaces, primarily cellulose or hemicelluloses, are exposed. Hydrogen bonding between these carbohydrate surfaces gives papers its strength. Fibres can be separated chemically, mechanically, or via a combination of the two.

Most chemical pulp is made using the Kraft process. The purpose of a chemical pulping process is to break down the chemical structure of lignin and render it soluble in the cooking liquor, so it may be washed from the cellulose fibres. Because lignin holds the plant cells together, chemical pulping frees the fibres and makes pulp. After Kraft pulping the pulp can be used directly for bags and boxes or further de-lignified, during bleaching, to produce white pulp for printing and writing. Chemical pulps tend to cost more than mechanical pulps, largely due to the low yield, 40-50% of the original wood. Since the process preserves fibre length, chemical pulps tend to make stronger paper. Another advantage of chemical pulping is that the majority of the heat and electricity needed to run the process is produced by burning the lignin removed during pulping.

There are two major mechanical pulps, thermo-mechanical pulp (TMP) and ground-wood. In the TMP process wood is chipped and then fed into large steam-heated refiners where the chips are squeezed and “fibreized” between two steel discs. In the groundwood process debarked logs are fed in into grinders where they are pressed against rotating stones and fibreized. Mechanical pulping does not remove the lignin, so the yield is very high, > 95%, but also causes paper made from this pulp to yellow and become brittle over time. Mechanical pulps have rather short fibre lengths and produce weak paper. Although large amounts of electrical energy are required to produce mechanical pulp, it costs less than chemical pulp. Paper made from either chemical or mechanical pulp can also be recycled. By mixing with water and applying mechanical action the hydrogen bonds in the paper can be broken and fibres separated again.

After the paper web is produced, the water must be removed from it in order to create a usable product. This is accomplished through pressing, filtration and drying. The methods of doing so vary between the different processes used to make paper, but the concepts remain the same. Pressing the sheet removes the water by force. Once the water is forced from the sheet, another absorbent material must be used to collect this water. On a paper machine this is called a felt (not to be confused with the traditional felt). When making paper by hand, a blotter sheet is used. Drying involves using air and or heat to remove water from the paper sheet. In the earliest days of papermaking this was done by hanging the paper sheets like laundry. In more modern times, various forms of heated drying mechanisms are used.

The strength of paper is a result of properties of the network as well as the component fibres. Fibre length, fibre-fibre bond strength, bond area, fibre dimensions, fibre cross section are some of the important properties used to describe paper. It is of utmost importance to understand the relationship between the strength of paper and the fundamental properties in order to make better and stronger papers. Models have been developed to describe this relationship, but no single model has found widespread acceptance. A complete model will help paper manufacturers around the world optimize the quality of their product, reduce wastes and help the manufacturing process become more economical.

The shear bond strength is one such fundamental property that is believed to govern the strength of paper. Numerous studies over the years have tried to measure the shear bond strength but none of the studies as yet report an accurate method to measure the shear bond strength of paper. A loss in shear bond strength is also believed to be responsible for the strength loss observed after drying and recycling of fibres. Recycling in itself is a very important field and helps reduce the negative impact of modern lifestyle on the environment. Recycling of paper is thus of significant importance and to understand and optimize recycling processes it is necessary to measure the shear bond strength, the reasons for loss of shear bond strength and the possible ways and means of restoring shear bond strength.

The objective of this thesis is to establish a simple method to measure the shear bond strength. This thesis forms a part of the continuous and ongoing studies in the field of paper and aspires to be a starting point for future experimentation and developments to complete and present a model which describes paper mechanical properties thoroughly and accurately.

Chapter 2 reviews the literature and the studies carried out so far in the pursuit of measuring shear bond strength. It also discusses the difficulties in measuring shear bond strength and the various pros and cons of the previously used methods.

Chapter 3 presents the new experimental methods designed in the studies for this thesis and explains the idea behind the design. It also describes the various steps in designing the new experiments and the equipment used.

Chapter 4 presents the results generated in the course of the experiments and goes on to discuss the relevance of the results and how they are used to measure the shear bond strength. The calculated values of the shear bond strength are presented in this chapter.

Chapter 5 presents the conclusions of the studies and recommends some of the work that needs to be done in the future.

Chapter 2: Literature Review

2. 1 A brief history of studies of paper structure and strength

Paper is a network of randomly stacked fibres. It is a composite and many theories of composites have been applied to paper to try and understand its properties. Properties like bond strength, network structure, and relative bonded area (RBA) and in general the structure of paper has been of interest to researchers for many years. Even today there is a great deal about paper that we do not know! We are not well informed about the nature of crystalline and amorphous zones and the changes that occur in cellulose during bonding on paper. The point to be noted is that after hundreds of years of paper manufacture and few decades of dedicated study, we still haven't been able to measure and define all the factors which govern the properties of paper. The following few paragraphs will give an overview of some of the different studies conducted in the area of paper science. These studies were helpful in designing and developing the experiments presented here in this thesis, though many of them may not directly relate to bond strength.

2.1. 1 Paper Mechanical Properties and Theories

The Paper mechanical properties have been studied for decades and there has been considerable effort to present models for tensile strength, which is one of the more important mechanical properties of paper. The other important mechanical properties of paper are fracture toughness, elastic modulus and load-elongation properties.

Models for tensile strength have been developed using different approaches, viz:

1. Analytical Network models
2. Pull-out models
3. Computer simulations

The analytical network models include the Cox model [1], Kallmes-Bernier-Perez (KBP) model [2], Page equation [3] and Allan-Neogi model [4]. They are based on the assumption that tensile strength of paper is controlled by the strength of the component fibres and of the bonding between the fibres.

The other group of Kane model [5, 6]and Shallhorn and Karnis [7] model assume that paper can be treated as a fibre reinforced composite. The third group of models include those by Niskanen and Astrom [8] and Raisanen [9] which have used computer simulations to study tensile strength and fracture mechanics.

2.1. 2 Details of Tensile strength theories

Cox [1] was one of the first to come up with the idea of treating paper like a mat of fibres. Cox defined an ideal mat of fibres consisting of homogeneous plane or solid mat of long thin fibres oriented either at random or according to some definite law of statistical distribution. The flexural stiffness of the fibres was assumed to be negligible so that the fibres could transmit load only in tension and the loading applied to the edges of the fibres satisfied this condition. Theories were also developed for a planar mat of fibres having strains in two directions and for parallel fibre distributions, asymmetric fibre distributions and symmetric fibre distributions. The effect of the changes on the Shear modulus and distribution of fibres was also investigated. Cox analyzed the effect of orientation of fibres on the stiffness and strength of paper and other fibrous materials and concluded that the means of transfer of load from fibre to fibre could be represented merely by the use of reduced value for their modulus of elasticity in practical applications. The experiments conducted for this research by Cox were shown to be applicable to resin bonded fibrous materials and showed good agreement with the theory. A lot of subsequent development of fibre reinforced composites is based on this pioneering work by Cox, later known as the “Shear lag analysis”.

The KBP model furthers the basic concepts of Cox. The failure of weakly bonded sheet is predicted to occur when the sheet strain reaches a critical strain at the maximum point of the stress strain curve [2]. Sheet strength is obtained by calculating the stress corresponding to the critical sheet strain. The important idea advanced by this model is that strongly bonded sheets fail when the sheet strain reaches the failure strain of fibres.

The Page equation assumes that only a fraction of the fibres break across the sheet failure line at rupture and the strength of sheet is therefore dependant on the zero span strength and fraction of fibres that break. The second assumption was that ratio of pulled out to broken fibres across the failure line is dependant on the ratio of fibre strength to bond strength.

The Page equation [3] is given as:

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho}{PLb(RBA)}$$ **.....Equation 2. 1**

Where,

T = Tensile strength of paper (Nm/g)

Z = Zero span tensile strength (Nm/g)

RBA = Relative bonded area

P = Perimeter of fibre (μ m)

L = Fibre length (μ m)

A = Average cross sectional area of fibre (μ m^2)

ρ = Density of fibre (g/m^3)

b = Fibre-Fibre shear bond strength per unit area (MPa)

The Allan-Neogi model [4] considers paper to be highly bonded, randomly oriented and a non woven cellulose fibre assembly. It assumes that the fibres, that have already de-bonded before the sheet reaches the peak stress, do not contribute to the strength of the sheet.

The Kane model [5, 6] assumes that paper is a thin, randomly oriented, fibre reinforced web; the tensile load of which is obtained by the sum of the force required to either break or pull-out the fibres that cross a line of separation.

The Shallhorn and Karnis [7] model considers paper to be short fibre reinforced composite material with all the fibres perpendicular to the fracture line and uniformly bonded to a network of other fibres.

Kallmes and Bernier [10] studied the bonded areas of fibres: The relative bonded area, the absolute bonded area and the maximum bonded area. They subscribed to the idea that bonded area is the area between fibres in optical contact. This concept, however, lacks direct proof.

Raisanen and co-workers [11] had by this time begun to wonder if the widely used Cox model did really apply to random fibre networks? They pointed out that though the Cox model was absolutely convincing for composites, it could not be applied to paper networks where the fibres are more flexible. They pointed out that Cox's Shear lag theory did not work for random fibre networks. The reason stated for the failure of the shear lag model was that, in the model, external stress is transferred to the fibres through a small, density-independent number of bonds at the fibre ends and thus the fraction of loaded bonds is inversely proportional to density. In reality, the number of loaded bonds seems to be comparable to the number of load-carrying fibre segments at all densities [11]. They also stated that the pure shear lag model is possible only when the stress mediating segments are aligned precisely in the transverse direction. Raisanen went on studying the simulations and found one of the reasons why small amounts of reinforcement fibre did not improve the strength of paper. Raisanen's simulation studies [9] state that in the case of fibre failure, the observed effect of the strength properties of the model network is much smaller than the local stress disturbances would predict but still in the same direction. In case of fracture driven by bond failure, as is usually the case in paper, the effect would presumably be larger since the local shear stresses turned out to be more sensitive to the presence of the reinforcement fibre than are the axial stresses. Also stated was the fact that reinforcement effects could only be expected when the added fibres are so closely located that the stress disturbances caused by their ends were compensated by the axial stiffness of other reinforcement fibres located close by. Raisanen and Niskanen have thus contributed quite significantly in understanding the fibre networks through their simulation studies.

2.1. 3 Factors affecting sheet strength

It can be seen from the theories (2.1. 2) that the main factors affecting the sheet strength are:

1. Fibre Strength: The strength of the individual papermaking fibres affects the strength of the sheet. Weaker fibres will give a weaker sheet; hence the choice of papermaking fibre should consider the strength of the fibres. The strength of the fibres can be measured using the zero span tensile strength [12-14].
2. Fibre Length: A long fibre can bond to many more fibres and thus be more strongly held in the network than a short fibre.
3. Relative Bonded Area (RBA): The RBA is the bonded surface area of the fibres divided by their total surface area available for bonding.
4. Bond strength: Bond strength can be either the axial shear bond strength for tensile loading or the z-directional bond strength. The values of both of these will be different.

Most of the above factors have been measured and there are continuous developments to try and measure factors like Bond strength and RBA which are very difficult to measure. As mentioned, the zero span strength is used as a measure of the fibre strength (axial strength). The Kaajani Fibre analyzer or any other similar type of fibre analyzer can be used to measure the fibre lengths. There have been two methods to measure the RBA- Nitrogen adsorption BET method [15] and the Light scattering method by Ingmanson and Thode [16]. There are some difficulties with measuring the RBA because one can never be sure about the area of the fibres in actual contact and the measurements given by the techniques. This has been elaborated further. Light scattering has been preferred over nitrogen adsorption because it is a quicker method. However, the relationship between scattering coefficient and tensile strength which is essential for calculation for RBA by the Ingmanson and Thode extrapolation method has not been well established. Batchelor et al [17] have described a new method to estimate RBA based on density. El-Hosseiny and co-workers [18] believed RBA to be related to both light scattering coefficient of a sheet and its density. This prompted them to investigate the connection between scattering coefficient and sheet density and whether this relationship could be used to test the theoretical relationships involving tensile strength and RBA. They modified Clark's equations [19] to calculate the RBA.

2.1. 4 Hornification

Hornification is the loss of swelling of the fibre wall resulting from drying which is not recovered on rewetting. It is associated with a stiffening of the fibres which reduces their ability to form inter-fibre bonds [20]. The hornified fibres thus lose their flexibility and have reduced ability to form bonds which is believed to result in a loss of shear bond strength.

There are two theories regarding Hornification. The first one by Jayme [21] looks at wet fibres being brought into contact as drying proceeds. The polysaccharide chains are thought to pack tighter with the removal of water upon drying and micro fibrils join in flat ribbons as a result of tight packing. The drying process is thought to progressively close the capillary voids which might not be completely re-opened by newly intruding water. As a consequence, the irreversible hornified cell wall is believed to be less swollen and less flexible compared to the state before drying. When re-moistened some surfaces remain coalescent, thus reducing the fibre surface accessed by water [22]. Scallan and Laivins in their work relating to comparison of low yield and high yield pulps, describe Hornification as a partially irreversible connection of inter fibril hydrogen bonding [20].

The alternative mechanism by Ruffini [23] states that Hornification is a result of thermal cross linking through the formation of esters. The pulps used for the study were a sulfite pulp with 17% lignin content, unbleached Kraft pulp (2% lignin) and commercial bleached sulfite pulp. The presence of ester groups was confirmed by hydroxylamine-ferric chloride test, wet strength and carboxyl content before and after the drying process.

2.1. 5 Other notable contributions

Some other notable contributions to the study of paper mechanical properties are listed in this section.

Jentzen looked at the stress applied during drying [24]. The studies state that the changes in mechanical properties of paper with drying restraint are due to the changes in the crystalline orientation. One of the important things noticed was that appreciable tensions were developed in the fibres during the drying of handsheets, but this was more on account of beating rather than degree of straining.

Kettunen and Niskanen described a geometric characterization method that arises when a crack propagates through the paper. They then applied their new technique to study the effect of fibre properties [25, 26], concluding that the pull-out width can be used to estimate the length of fibre ends that can be extracted from paper along a fracture line. The damage width measures the area in which the fibre de-bonding takes place. They also found that both these parameters decrease at the same rate if fibres break along the fracture line.

Page et al. [27] were trying to calculate fibre-fibre bond strength of once dried pulps. They calculated their bond strengths using the Page equation [3] to find that the primary cause of tensile strength reduction upon drying was the loss of shear bond strength with a minor reduction caused by a loss in the bonded area.

Batchelor and co-workers came up with a new approach for quantitative analysis of paper [28]. In this first time technique for quantifying paper structure at fibre level, they measured the fibre dimensions, fibre orientation and fibre collapse directly using Confocal Laser Microscopy. This particular study by Batchelor et al forms a key to the successful design of experiments in this thesis. To try and further the understanding of paper at a fibre level, He, Batchelor and Johnston directly measured fibre-fibre contacts for a number of samples [29].

The main experimental findings were:

1. Fibre cross sectional shape has no significant effect on the frequency of fibre bonding along a fibre and distribution of free fibre length.
2. The distribution of a free fibre length is narrowed and shifted to a lower value range by wet pressing.
3. Fibre length alone has no effect on the properties of fibre-fibre contacts.

Batchelor and co-workers also proposed an analytical model for fibre-fibre contacts relating the average number of fibre-fibre contacts per unit fibre length with the cross sectional dimensions of the fibres in a sheet and sheet density. This study was responsible for developing new expressions for RBA which were experimentally verified. Batchelor et al [30] further investigated the behavior of fibres in wet pressing and found that fibre twist, fibre collapse and gap closure occurred simultaneously at low pressing pressures and gap closure was the predominant mechanism in paper structure densification at low pressures. Increasing pressure only increased the apparent density slightly and the density increase was mainly contributed by the additional twist and collapse of the fibres at the high pressing pressure. The distribution of lengths between fibre-fibre contacts was shown to be similar to the gamma distribution derived theoretically by Dent [31].

Batchelor followed up the work by trying to verify the models for tensile strength using the new techniques [32]. Many researchers have been working on many more aspects of paper strength and other properties and this study is an ongoing process.

2. 2 Zero span tests: A brief description

Zero Span tests form quite an important part of the experimental techniques used in the experiments and is used to measure the fibre strength. It therefore becomes important to know a little bit about these kinds of tests. Zero span tensile tests involve performing a tensile test with as small a gap between the jaws as possible, while short span tensile tests involve setting the jaws at a small distance apart (usually 0.1 to 0.6 mm). The gap between the jaws of the tester is known as the span [33].

Van den Akker [34] has shown that zero span strength of an isotropic sheet is 3/8 the strength of the sheet if all the fibres were aligned in the stress direction.

Defects in the fibres can have a major influence on the measured zero span strength [35-37]. El-Hosseiny and Bennett were the first to appreciate and point out the residual span. It should be noted that an increase in the number of curls and kinks were found to significantly reduce the measured zero span strength. Though the test is said to be a zero span test, Cowan and Cowdrey [38] mention that a residual span (0.2mm) exists. They observed differences in wet and dry zero span strength and believed that this was an effect of the residual span. They suggested that the true zero span strengths should be obtained by extrapolating a plot of zero/short span strengths vs. span to "-0.2mm". Later investigations by Gurnagul and Page [39] have led researchers to believe that wet fibre strength is actually less than dry fibre strength which is the reason for a difference in the wet and dry zero span strengths and hence it is not clear whether a residual span really exists.

Measurements of zero span strength as a function of grammage have shown that tensile strength decreases as grammage increases [14] due to the effect of non uniform stress field through the thickness of sample. This paper proposed that the true, intrinsic zero span strength should be obtained by extrapolating a plot of zero span tensile index vs. grammage to 0 gsm. A more detailed description about the zero span tests is given in the Experimental methods chapter.

Wathen et al. [40] studied the effect of different degradation mechanisms on axial and z-directional fibre strengths and found that acid vapour treatment is more detrimental to axial fibre strength than ageing treatments at elevated temperatures and humidity. They found that the z-directional strength of softwood decreases only after a harsh degradation. They used spruce (3000 revs in PFI mill) and birch (2000 revs in PFI mill) fibres for their studies. Handsheets were made as per ISO 5269-1. Acid vapour treatment was performed using a dessicator and by hanging the handsheets on a rack inside the dessicator for specific times (3:45 minutes to 960 minutes). The treatment times were dependant upon the type of pulp. Thermal treatment (80°C oven dried and 65% RH for 5-10 days and 90°C and 80% RH for 1, 2, 5, 6 days) was performed only for the spruce handsheets. After treatment the handsheets were conditioned and aerated. Wet and dry zero span measurements (ISO 15361), tensile strength and stiffness, modified Scott bond measurements (TAPPI T 833) were made. Pulp viscosity was used as a measure of degree of polymerization and hence degradation. Their findings are as follows [40]:

1. Dry zero span strength at same viscosities is higher for aged handsheets
2. At the same dry zero span strength, acid vapour treatment yields higher wet zero span strength; their explanation being that hydrogen bonds reinforce aged fibres more effectively than do acid vapour treated fibres and their removal during wetting causes the larger drop in wet zero span strength.
3. When evaluated at same fibre strength, dry zero-span vs. ordinary tensile strength reveals that acid vapour treated handsheets have higher tensile strength; the fibre network being able to compensate for the few larger local fibre defects but not for the numerous smaller defects which in combination cause failure at lower tensions.

Wathen et al. do not provide a single value of bond strength, however while studying the Scott bond measurements they found no change in inter-fibre bonding or z-directional strength above viscosities of 400 ml/g for spruce and 700 ml/g for birch and concluded that degradation treatments do not influence bonding above the viscosity levels mentioned and below these values the fibres are so weak that inter-fibre bond failure doesn’t occur and the effect on tensile index cannot be observed.

2. 3 Introduction to Bond Strength

Bonding between fibres is extremely important. Without bonding, there is no fibre network. In the paper making process, bonding arises from the intrinsic tendency of cellulosic fibres to bond to each other when dried from water or other polar liquid. The bonding between papermaking fibres is considered to be primarily due to hydrogen bonds. Van der Waals forces may also contribute. Inter fibre bonds in paper form gradually as solids content increases in the papermaking process. At first, the tension forces such as colloidal interactions and mechanical interlocking of the fibrils pull fibres closer together when the water is removed from the wet web. This is known as the Campbell effect [41]. The solids content at which the actual inter-fibre bonds form is not exactly known, since the Campbell effect gradually changes into hydrogen bonding. The mechanical properties of the bond cannot be separated from the response of the bonded fibre segments. The mechanical properties of paper can be entirely described by the properties of the bonded and free fibre segments. The strength of an inter fibre bond usually refers to its shear strength [41]. The statement is true in case of in-plane loading which is important from the perspective of this study. There are several out of plane testing methods for which the above statement does not hold.

Shear Bond strength is the shear force per unit area. The shear bond strength is defined as "the maximum load per unit area that the bond can carry when the bonded fibres are displaced relative to one another, parallel to the plane of bonding [41].

Retulainen and Ebeling [42] tried to compare the different methods of measuring bond strength. They mentioned that there were four types of loading modes, viz:

1. In plane tensile loading
2. In plane shear loading
3. Z-directional tensile loading
4. Z-directional peel loading.

They tried to measure the specific bond strength, defined as the strength of the bond per unit area of the bond, in eight different ways (Table 2. 1). Retulainen and Ebeling conducted two sets of experiments. In the first set two pulp fractions of different coarseness (springwood and summerwood) were compared with un-fractionated pulp. Bleached pine sulphite pulp was used for the experiments. In the second set unrestrained drying, drum drying (between blotters) and restrained drying (in drying rings) was used. The RBA was evaluated from tensile strength values and light scattering values (using Elrepho with 620 nm filter). Nordman bond strength was measured according to Nordman's theory about Nordman Bond strength [43]. Page's equation [3] was used to determine the specific bond strength and fibre strength was evaluated based on zero span tensile strength values. Scott bond strength was determined using TAPPI 308. They observed that NBS increases with beating. At low RBA, summerwood pulp seems to have better NBS than coarser fractions. Page's equation predicts that bond strength increases with beating. Summerwood fibres showed better specific bond strength at constant RBA in the Scott Bond strength, Clark's cohesiveness, fibre pull out method and drying stress method.

Method	**Loading mode**
Nordman Bond strength	In-plane
Skowronski	Peel, duplex sheets
Clark's cohesiveness	Shear, duplex sheets
SBS-Page equation	In-plane, calculation
SBS-pull out length	In-plane, tagged fibres
Tensile strength at constant density levels	In-plane, extrapolation
Scott bond/ RBA	z-directional, energy
Drying stress	In-plane

Table 2. 1: Methods used to characterize specific bond strengths [42]

For a constant level of beating summerwood fibres showed higher values of bond strength in case of Scott bond strength, Page equation method, pull out method and drying stress method, whereas the springwood fibres showed higher values of bond strength in case of the cohesiveness method and tensile strength at constant density. The results of the drying mode were not so contradictory and clearly showed that restrained drying was a better drying mode for increasing bond strength at a constant RBA level. It is not clear how the shear stress measurements were done. They concluded that amongst the methods they studied, there was no ideal method to calculate the specific bond strength. They also stated that the shear strength should be measured directly instead of measuring some parameter correlated to the shear strength.

Lindstrom et al. [44] reviewed the effects of wet and dry strength resins on the strength of paper. The additives they reviewed and their effects on joint strength are summarized in Table 2. 2 and Table 2. 3. They do not mention any values of the shear bond strength but their discussions regarding the bonding mechanisms are worth noting. Lindstrom et al. state that when the distance between fibres in the wet state is short enough, the fibre-fibre interaction represents a balance between the capillary forces pulling the fibres together, the attractive Van der Waals forces and the repulsive electrostatic forces emanating from the negative charges on the fibres. Their discussion mentions that Hydrogen bonding has been the mechanism most commonly cited to explain the development of molecular interactions in the fibre-fibre joint. Van der Waals interactions are also said to be responsible for interactions between surfaces. They state that there are no quantitative evaluations of the relative importance of hydrogen bonding to the development of strong fibre-fibre joints. Fibres are usually treated as cylindrical objects, but in reality they are highly fibrillar. The current theories of hydrogen bonding and Van der Waals forces cannot fully describe the fibre-fibre bonding process and hence a new mechanism needs to be developed to account for the way bonding takes place between cellulosic surfaces in sheets of paper.

Dry strength additives	**Effect on strength**
Starch	Increases specific bond strength
Acrylamide based polymers	Improvement in internal bond strength
Chitosan	Efficient strength additive
Gums	Improves formation, improving strength
Wood hemicelluloses	Tensile strength improvement
Latex additives	No effect on unfilled papers
Carboxy methyl cellulose	strength improvement > cationic starch
Polyelectrolyte multilayers	Tensile strength increases without significant increase in sheet density

Table 2. 2: Dry strength additives summary by Lindstrom et al. [44]

Dry strength additives	Effect on strength
Urea formaldehyde	Protective action increases strength
Melamine formaldehyde	Limited to use under acidic conditions
Alkaline curing polymeric amine-epichlorohydrine resins	Increases creep strength
Glyoxylated polyacrylamide resins	Reduce moist creep
Oxidized polysaccharides	Improves fracture resistance

Table 2. 3: Wet strength additives summary by Lindstrom et al. [44]

The other interesting point they make is regarding light scattering measurements for RBA. They state that the wavelength of light is much too large to enable detection of dimensions of relevance for interactions between the fibres.

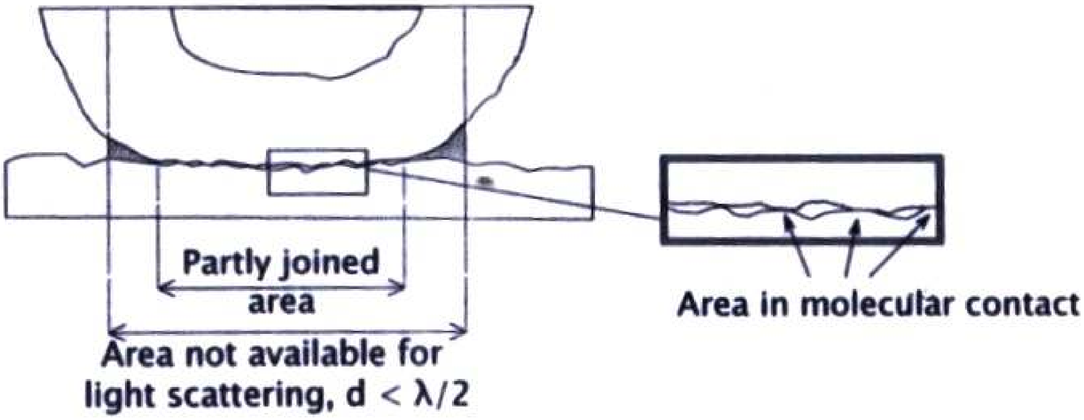

Figure 2. 1: Schematic diagram of fibre-fibre contact-related to Light scattering [44]

Figure 2. 1 [44]shows the area that might be detected using light scattering and the areas that might be in actual contact. As can be seen, the actual area in contact is much less than the area in contact detected by the light scattering measurements. Hence Lindstrom et al. state that light scattering measurements cannot be used for determining the

fundamental properties of the joined area in paper. They also state that it is important to distinguish between areas that are close enough to be affected by molecular forces but not in direct molecular contact and areas in direct molecular contact.

They describe a few mechanisms of various types to explain interactions between two surfaces (Figure 2. 2)[44]. Fibre surfaces are both rough and rather soft and might adjust towards each other during pressing and drying operations. In this case an interlocking mechanism is more likely to occur.

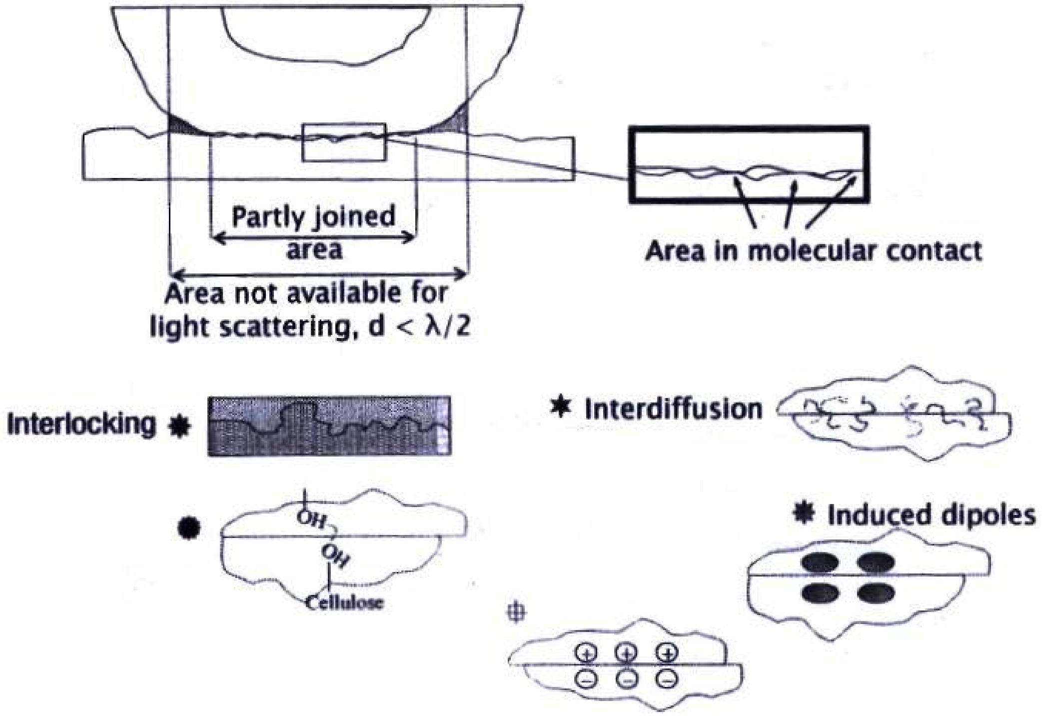

Figure 2. 2: Schematic diagram of various mechanisms of interactions of surfaces [44]

They also mention a diffusion mechanism by which molecules from opposite surfaces migrate across the interface to create linkages between the surfaces, thereby increasing the adhesion.

Niskanen et al. believed that none of the then existing theories connect the tensile strength with an independently measurable value of bonding degree or bond strength, hence they presented a macro-mechanical study that connects tensile strength with independently measured values of tensile stiffness and z-directional fracture energy (i.e.: the Scott bond strength or z-directional tensile index). They believed that tensile strength of paper is not governed by the macroscopic defects that are present in the paper from the beginning; instead they might be governed by microscopic structure and microscopic properties [45]. The fracture process zone (FPZ) was defined as the area where plastic deformation and damage is distributed during the fracture and the longitudinal width of the fracture process zone measured after crack propagation was called damage width. Niskanen et al. measured the size of the FPZ when a crack starts to propagate from a cut made to the specimen.

They compared the z-directional fracture energy from experiments on softwood craft pulps (0, 1000 and 3000 revs at PFI-mill) and their calculations. The nip-peeling test was used to measure the fracture energy (G_z). The best agreement between their theory and actual values was obtained for a fibre grammage 7 gsm. The fibre width to thickness ratio was best at a value of 2. They also discovered that measured tensile index(Average value 75 NM/g) for bleached Kraft pulp has higher values than unbleached Kraft pulp (average value 60 Nm/g).

In their experiments, Lindstrom et al had to use the Scott bond strength values to estimate G_z and found that it's difficult to model the complicated properties of paper using simple geometric considerations. They also said that some of the values they used for agreement between their theory and experiments were far from realistic values and effects of low fibre strength were missing from their analysis. The main point of their conclusions was that z-directional fracture energy does not capture all aspects of inter-fibre bonding that are important for the in-plane tensile strength.

2. 4 Previous Studies

Bond strength is a very difficult quantity to measure. It is therefore, not surprising that not many studies have been carried out in this area. Most of the work carried out is either related to the field of Materials engineering or to Composites. Since polymer composites find wide use in areas such as aerospace, automobile sector etc, a lot of work has been done in this field. In contrast, not as much has been done to understand the bond strength in paper and cellulosics. One may note that for years the polymer composites and fibre theories applied to composites were assumed to hold for paper networks as well. It was later suggested that the Cox model [1], which was the basis for all the tensile strength and bond strength research, did not apply to paper networks completely [46]. In fact, Page and Seth [46-48] have argued that Cox did not consider important factors like curl and kinks and micro compressions which influence the behavior of paper greatly. Pioneering work in the measurement of Bond strength in paper was done by McIntosh [49]. The following graph gives an idea about the studies carried out in this area since 1960.

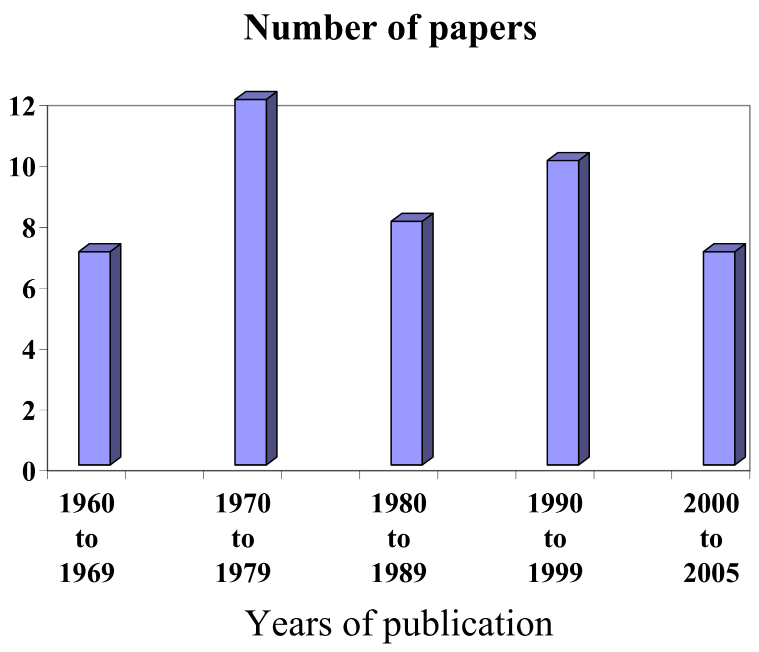

Figure 2. 3: Number of papers over the years of publication

One of the main reasons why so less a work has been done in this area is that the quantity to be measured, i.e.: Shear Bond Strength, can’t be measured easily and one needs to design experiments with great care.

From the graph (Figure 2. 3) we can conclude that there were numerous studies carried out from 1970-1980. However there was a bit less done from 1980 to 1990. The study in the 1960's focused mainly on forming single fibre joints and testing them to get the bond strength. The 1990's saw the advent of a new approach to measure shear bond strength using Page's equation instead of single fibre bond measurement techniques.

The studies undertaken by different researchers will now be discussed in the following subsections. The studies are divided into two groups, depending on whether the shear bond strength was measured directly or indirectly from measurements on the sheet.

2.4. 1 Direct Measurements

2.4.1. 1 McIntosh and Leopold [49, 50]

In order to obtain direct information on the bonding strength of fibre surfaces, a method was devised of bonding the individual fibres on cellophane or on a radial group of shives one cell thick (shive) (Figure 2. 4). The shear stress required for separating the fibre from the cellophane or shive was measured. Loblolly pine, Springwood and Summerwood chips were used for this study. Cooking time was varied to obtain yields between 94% and 46 %. A wet fibre shive was placed on a foil wrapped glass microscope slide and a drop of water was applied to the shive. A single wet pine fibre from the same pulp as the shive was placed carefully across the shive at 90 degrees with the shive close to one end of the fibre. This was covered with another foil wrapped glass slide and allowed to dry overnight in an oven at 90°C under a 300 g weight. The assembly was removed from the oven into controlled conditions of 50% R.H. and 23 degrees C. In preparation for mounting on a test apparatus, one end of a small piece of cellophane was glued to a paper tab of the type used for single fibre testing. Both ends of the shive, with bonded fibre attached, were then glued to the opposite end of the cellophane in such a way that the free end of the fibre extended beyond the edge of the cellophane for about one half the fibre length. This was then photographed on a microscope in transmitted polarized light for a record of the area available for contact between fibre surfaces [49].

A shive was also bonded to the cellulose film directly to get another assembly and the results showed that the strength of fibre-shive bonding was about 7 times the strength of fibre-cellulose film bonding.

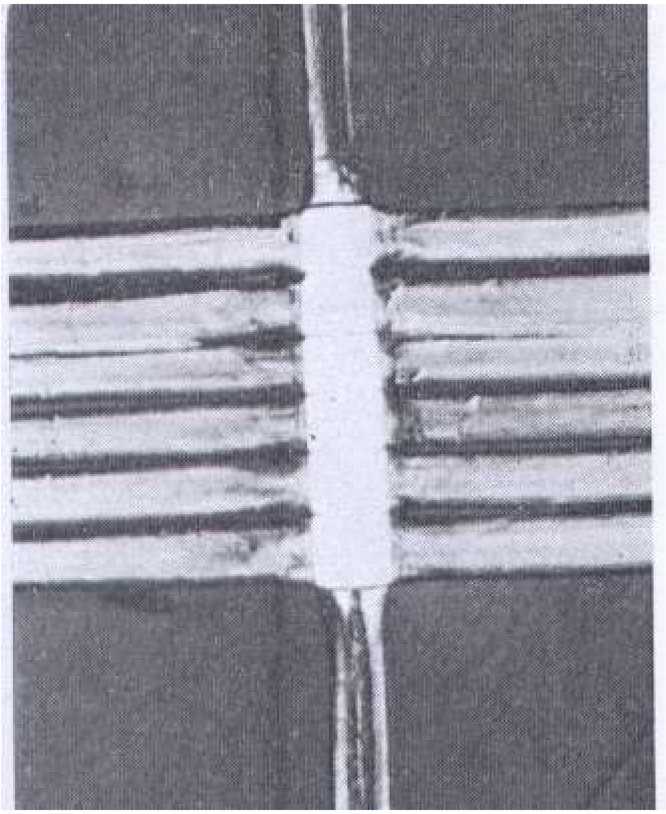

Figure 2. 4:McIntosh's Shive Arrangement for testing fibre-fibre shear bond strength [49]

The results are summarized in Table 2. 4

Fibre type	Assembly type	Bond strength (MPa)
Springwood	Fibre-Cellulose film	0.3
	Fibre-Shive	2.7
Summerwood	Fibre-Cellulose film	1
	Fibre-Shive	7.1

Table 2. 4: Bond strength Values by McIntosh and Leopold [50]

2.4.1. 2 Russell, Kallmes and Mayhood [51]

Russell, Kallmes and Mayhood studied the effect of Melamine Formaldehyde resin and a polyamide resin on factors which influenced the stress- strain behaviour of paper. The three factors they studied were:

Stress Strain Properties of Fibre
Shear resistance of inter fibre Contact areas
Degree of inter fibre bonding.

They used a St.Regis unbeaten pulp and unbleached bisulfite pulp. Handsheets were prepared using TAPPI, T-205 m. After drying, all the sheets were oven dried at 120°C for 10 minutes. Wet strength additives were added to the pulps. The single fibres were mounted on tabs with Epoxy 907 (Miller Chemical Co.) and were held in a pair of specially constructed clamps.

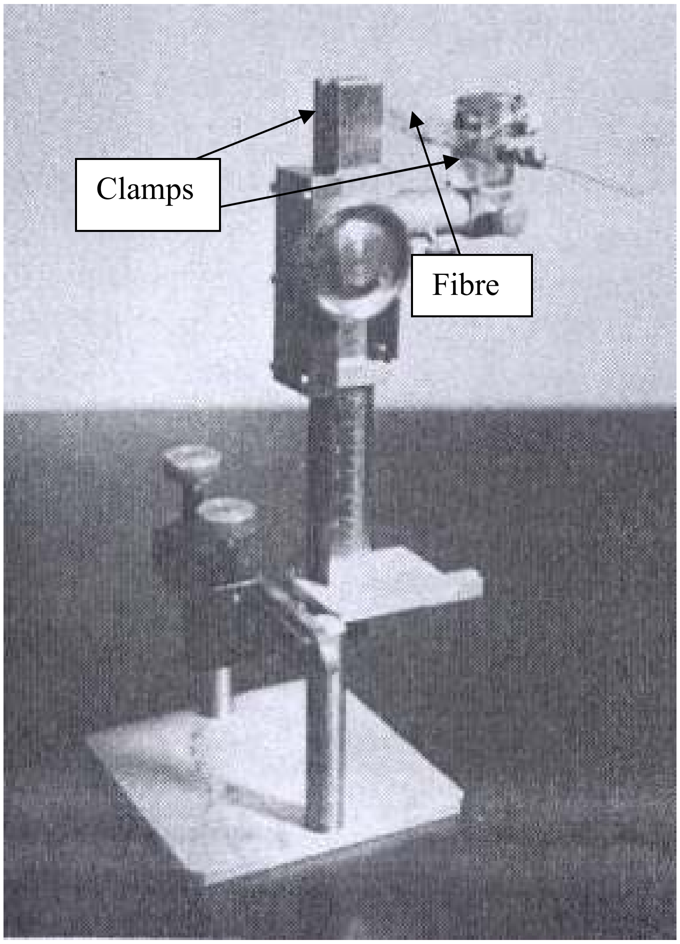

Figure 2. 5: Sorbtometer [51]

The apparatus used for measurement of shear resistance of contact areas was an analytical balance with a special pair of clamps. A hypodermic needle was placed such that a drop of water was easily transferred from the tip of the needle onto the contact. This whole assembly was the Sorbtometer (Figure 2. 5) which was used to measure the degree of bonding. The dry area in optical contact was measured by observing the area of optical contact under crossed Nichols.

The Bond strength values are displayed in Table 2. 5

Type of sample	**Dry Strength (MPa)**	**Wet strength (MPa)**
Untreated Sample	2.56 ± 0.98	0.29 ± 0.1
2% melamine resin	2.39 ± 1.67	0.86 ± 0.52
2% polyamide resin	2.49 ± 1.19	1.04 ± 0.76

Table 2. 5: Shear Bond strength values by Russell et al.[51]

It was also concluded that the addition of Melamine Formaldehyde and polyamide resin does not change the dry shear bond strength much, but the resins have a protective action on the contacts and increases wet shear bond strength values [51].

2.4.1. 3 Schniewind, Nemeth and Brink. [52]

Schniewind et al developed a method to determine the Shear strength of fibre to fibre bonds of individually prepared single fibre crossings. A test specimen was prepared by placing two never dried wet fibres on a Teflon block crossing each other at an angle of 90 degrees. A small drop of water was placed at the point of overlap to prevent premature drying of the fibres. The work was done with Fir fibres prepared suing an experimental nitric acid pulping procedure. The Teflon blocks measured 1 X 1 X 1/4inch. Four fibre crossings were placed on each block and each crossing was covered with a 15 mil Teflon disk 5/16inch in diameter. Ten such assemblies were placed in a screw press with pressures ranging between 25 and 250 psi for different experiments. However a standard pressure of 75 psi was adopted. The press was kept in a humidity room at 23 degrees C and 50% R.H. for three days. The samples were then removed and mounted on paper tabs, about 1/4 X 1 inch in size. One end of the tab was covered with masking tape with adhesive on both sides and a slot 1 to 1.5 mm wide was cut into this end of the tab. The specimen was mounted on the tab by placing one of the fibres across the slot and pressing its ends into the masking tape. The point of fibre overlap was placed in the centre of the slot and the other fibre then protruded beyond the tab. Area of bonding was measured using polarized light technique. Testing was done on an Instron tensile tester and the speed of testing was 0.1 inch/minute. White fir fibres (Summerwood and springwood) were used for the studies. Pulp had been prepared from air-dried chips cooked to a yield of 68.4% and refined in a Bauer mill. Other pulps like the Douglas fir holocellulose fibres and bleached pulp from Weyerhaeuser Co. were also used for some measurements.

Type of bond	**Bond strength Values(MPa)**		
	Holocellulose fibre	**Dried Kraft pulp**	**Dried Sulphite Pulp**
Springwood-Springwood	1.93	0.37	0.21
Summerwood-Springwood	2.83	0.99	N.A.
Summerwood-Summerwood	3.74	0.77	0.32

Table 2. 6: Shear Bond strength values, Schniewind et al [52]

There were a lot of misalignments and variations in the results. The bonds were also prepared using one summerwood-one springwood fibres. The reported shear bond strengths are given in Table 2. 6. They could not state definitely the reason for the difference in bond strength values between the summerwood and springwood fibres, but they suspected this was due to an actual physical or chemical change in the characteristics of fibres.

2.4.1. 4 Button [53]

Button did a lot of work relating to joint strength in paper and tried to estimate the shear bond strength using a linear elastic model. Button's entire PhD dissertation focused on the study of the linear elastic model as applied to fibre-fibre bonds. Holocellulose Loblolly pine tracheids, Cellophane strips (fibres) were used for experiments. Most of Button's work focused on cellophane fibre joints, but a part of the work was also on loblolly pine fibres. Different types of fibres like latewood and earlywood fibres were used. Different solvents like carbon tetrachloride, ethyl alcohol and distilled water were used for treatments at different stages of sample preparation (i.e.: caustic extractions to a 58% yield). Three layers of membranes were placed before the fibres were sandwiched between 20 layers of filter papers. These were then covered with stainless steel plates, placed under a pressure of 100 psi for 24 hours. The joints were then mounted on metal pins. The pins were then pushed closer together to give the desired amount of overlap. The testing was done at loading rate of 0.35 g/sec on a Fibre load/elongation recorder. Button found that the bond breaking load is almost independent of the area of the bond because of stress concentrations in the bond. The bond strength results are shown in Table 2. 7.

Type of fibre	**Average Breaking load (g)**	**Average Bond Area (sq.microns)**	**Average Shear Bond strength (MPa)**
Latewood	7.862	11048.4	13.908
Earlywood	5.494	6128.2	8.954

Table 2. 7: Button's Shear Bond strengths (Loblolly Pine) [53]

2.4.1. 5 Thorpe, Mark, Eusufzai and Perkins [54]

Thorpe et al focused on determining experimentally a range of stiffness values for fibre to fibre bonds.

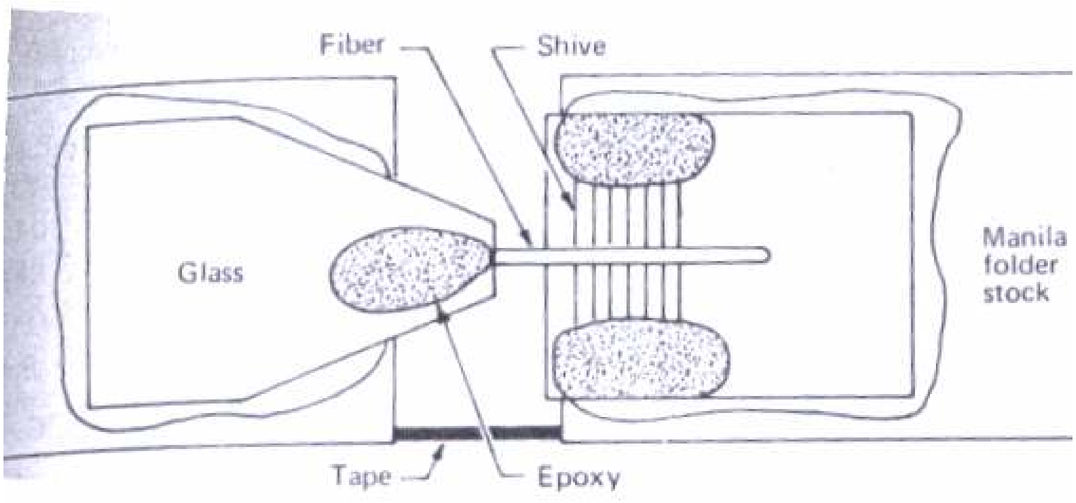

Figure 2. 6: Thorpe's Manila Folder type measurement design [54]

They believed that fibre straightening is not an important phenomenon and the determination of mechanical properties of fibre bond regions may hold the key to better agreement between theory and experiments for predicting mechanical behaviour of bonded fibre networks. The system developed was used to determine the properties of bonds between fibres and shives from holocellulose and high temperature TMP. Specimens were made using the techniques specified by McIntosh [50]. The only significant change was that the bonds were formed at 110-115°C or at 210°C under 21-25 psi pressure. The bonding was observed using the Zeiss Universal Light microscope. After bonding, the assembly (Figure 2. 6) was carefully placed in position on a testing assembly and glued on with Epon 907 epoxy adhesive. The testing assembly consisted of two 3/8 X 1/8 inch manila folder stock covered with shards of broken microscope slide cover glasses and connected together along one edge with a narrow piece of scotch tape. Photomicrographs were taken using the Zeiss Universal microscope polarized light technique and were used to determine the bonded area. The values of bond strength are displayed in Table 2. 8.

Type of Fibre bond	Average Shear Bond strength (MPa)
Holocellulose bond formed at R.T.	4
TMP bond formed at 110°C	2.86
TMP bond formed at 210°C	8.16

Table 2. 8: Thorpe et al. Bond strengths [54]

They concluded that holocellulose bonds showed least damage to the fibre and shive walls in de-bonding, TMP at 110°C show more damage to cell walls than in case of holocellulose and TMP at 210°C derive their much higher stiffness and proportionately lower bond elongation from the thermal flow of lignin and hemicelluloses at higher temperatures. They suspected that on drying, the lignin and hemicelluloses acted as a continuous cementing agent between the cellulosic reinforcements.

2.4.1. 6 Stratton and Colson [55, 56]

Stratton and Colson [56] have done extensive work in the area of bond strength measurement, studying the strength of individual fibre-fibre bonds and the resulting damage during rupture to the fibre walls under varying conditions. Southern Pine chips were pulped using conventional Kraft cook process and cooked to 47.5% yield. The freeness was varied to study its effect on the bond strength as well. In addition Loblolly pine chips, earlywood and latewood were Kraft cooked and used without refining. Individual fibre-fibre bonds were prepared by positioning a pair of wet fibres at right angles to each other on a Teflon-faced rubber disc (Figure 2. 7). The pair was dried at 105°C for one hour in an oven under a nominal compressive load of 0.12 MPa. The bonded fibre pair was cemented at the ends of the fibres to a special Mylar mount. Bonded area was measured using the Page's polarized light technique. The tongue area of the mount was painted with black ink before the fibres were attached to it to reduce reflection and enhance contrast between bonded and non bonded regions.

Pulp Type	Additives/Treatment	Bond Strength (MPa)
Earlywood Loblolly Pine	-	2.1
Latewood Loblolly Pine	-	6.4
Earlywood Loblolly Pine	Polyamide polyamine epichlorohydrin	3.9
570 ml CSF Southern Pine	-	2.8
570 ml CSF Southern Pine	Polyamide polyamine epichlorohydrin	7.5
570 ml CSF Southern Pine	Polydiallylmethyl ammonium chloride + sodium polystyrene sulfonate	9.3
345 ml CSF Southern Pine	-	3.7

Table 2. 9: Stratton and Colson, Bond strengths [56]

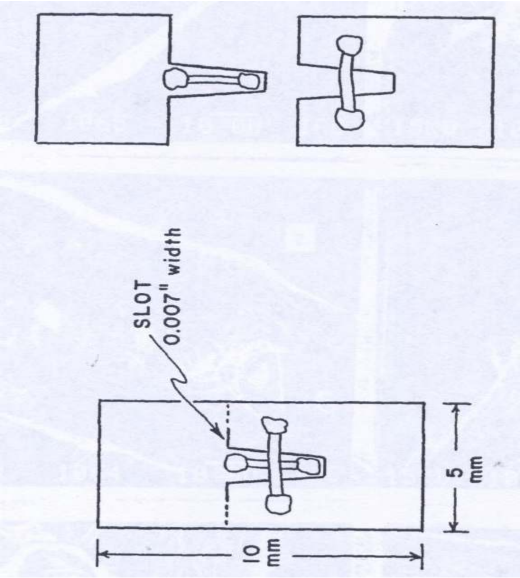

Figure 2. 7: Stratton's Teflon Disc Arrangement [56]

The breaking load of the bonds was determined using the FLER II, a second generation fibre elongation recorder. The experiments were done at 23°C and 50% R.H. The bond strengths are shown in Table 2. 9. They also studied the dependence of fibre–fibre bonding on some papermaking variables [55]. Their definition of bond strength is as follows**:** "Bond strength is the force required to cause the failure of a single fibre-fibre bond divided by the bond area of that bond".

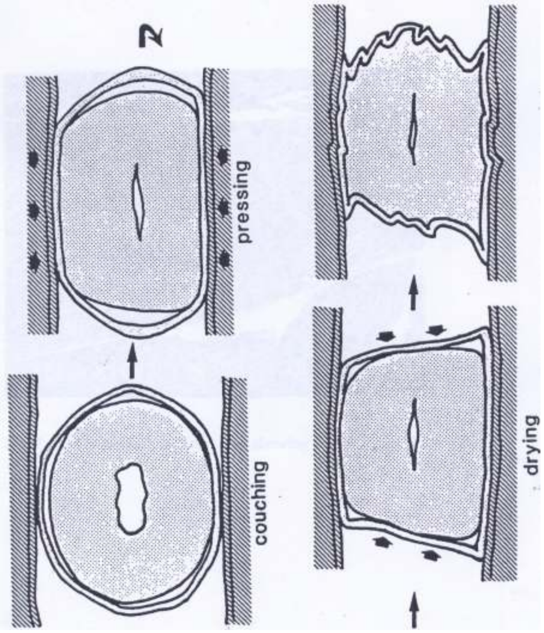

Figure 2. 8: How Fibres appear during different stages of pressing and drying [55, 57]

The variables tested were refining, wet pressing and polymeric strength aid and their effects. They found that latewood fibre bonds had higher strength than earlywood fibre bonds, refining did not have a significant effect on the bond strength and wet strength aids are effective in improving the bond strength. In further studies by Stratton [57], fibre properties were measured on classified pulp. Hand sheets were made using the Noble and Wood hand sheet making procedure. The standard couching and pressing operations were performed on the sheets (Figure 2. 8).

The Z-toughness test was calculated by measuring the energy of delamination and change in optical contact area. Shear Bond strength was not measured in the later work The optical contact area was measured using light scattering technique. Stratton argued that the pre-test and post-test scattering co-efficient should be different and hence it is possible to calculate the bond area from there. Stratton concludes that Density is not a good predictor of bond strength in a sheet

2.4.1. 7 Torgnysdotter and Wagberg [58]

Torgnysdotter and Wagberg [58] examined the possibility of changing the properties of the contact zone between fibres to control the physical properties of paper. The data generated from their experiments has been used to calculate the Shear Bond strength, though Torgnysdotter and Wagberg have not calculated the shear bond strength. They believed that yield of pulps has a great influence on the mechanical and chemical properties of the fibre and fibre surface and also that recycling and drying operations have a significant effect on the paper properties like tensile strength. Spruce wood chips were used to cook up the pulps with target kappa numbers 110, 80 and 16. All pulps were disintegrated and fractionated in a Britt dynamic drainage jar equipped with a 125P screen to remove the fines fraction. The pH was adjusted to 2 with HCl. The pulp was dewatered and washed with de-ionized water to pH 4.5. The pulp was then washed with NaOH to pH 8 and the pulp was allowed to dry before testing and stored at 4°C with a solid content of ~ 20%. The pulps for the drying experiment were oven dried at 105°C overnight and soaked in water at pH 9. The high yield pulp was heated at 80°C before disintegration. Polyelectrolyte multilayers and polyelectrolyte complexes were added to fibres to increase the paper strength properties. Sheets of 110 gsm were prepared using the Rapid-Kothen Blattbildner (EN-ISO 5269-2).

Type of Fibre	**Yield (%)**	**Average Shear Bond strength (MPa)**
Never dried	60	2.1
	52.1	1.5
	40.9	1.6
Once dried	60	1.8
	52.1	1.5
	40.9	1.4

Table 2. 10: Calculated bond strength values from Torgnysdotter and Wagberg's data [58]

Fibre crosses were tested using the methods outlined by Stratton and Colson [55]. The calculated bond strength values are shown in Table 2. 10. The bond strength values were calculated using the values of fibre-fibre joint strength and average fibre width.

They explained that after drying the wet-fibre flexibility and contact zone properties deteriorated resulting in lower tensile and compression strengths and lower water retention capacity of sheets. They also believe that increase in paper strength properties was most likely caused by increased fibre-fibre joint strength arising from enhanced fibre contact zone properties. Contact area was measured in a very different manner using light microscopy (Leica DMRX), operating in the diffraction interference contrast mode. The paper was soaked in ethanol, allowed to dry and then delaminated to expose the contact areas.

2.4. 2 Indirect measurements

2.4.2. 1 Jones [59]

Jones conducted a study on the techniques to characterize the strength of different pulps. He studied unbleached Kraft pulp from several different wood species. Slash Pine and spruce pulps of 47%, 53%, 51.1%, 60.2%, 54.4%, and 46% yield were used. The Tensile strength of individual fibres and zero span strength of sheets are the topics of interest as far as this project are concerned. Jones did measure a lot of other properties as well, but they won't be discussed here. For measurement of Zero span tensile strength, specially designed jaws were used. Jones mentions the designer of these jaws as Wink [12] who also produced the first zero span tester [59]. The jaws were lined with cellophane tape and a clamping pressure of 15000 psi was used. Individual fibre strength was determined by using a table model of the Instron and a type "A" load cell. The cross head drive motor was isolated on a separate table by means of a flexible shaft to minimize vibration. The fibres tested were dried from water after they had been gently straightened out with a dissecting needle. The fibres were dried on a glass plate which had been lightly filmed with silicone grease so that adhesion between the plate and the fibre was sufficient to prevent twisting as the fibre dried but would allow the fibre to be easily removed when the water was gone.

Jones concluded that as the zero span strength changes the bond strength changes in such a way as to compensate for the zero span strength. Surface area measurements were made with a dynamic nitrogen adsorption apparatus. Sheets were made for the zero span tensile tests.

Type of Pulp	Shear Bond strength (MPa)
Slash Pine 50% yield	7.1
Slash Pine 60% yield	9.3
Spruce	8.7

Table 2. 11: Shear Bond strengths of different yield pulps by Jones [59]

The pulp was refined in a valley beater at 1.57% consistency from about 705 ml CSF to 135 ml CSF. 60 gsm sheets were made on the British sheet mold, pressed and dried on plates.

The Shear Bond strength values are given in Table 2. 11

2.4.2. 2 Gurnagul, Ju and Page [27]

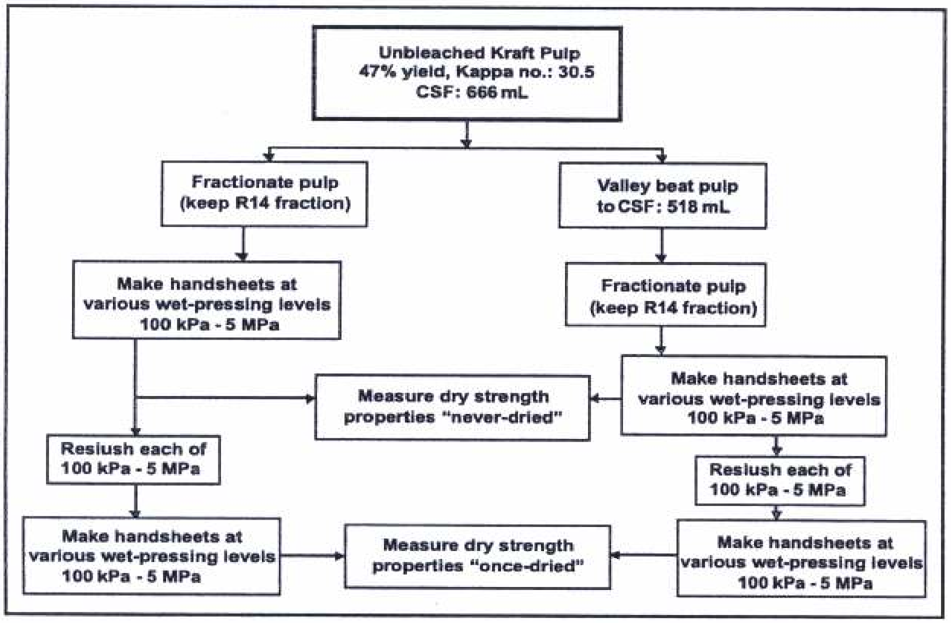

Figure 2. 9: Flowchart of Gurnagul et al. experimental method [27]

Gurnagul et al used the Page equation [3] for tensile strength to determine the contribution of the relative Bonded Area and the shear bond strength to the loss of tensile strength of a northern softwood unbleached Kraft pulp when it is dried. They found that the primary cause of tensile strength reduction upon drying was the loss of shear bond strength, with a minor reduction caused by a loss in the bonded area.

They wanted to apply their study to enhance the way in which the recycled fibres are treated to be able to make better paper. To make things easier for the reader, they have summarized their work in the form of a flow sheet (Figure 2. 9).All the tests were done at 50% R.H. and 23 degrees C.

The bond strength value was not directly calculated by Gurnagul et al, but has been obtained from graphs of Tensile Index versus scattering coefficient (Figure 2. 10), Specific Elastic Modulus versus scattering coefficient (Figure 2. 11) and Page Bonding strength versus scattering coefficient (Figure 2. 12), by assuming the fibre perimeter to be 100 microns and by using Equation 2.2.

$$\frac{\mathbf{b}}{\mathbf{k}}-\left[\frac{\mathbf{b}}{\mathbf{kS_0}}\right]\mathbf{S}=\left[\frac{\mathbf{1}}{\mathbf{T}}-\frac{\mathbf{9}}{\mathbf{8Z}}\right]^{-1} \text{ and } \mathbf{k}=\frac{\mathbf{12c}}{\mathbf{PL}}$$ **.....Equation 2. 2**

Where,

b = Shear bond strength per unit bonded area

S_0 = the scattering coefficient of a sheet of unbonded fibres

S = the scattering coefficient for paper

T = Tensile index

Z = Zero span tensile index

c = Coarseness

P = perimeter of the fibre cross section

L = fibre length

The equations are used to calculate the Bond strength, where all the terms are from the Page's equation. The first term in Equation 2.2 is termed as the Page bonding Strength index.

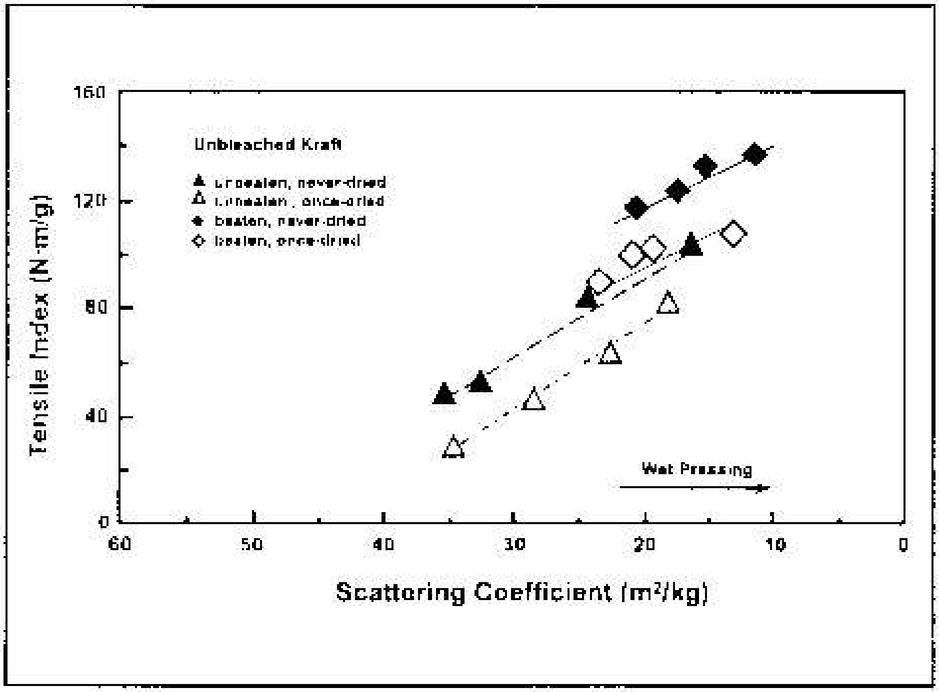

Figure 2. 10: Tensile index vs. Scattering coefficient [27]

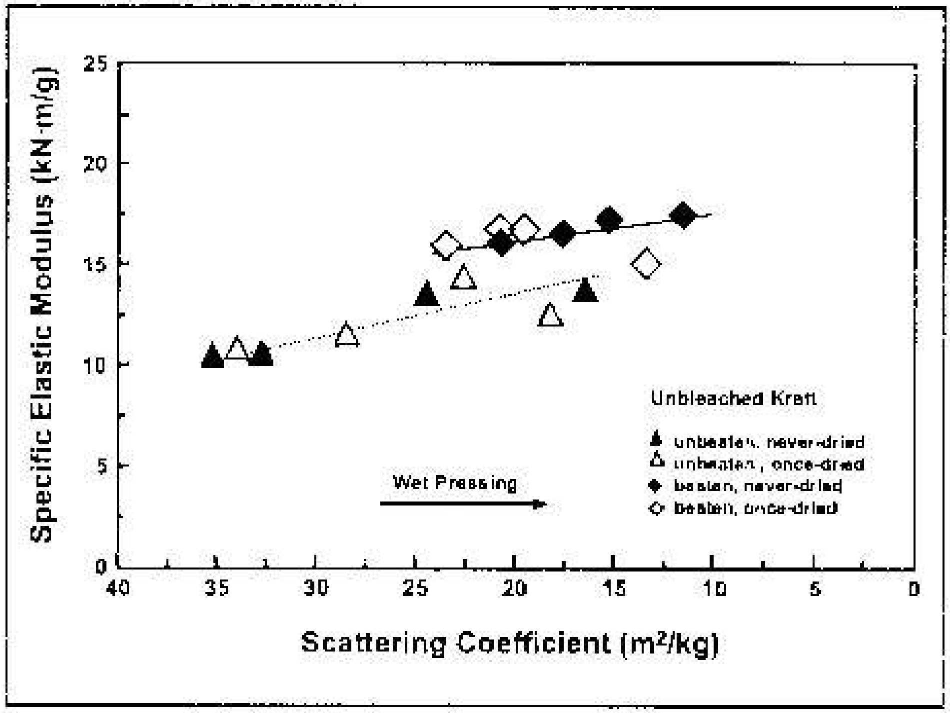

Figure 2. 11: Specific Elastic Modulus vs. Scattering coefficient [27]

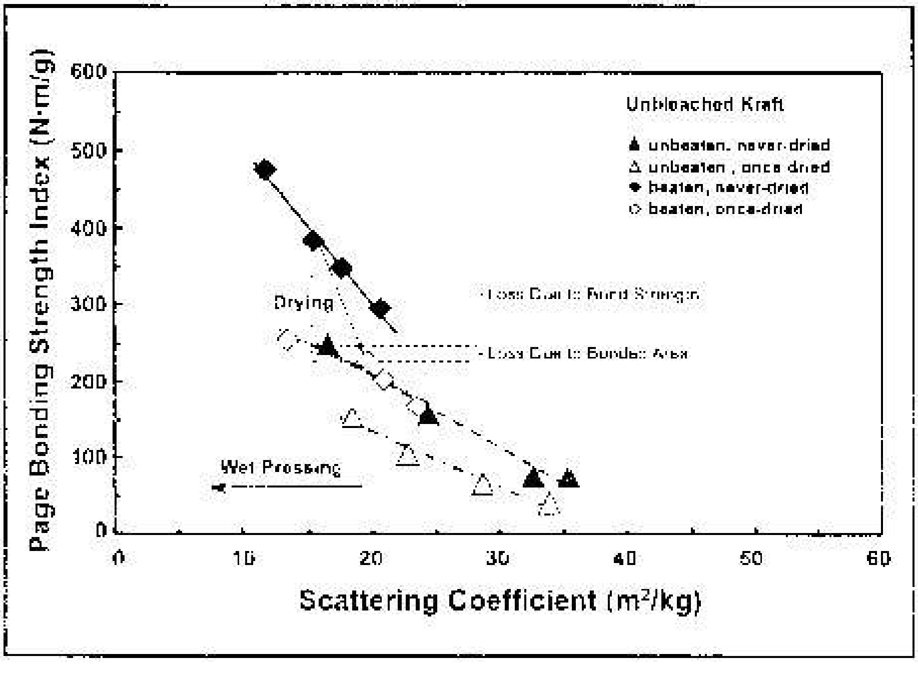

Figure 2. 12: Page Bonding Strength Index vs. Scattering coefficient [27]

Sample type	**Value of intercept** $(\frac{\mathbf{b}}{\mathbf{k}})$	**Value of “c” (mg/m)**	**Fibre Length(mm)**	**Shear Bond strength (MPa):not calculated by Gurnagul et al.**
Unbeaten, never dried	399	0.171	2.82	5.59
Unbeaten, once dried	278	0.171	2.81	3.04
Beaten, never dried	698	0.177	2.65	2.90
Beaten, once dried	373	0.161	2.60	2.03

Table 2. 12: Calculation of Bond strength values from Gurnagul et al. data [27]

The y-intercept (Figure 2. 12) gives the value of $\frac{\mathbf{b}}{\mathbf{k}}$. The bond strength values are shown in Table 2. 12. Gurnagul et al [27] concluded that drying or refining and drying together caused a significant loss of bond strength.

2.4.2. 3 Nordman [43]

Nordman’s approach to measuring bond strength was to use the irreversible work done during straining of paper sheet as a measure of bond strength [43].

The Nordman bond strength is defined as the ratio of work done during straining of paper to the change in the scattering coefficient.

$$\mathbf{NordmanBondStrength(NBS)} = \frac{\Delta \mathbf{W}}{\Delta \mathbf{S}} \quad \text{.....}\mathbf{Equation\ 2.\ 3}$$

Where,

ΔW = work done during the straining of paper.

ΔS = change in the scattering coefficient due to the straining of paper.

Seth [60] was convinced that the Nordman Bond strength as interpreted by Page [61] needed some further thought and modification. The idea was to correct the Nordman bond strength and show it was independent of the pressing pressure which gave the Nordman bond strength as:

$$\mathbf{NBS} = \frac{\mathbf{\Delta W \times RBA}}{\mathbf{\Delta RBA}} \quad \textbf{.....Equation 2. 4}$$

Where,

RBA = Relative Bonded area, defined as the bonded surface area of fibres divided by their total surface area

ΔRBA = Change in the RBA

ΔW = work done during straining of the paper

Page [61] also suggested that the Nordman bond strength is not a useful measurement technique since most of the work done in plastic deformation is due to straining of fibres. The results obtained by direct and indirect methods are sensitive to how the bonds are loaded.

Nordman [43] had proposed a method of measuring the specific bond strength by determining the irreversible work of straining sheets and the change in optical scattering coefficient that was observed. This method, proposed about 40 years ago has been proved to be unsound. Page [61] examined the work of Nordman more closely and concluded that under certain experimental conditions, Nordman bond strength is a relative index of specific bond strength, in other circumstances it is not. Seth [60] was puzzled why the work to break bonds per unit bonded area, which is supposed to be a property of the pulp, should depend on the basic variable of specimen preparation, i.e.: wet pressing pressure.

This prompted Seth to re-examine the phenomenon of Nordman Bond strength. In the study, Seth concluded that increased wet pressing pressure during sheet making increases the RBA and therefore the tensile strength. Seth started by using a commercial bleached Kraft pulp containing mostly black spruce.

Pressing pressure (kPa)	$\frac{\Delta W \times RBA}{\Delta RBA}$ **(J/kg)**
34.5	8.21
345	8.12
3450	8.11

Table 2. 13: Seth's data after re-examining NBS [60]

The pulp was beaten for 5000 revolutions in a PFI mill. Standard procedures of PAPTAC were followed for handling pulp and making handsheets. After couching, the sheets were pressed against Teflon plates at three different wet-pressing pressures. The sheets were then dried without restraint at constant temperature and humidity. Test strips 3.8 cm wide and 12 cm long were cut from each set of sheets. Scattering coefficient at 681 nm was measured on each strip at three different locations. Instron Tensile tester was used for testing all the strips. The gauge length was 10 cm and elongation rate was 0.5 mm/min. Over 20 strips were tested for each handsheet. All the tests were carried out at standard conditions of 50% R.H. and 23 degrees C. Seth showed that the results are independent of the pressing pressure. Seth's method does not account for the work done in plastic deformation of fibres and so is an indirect measure of bond strength. Seth's data is shown in Table 2. 13.

2. 5 Analysis: Relevance of previous work

Researchers	Type of Fibre	Earlywood (E)/ Latewood(L) or any other parameter	Yield (%)	Bond strength value (MPa)
McIntosh and Leopold [50]	Loblolly Pine	(E)	46	2.7
		(L)	46	7.1
Russel et al. [51]	St.Regis unbeaten	N.A.	N.A.	2.56
Schniewind et al.[52]	Fir	(E)	68.4	1.93
		(L)	68.4	3.74
Button [53]	Loblolly Pine	(E)	58	8.9
		(L)	58	13.9
Thorpe et al. [54]	N.A.	110°C	TMP(~95)	2.86
		210°C	TMP(~95)	8.16
Stratton and Colson [55, 56]	Loblolly	(E)	N.A.	2.1
		(L)		6.4
	Southern	345 CSF	47.5	3.7
		570 CSF	47.5	2.83

Torgnysdotter and Wagberg [58]	Spruce	Never dried	60	2.1
			52.1	1.5
			40.9	1.6
		Once dried	60	1.8
			52.1	1.4
			40.9	1.5

Table 2. 14: Summary table of all bond strength values and involved variables (Direct measurements)

Researchers	**Type of Fibre**	**Earlywood (E)/ Latewood(L) or any other parameter**	**Yield (%)**	**Bond strength value (MPa)**
Jones [59]	Slash Pine	N.A.	50/60	7.1 / 9.3
	Spruce		60	8.7
Gurnagul et al. [27]	Northwood Kraft	Never-Dried unbeaten	47	5.59
		Never-dried beaten	47	2.9
		Once-dried unbeaten	47	3.04
		Once-Dried Beaten	47	2.03

Table 2. 15: Summary table of all bond strength values and involved variables (Direct measurements)

As seen from the literature cited, there has been some very interesting work done in measurement of fibre-fibre bond strength. The range of the bond strength values comes as a surprise initially, but a closer look at the methods employed for measurements tend to suggest that some points have not been considered while conducting the experiments. E.g.: The bond strength values range from 1 MPa to 13.9 MPa depending upon the type of experiment and the type of pulp. Observe Table 2. 14 and Table 2. 15. It can be seen that there is a really strong trend showing that latewood fibres tend to form stronger bonds than earlywood fibres. No notable trend can be observed between yield and bond strength. McIntosh [49] conducted the pioneering work in the measurement of sheer bond strength (2.4.1. 1). The idea of using cellophane and fibre shives is a very clever way of experimentation. It does not, however, consider that the wetting of the fibre-fibre bond may have an effect on the strength of the bond. It also fails to consider that a bond made between a fibre and a shive cannot be a representative of the fibre-fibre bond in paper sheets. Thus these bond strength values cannot be an accurate representation of the actual bond strength values. One of the major problems with this type of assemblies is also that of stress concentration [53]. It means that the bonds break earlier than if the stress was uniform.

Russell and co-workers [51] (2.4.1. 2), Torgnysdotter and Wagberg [58] (2.4.1. 7) conducted similar experiments. Thorpe et al [54] (2.4.1. 5), Stratton and Colson [55-57] (2.4.1. 6), all carried out experiments of similar nature for determining the bond strength values. They also aimed at measuring a few other variables and their relation to the bond strength values. Thus, though their objectives were wider than just measuring the bond strength, they effectively used one similar technique in their experiments; i.e.: Making a single fibre bond with another single fibre, gluing the assembly using tapes and paper and then using a tensile tester for breaking the bond. Most of them used the polarized light measurement technique for measurement of area. Almost all of them thought that the bond would go dry and hence tried to place a drop of water at the point where the two fibres came in contact.

The above works do not consider the effect the water drop may have on the hydrogen bonding and also on the strength of the individual fibre. More importantly, they take a fibre-fibre bond to be a representative of all the bonds in a sheet of paper and this may not be the best way of judging the strength of bonds in a network, especially paper which is a very complex network. In a sheet of paper, stress is produced as the fibres dry [24]. In fibre crossings, one will observe a build up of stress and reduction in the bonded area. It is very difficult to replicate this stress behaviour while forming an individual bond. It should be noted that in some instances, the researchers have used a drop of water as a means of actually positioning the fibres and allowing it to dry out so that a good bond is formed.

Amongst the above, the work done by Stratton and Colson [55-57] and further Stratton [57] were interesting because they actually considered the effect of friction between fibres while designing the experimental setup. The specially designed Teflon plates with the slots come very close to simulating the actual way in which fibres arrange themselves in the network.

Schniewind et al. [52] (2.4.1. 3), also used Teflon block assemblies to give the fibres the desired stiffness without them curling up. However, their assembly was plagued with misalignments and hence there was a lot of variation in the results. Another point to be noted here is that the speed of testing and spans used for testing in all the studies were not uniform. Paper tabs and adhesive tapes used for holding the fibres are also not a good way of fixing the bond in place.

Button [53] (2.4.1. 4) did an amazing amount of work on fibre-fibre bonds. The work was based on linear elastic model and different types of joints. This was again a single fibre bond measurement technique and hence cannot be considered representative of the entire fibre network.

Nordman’s idea was using the irreversible work done during the straining of sheets as a measure of bond strength. The method by which Nordman measured the bonded area was not correct since the fibres might not be in actual contact, yet appear to be in optical contact since the space between the fibres may be smaller than the wavelength of light. This is also true in case of most of the direct sheet measurements. Seth [60] (2.4.2. 3), proposed some modifications to the Nordman Bond strength as explained by Page [61].

His work concentrated on defining the bond strength in paper as a factor dependant upon the work done in straining the paper and the changes in the scattering coefficient. Non-standard size of test strips and a different elongation rate seem to be the drawbacks associated with this technique. Seth was very careful in designing his experiments, except for the fact that he tried to depend too much on the accuracy of light scattering experiments. It must be noted, that he realized the importance of measuring the bond strength in sheets and so used hand sheets for his studies rather than bonds between single fibres or between fibres and shives.

Gurnagul and co-workers [27] (2.4.2. 2), realized that experiments needed to be carried out on a sheet of paper rather than on individual fibres to be able to determine the bond strength of fibres. Their experimental techniques seem solid. The major drawback in their technique is the way in which the bonded area and bond strength was measured. They measured the bonded area using Ingmanson and Thode extrapolation method [16]. The bond strength which they measured was using different graphs of Tensile Index versus scattering coefficient, Specific elastic modulus versus scattering coefficient and Page Bonding strength versus scattering coefficient. It should be noted is the fact that Page's equation has never been verified completely and assuming its validity in itself is a big step. One would expect the relative change in bond strength to be reasonably accurate but the absolute values depend on the constants in the Page's equation which have never been fully verified.

2. 6 The Objective

As seen in the previous sections some work has been done on measurement of Bond strength. However, one must note that the work done is actually as a part of some other experiment in many cases. The fact that bond strength is a difficult quantity to measure is accepted. The question then is what can be done about it?

Based on the literature reviewed, the ideal solution for bond strength measurements should be based on the following points:

1. Sheet measurements should be done instead of single fibre measurements because the latter were tedious, time consuming and not necessarily representative of fibres in an actual sheet.
2. The measurement procedure should be quick
3. In-plane testing methods should be used in preference to out of plane methods as the latter will give different answers.

The start of the next chapter will discuss and justify the solutions that have been found.

Chapter 3: Experimental Method

3. 1 Introduction

First Design (Researchers)	**Brief experimental apparatus design**	**Later modifications based on similar idea (Researchers)**
McIntosh and Leopold [49, 50]	Gluing fibre to shive or cellophane + heat and pressure + glass slide mounting	Thorpe [54]
Schniewind et al [52]	Teflon Block mounting	Stratton [55-57] Torgnysdotter [58]
Russell et al [51]	Single fibre joints + drop of water and needles for wetting fibres during testing	Thorpe [54]
Button [53]	Fibre shive joint using cellophane + Mechanical joint theory	No one has followed up this approach as yet
Nordman [43]	Work of straining sheet	Seth [60] Page [61]

Table 3. 1: Previous methods of research and brief idea of apparatus

Shear Bond strength measurements have been carried out by researchers for more than the last forty years. The techniques they have used can be summarized in the form of a table (Table 3. 1). It is seen that many of the approaches overlap. The researchers have tried to use single fibre joints, handsheets, mechanical joint theories and much more but have not been able to get fully consistent and reproducible results. The major point against the single fibre joints is that these joints are not representative of the whole sheet of paper. The difficulty in preparing the joints and the effect of pressure and heat on the values obtained are some of the other points to consider.

3. 2 Development of method

Considering the difficulties faced by previous researchers, a method had to be developed which overcomes the major drawbacks of previously used methods. Gurnagul et al [27] had realized the importance of carrying out the in-sheet measurements for calculating the bond strength in their procedures. However, they relied heavily on the Page equation for measurement of bonded area and bond strength. The points to be considered were:

1. Measurements need to be done in the sheets so as to avoid the problem of preparation of individual bonds.
2. Measurements should not rely on the assumptions of the Page equation.

The starting point for the development of a new method was considering the fracture process of paper.

Fracture refers to the macroscopic fracture of paper in a tensile test. The fracture of paper can be triggered either by fracture of fibres or fracture of bonds in the paper. Two view points exist regarding the mechanism of paper fracture.

Page [3] and Kallmes et al [2] believe that the fracture of paper is started by the failure of fibres oriented in the direction of the applied load. Van den Akker et al [34] and Niskanen [62] on the other hand believe that fibre bonds control the tensile strength of paper, assuming that paper fails when the external stress equals the bond yielding threshold. While Page [3] has provided some evidence to support his claims, Van den Akker [34] has shown that many bonds fail before macroscopic failure has commenced. It is to be noted that none of the evidence is strong enough to support one viewpoint against the other and hence it can be said that the fracture process is a result of bond breakage and fibre fracture. However it is clear that fibre segments become permanently elongated and the fibre-fibre bonds rupture in small steps, when paper is stretched, and before the macroscopic fracture. The partial bond ruptures and related yielding of fibre segments will result in relaxing of local stresses, thus increasing the stresses in the neighbouring elements. When the stresses in the fibre exceed its strength, then the fibre breaks and triggers off the macroscopic fracture of paper. Once initiated, this rupture proceeds rapidly through the fibre network. The fibre break or pull-out depends on the bonding degree of the fibres.

The combination of fibre and bond failure makes it difficult to analyse the process and also makes it difficult to obtain information about the bond failure alone. To simplify the analysis, one needs to set up a situation where either all the bonds fail or all the fibres fail. In a sheet, if the bonds are weakened so that all the fibres pull-out, the bond strength will have changed. The same is also true if all the fibres are broken by increasing the bond strength. The main idea for the experiments reported in this thesis is to weaken the fibres so that they break before any of the bonds.

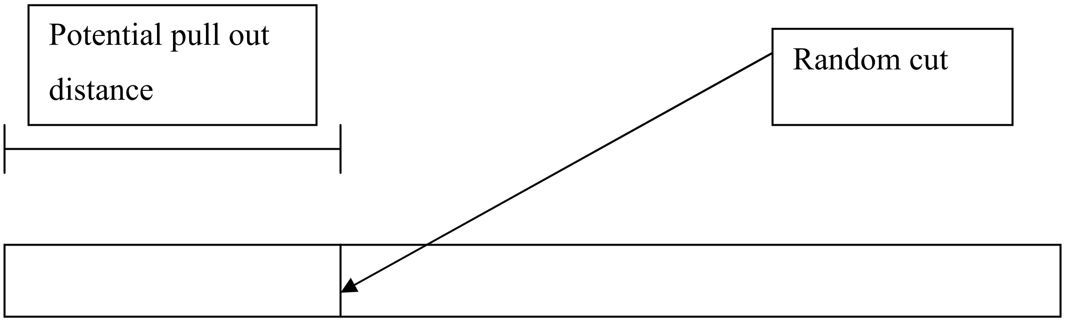

Figure 3. 1: Schematic diagram showing a random fibre aligned perpendicular to the fracture line, cut at some random point

If all the fibres break then it means that they are weaker than one bond. This can be visualized with the help of Figure 3. 1, which shows a fibre aligned perpendicular to the fracture line. The fracture line has cut the fibre along some random position. The fibre would pull-out if the bonding strength in the shorter length is less than the fibre strength at that point. However, if there are several bonds along the shorter segment, then the bond strength estimation becomes difficult because all the bonds are not equally loaded (as per the Shear lag analysis) and some bonds may have broken even before the fracture begins [25, 26]. If all the fibres are breaking, then they are breaking even when there is only one bond holding the shorter segment. Under these conditions the fibre strength is less than the strength of one bond. The heart of the method that has been developed here is to weaken the fibres so that their strength is equal to the strength of one fibre-fibre bond.

3. 3 Method to weaken the fibres

It is clear that there needs to be a method to weaken the fibres without changing the bond strength and the sheet structure. Degradation of the fibres is necessary to weaken them. Degradation can be defined as a detrimental change in the chemical structure or physical properties. Degradation can be either mechanical or chemical [63]. Mechanical degradation introduces disorders into the fibres like curls, crimps, kinks etc; whereas in chemical degradation the cellulose chains are clipped.

Chemical degradation can be classified into:

1. Acid hydrolysis
2. Oxidative
3. Alkaline
4. Thermal
5. Microbiological

Degradation can be either homogeneous or heterogeneous. Berggren et al [64, 65] have studied the degradation mechanisms in detail and their schematic illustration (Figure 3. 2) helps one understand the homogenous and heterogeneous degradation. Acid degradation is more detrimental to the fibre strength than alkaline degradation. Acid degradation is more heterogeneous whereas alkaline degradation is more homogeneous (Figure 3. 2). De Souza Lima and Borsali [66] have found that the effect of the acid on degradation depends upon acid species, concentration, exposure time and temperature. They do not mention which acid is more favourable for degradation.

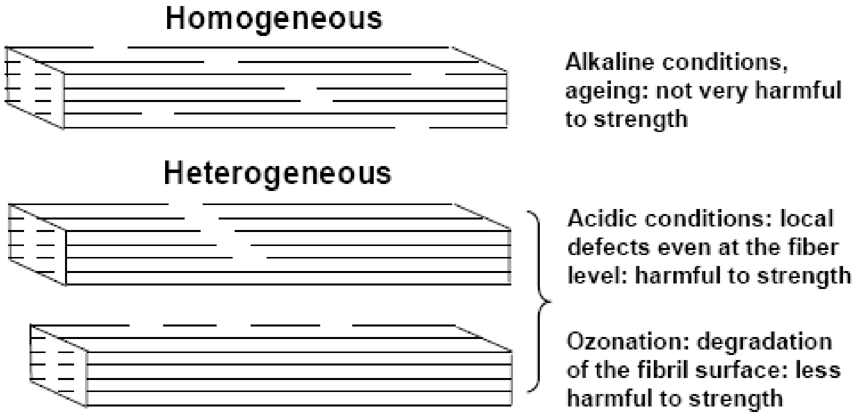

Figure 3. 2: Schematic diagram showing homogeneous and heterogeneous degradation [65]

Weakening of fibres using acid hydrolysis to study changes in fibre properties has been used previously by Seth and Page [67] and Wathen et al [40, 63]. Considering this and also considering that the acidic conditions lead to a more heterogeneous degradation, acid hydrolysis was chosen as the means to weaken the fibres. It can be seen (Figure 3. 2) that the heterogeneous degradation is more localized than homogeneous degradation which means that a heterogeneous degradation is more likely to cause a reduction in fibre strength than a homogeneous degradation. While using acid hydrolysis it is important to note that preference had to be given to acid gas vapours. Aqueous liquids will act on the sheet of paper effectively and bring about acid degradation; However they will also bring about changes to the bonding. Acid vapours on the other hand will degrade the fibres in an equally effective manner and won’t bring about changes to the bonding. There is no clear evidence linking the acid exposure and bonding and this is one of the unanswered questions still under investigation by researchers around the world.

While designing the complete experimental setup presented in this thesis, the following points were considered and the apparatus was designed accordingly:

1. A method for exposing the sheets uniformly with reproducibility had to be designed.
2. A method to estimate the fraction of broken and pulled out fibres was needed.
3. There was need of a method to measure fibre strength of single fibres

The design of the equipment can be observed in the following subsections.

3. 4 Acid Exposure Procedures

It was thought that the method used by Wathen [40] would be the most ideal one for acid exposure of sheets because it is simple and straightforward.

Figure 3. 3: Desiccator

Wathen et al [40] used a tank filled with acid and the paper samples suspended above the acid bath. The samples were removed from the acid tank and aerated to stop the exposure of the sheet to the acid gas. The aerated samples were then conditioned and used for testing in the original method. This method was modified slightly for the work here by replacing the tank with a glass desiccator (Figure 3. 3). The dessicator is a glass chamber with a lid, designed such that the bottom part can be filled with desiccant and the samples can be placed on a ceramic or metal mesh resting in the middle of the lower part of the dessicator. This glass "bowl" is covered with a glass lid and the lid has protruding outlets for connecting to a vacuum apparatus if needed. Some desiccators are also made of plastic materials, but the one used in the experiments here was made of glass.

The desiccator was filled with conc. HCl (32%) and a metal mesh was placed above it to hold the samples. The sheets were kept on the mesh for about 5 minutes. The metal wires reacted with the acid gas and imprints were found on the sheets making them unsuitable for further testing. The metal mesh was then replaced with a mesh made of thin PVC wires; this time a change in colour was observed for the sheets. The further modification was replacing the plastic mesh with a ceramic mesh plate so as to eliminate the problem of the acid reacting with the mesh, but a change in colour of the sheets was still observed. The samples obtained from the desiccator exposure method also seemed very wet after aeration and in some cases were beginning to tear even as the sample was removed from the desiccator. This method was therefore considered unsuitable for the experiments and hence discarded.

It was thought that the TLC (Thin Layer Chromatography) chambers would be more useful and would give better results than the desiccator assembly. The TLC chamber was filled with about 50 ml HCl so that the bottom was sufficiently covered and there was enough acid to give off vapours to expose the sheet properly. The lid covering the TLC chamber was fitted with small hooks and the paper samples were suspended from the hooks into the chamber. The acid reacted with the adhesive used to fix the hooks and the hooks started falling off one by one. This assembly was also discarded.

3.4. 1 Design of the new assembly

It was then decided that the paper sample and acid should be kept in separate chambers. There was also a need to connect the two chambers and have a system which would help transfer the vapours from the acid chamber into the other chamber. There was also need to cut-off the vapours and rapidly remove the acid gas vapours from the paper and its surroundings so that the acid gas exposure time could be tightly controlled. The new assembly (Figure 3. 4) was designed using PVC as the material for construction of the chambers. The dimensions of the chambers are 220 mm x 220 mm x 40 mm. PVC was the preferred material because data charts show that PVC does not react with conc. HCl at room temperatures. To ensure safety while working with this assembly, the HCl was not directly poured into the chamber but was kept in small 100 ml beakers and then kept in the chamber to ensure that the HCl would not leak out. The assembly was placed under a fume hood as a further precaution. The chamber on the left held the acid beakers and the chamber on the right held the paper sample. A small connector was provided at the bottom of the chamber holding the paper to facilitate rapid acid gas evacuation of the chamber using a vacuum apparatus similar to the one used for a Buchner Funnel assembly.

The Buchner funnel type assembly was deemed suitable because the volume of gas from the chamber is very small as compared to the volume of water with which it is washed away. Safety officers were consulted before implementing this procedure to assure that the experiment did not cause environmental problems. The chambers were connected using a 350 mm plastic pipe with a binary valve. The connector for the vacuum apparatus was 0.5 mm and made of metal.

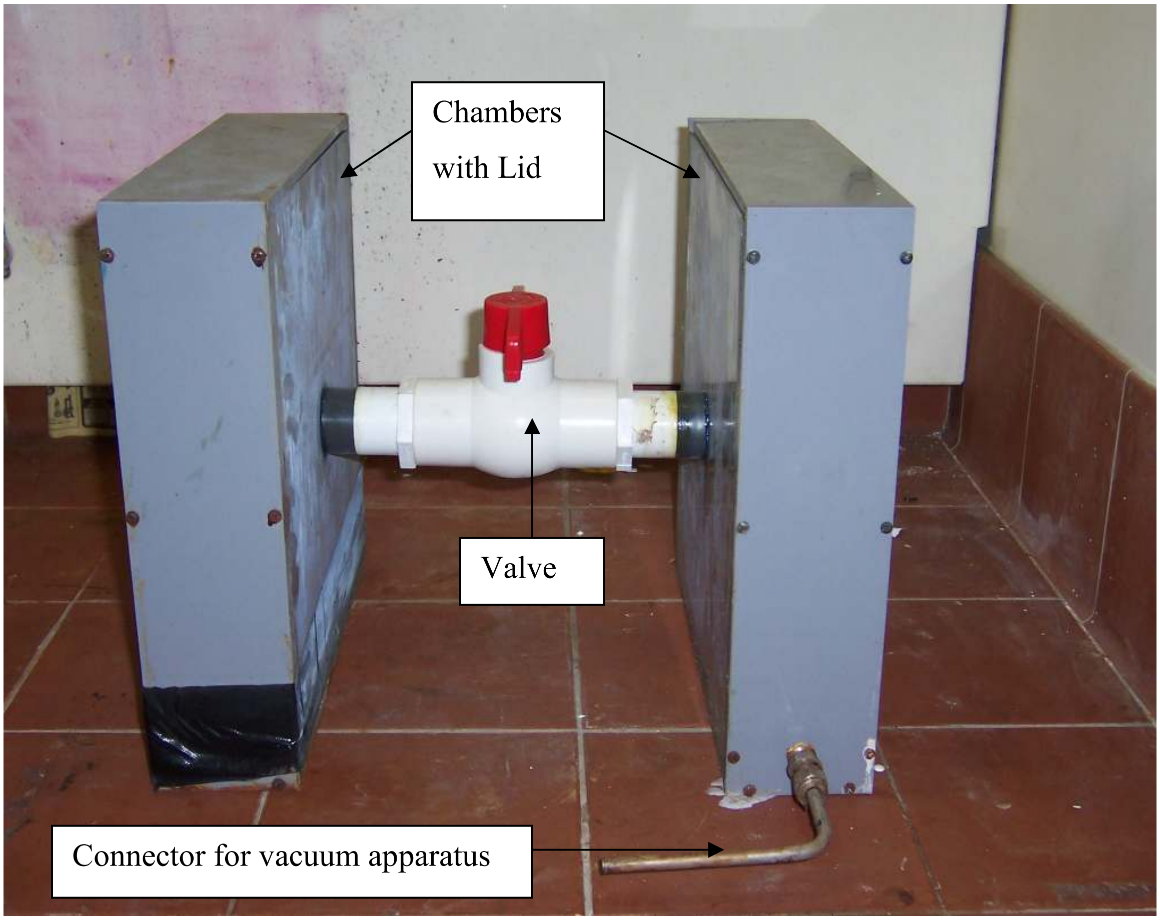

Figure 3. 4: Acid Exposure Chamber Assembly

Litmus papers were stuck at different heights and along all sides of the chamber where the paper was to be held. The valve was turned on and the vacuum system was operated so that the vapours would enter this chamber. It was found that the acid gas spread evenly throughout the chamber. This was evident from the uniform change in the colour of the litmus paper around the chamber. Handsheets of 30 gsm were acid exposed and tensile tested. The sheets were cut into four parts and the samples were cut from all the four parts and tested. This was necessary to ensure that the sheets were exposed evenly to the acid vapours and the exposure method could give reproducible results. 30 gsm sheets were chosen because of the low grammages. Thus an uneven acid exposure would be much more visible in a 30 gsm sheet than a 45 gsm or a 60 gsm sheet. It was found that the assembly provided an even acid exposure.

The operating procedure for the new acid exposure apparatus was:

1. The chambers were kept under a fume hood taking care that they were not twisted as this could have lead to breaking of the connecting pipe. The fume hood fan was turned on to take away the escaping gas if any.
2. Four 100 ml beakers were filled with conc. HCl (32%) and placed in the left hand side chamber of the apparatus. The lid was placed on top of the chamber to seal it off.
3. Paper samples were placed in the right hand chamber and the lid closed to seal off the chamber.
4. The valve was turned on.
5. Vacuum was applied using the Buchner funnel type arrangement and sheets were left for the desired exposure time in the chamber.
6. After the desired exposure time, the valve was turned off but the vacuum was still applied to rapidly remove the acid gas from the paper containing chamber (≈ 2 minutes).
7. The vacuum was turned off and the paper was removed.
8. The procedure was repeated for all the paper samples.
9. The fume hood fan was left on during the entire procedure as a safety measure.

3. 5 Sheet Making Procedures

Specialized procedures were used for sheet making. The pulp preparation, screening operations and the equipment used will be discussed in the subsections ahead.

3.5. 1 Pulp Preparation and Screening

The raw material used for these studies was unbleached Radiata Pine pulp, never dried, 60% yield and 24% dry content as sourced from Australian Paper's Maryvale mill. 316 gm oven dried pulp was mixed with 23 litres of water (0.01% consistency) and beaten in a Valley beater for 12 minutes. The Valley beater accommodates a maximum of 360 gm oven dried (O.D.) pulp and the beater operates with 23 litres of water. The freeness of the pulp was tested using the Canadian Freeness tester (Figure 3. 5) as per AS 1301.206s-88. The freeness of the pulp before refining was 720 CSF and after refining it was 610 CSF.

The next stage was screening the pulp to remove the shives and the fines. This was a multi-stage screening operation achieved with the help of two vibrating screen holders as shown in Figure 3. 6 The 0.2 mm slotted screen (Figure 3. 7) was used to remove the shives and the fines were allowed to pass through the 200 mesh screen (Figure 3. 8).

Figure 3. 5: Canadian Freeness tester

The screens were placed in the screen holder and the diluted pulp (23 litres of slurry at 0.01% consistency diluted to 69 litres at 0.003% consistency) was poured through the screens, 500 ml at a time and screening was done for 10 minutes before adding the next 500 ml of slurry. The screens vibrate using an electronic motor.

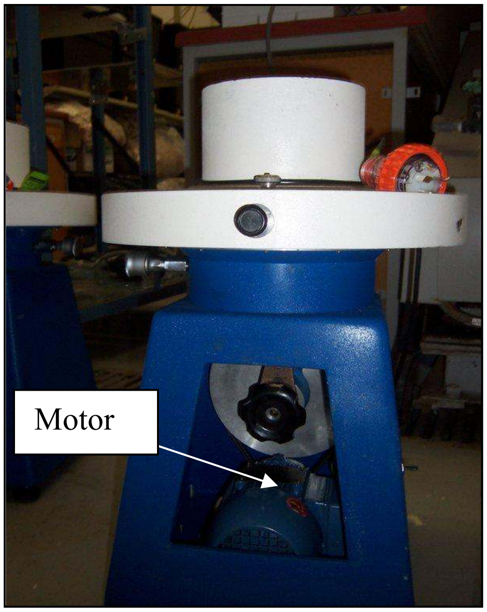

Figure 3. 6: Screen Holder with motor

The shives stay on the slotted screen whereas the fines pass through the 200 mesh screen thus leaving the middle fraction which was used in sheetmaking.

Figure 3. 7: Slotted screen (0.2mm)

The pulp slurry was then passed over a dewatering apparatus, again using a 200 mesh screen and the excess water was removed.

Figure 3. 8: Screen (200 mesh) used for removal of fines

Dewatering was done using a COW machine to help store the pulp. The COW is a vacuum apparatus which has a detachable funnel shaped container with a screen. Different sized screens can be fitted on the main screen. The assembly is connected to a vacuum pump. The slurry is poured into the funnel shaped container and the vacuum is applied. The water is sucked out from the funnel due to the vacuum and a dry mass of fibres is obtained. The operation can be repeated till the desired level of dryness is achieved. The dry content of the dewatered pulp was checked and found to be 24%. This pulp was then kept in storage. These operations were repeated for each set of experiments to measure the bond strength.

3.5. 2 Sheet making operation

The sheet making operation was carried out using specialized equipment known as the Moving Belt Sheet former (MBSF). The MBSF was developed by modifying the Moving Belt Drainage tester (MBDT) [68] used to study the drainage properties of pulp. The Conventional laboratory handsheet makers possess a constant or falling pressure head during sheet formation, whereas on a paper machine the fibre suspension experiences strong positive and negative pulses during the web formation. The constant pressure creates a z-directional distribution of fines and fillers which does not resemble that on the paper machine. In addition, suction application times; typically 1 to 30 seconds with the conventional handsheet makers do not correspond to those used on commercial paper machines (pulses of 1 to 5 milliseconds, cumulative suction time some hundreds of a millisecond). Scraping action by the leading edges of the suction box is also found to be essential. To overcome these limitations, a new type of laboratory drainage tester was built. The MBDT was originally designed to studies of vacuum assisted dewatering. The first version was built in 1990 by the laboratory of Paper Technology, Helsinki University of Technology, Finland. An enhanced version was built for the Australian Pulp and Paper Institute in 1995.

The essential features of the tester are:

1. An adjustable high vacuum pulse frequency.
2. A scraping of the underside of the wire imitating the operation of the leading edge of the suction boxes.
3. An adjustable suction profile during the sheet forming.
4. A timed injection of retention and drainage aids.
5. A stirrer to mix pulp slurry (has been modified at APPI).
6. Formed handsheet can be removed for testing purposes.

The tester is provided with the measurements of suction level and air flow rate through the formed sheet. Computer control enables an accurate and repeatable operation [69].

The following narration will now focus on how the MBSF works. On a paper machine, a web-wire combination moves over stationary dewatering elements. This results in short positive and negative pulses by foils and vacuum elements. In the MBDT the suction box and the wire are stationary. Between them there is a moving cogged belt with punched-hole rows (Figure 3. 9).

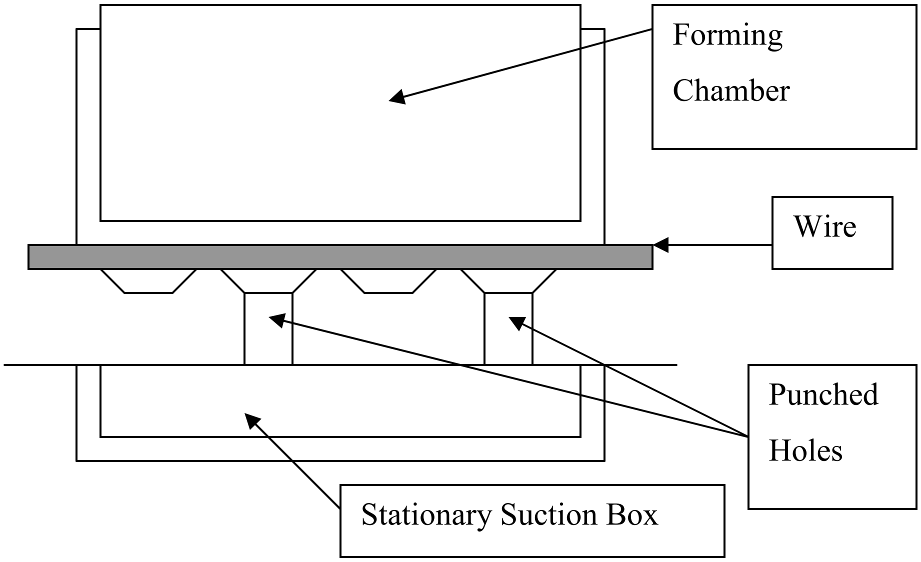

Figure 3. 9: Working of the MBSF (not to scale) [69]

The pulp slurry is exposed to the vacuum in the suction box through the cogged belt rows.

Figure 3. 10: MBSF

The duration of the individual pulses and pulse frequency depends on the speed of the belt given that the distance between the holes and the consecutive lines of holes is fixed for a given belt. This can be changed by changing the cogged belt.

One advantage of using the MBSF is its ability to affect the sheet structure in the z-direction. This is done by varying the pulse rate.

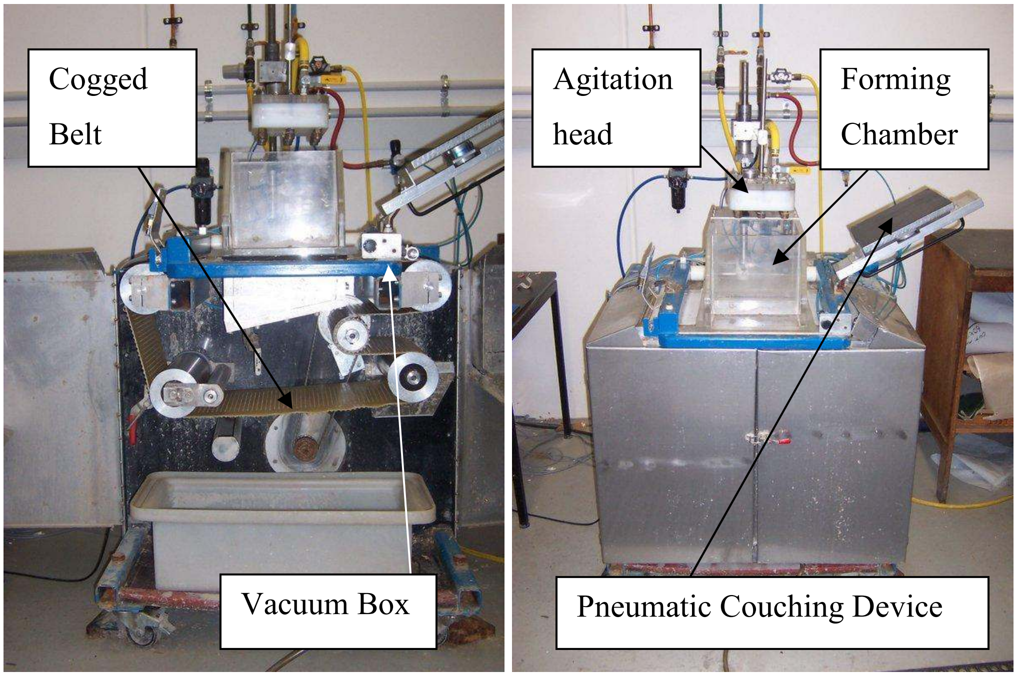

Figure 3. 11: MBSF parts

The higher the pulsation rate the more the fines and fillers are washed away from the wire side. The pulsation rate also affects the formation of the sheet. Depending on the furnish composition, the pulsation may disrupt the sheet or improve its formation. On a paper machine wire section, from the head box side to the couch, the vacuum profile is ascending. In the first wet section boxes the suction strength is typically from 2 to 10 KPa whereas in the flat boxes, the vacuum varies from 15 to 40 KPa and 40 to 80 KPa in the couch roll. This kind of ascending vacuum profile can be readily used with the MBSF. The vacuum level without a high vacuum pump can vary from 0 to 20 KPa. The maximum vacuum level with the external pump is up to 60 KPa, depending on the furnish type and the grammages of the formed sheet.

Fines content of the sheet is dependant on the vacuum profile used. High vacuum in the beginning of the drainage causes greater loss of fines and fillers than the slowly ascending vacuum profile. We are not concerned about the fines in particular in the experiments because ours was a furnish having both the shives and fines removed. One must note that while using very low freeness furnish, high vacuum in the beginning of the drainage seals the bottom layers of the forming sheet and consequently retards the drainage. As mentioned earlier, the MBSF is controlled by a computer.

There are two sensors in the MBSF: The pressure sensor and the airflow sensor. The pressure sensor sends direct voltage signal at a range 1 to 6 V, which is directly proportional to vacuum level it senses. Voltage value is converted by the software to engineering units of KPa using a calibration constant. The airflow sensor gives a voltage signal at range 1 to 5 V directly proportional to the air flow. The voltage is also converted to engineering units (l/min) by the control software.

Vacuum profile, frequency of suction pulses and the rotation rate of the stirrer (or in this case the injection speed) can be varied during experiments according to a preset program. Vacuum in the suction box is generated by three pneumatic ejector pumps. The ejectors generate suction according to their input flow. In practice it is easier to use the pressure control of the input flow which is provided with a proportional valve. The output pressure of the valve is directly proportional to the electric voltage signal. Thus if the pressure level of 3 bars into the ejectors is required, 3 volts is fed into the valve. The response time is approximately 150 milliseconds which enables some 7 pressure level changes in a second. The maximum vacuum is obtained with the feeding pressure of 5 bars. Pulsating suction is generated using a cogged belt with hole-rows between the suction box and wire. To vary the pulsation rate the belt speed must be changed. This is done using 3-phase inverter which changes the frequency of the electricity to the 3-phase motor according to the direct voltage signal given from the computer in the control file. The speed message is given in meters per second and it is converted to volts by the computer. The maximum belt speed is 12 m/s, but it has been found that one should not exceed 6 m/s for best results.

At APPI the forming chamber has a capacity of 9 liters with a forming area of 220 x 220 mm. The original stirrer used with the MBSF was a mechanical stirrer used to mix the pulp slurry and operated with the help of a motor. The MBSF (Figure 3. 10, Figure 3. 11) at APPI has however been modified [68, 70] and uses an injector stirrer (Figure 3. 12) instead of the conventional stirrer. It was found by researchers at APPI that rotating stirrers used with the MBSF produced “swirl marks” [68, 70] in the sheets which could possibly make the sheet inappropriate for further mechanical testing and studies [68].

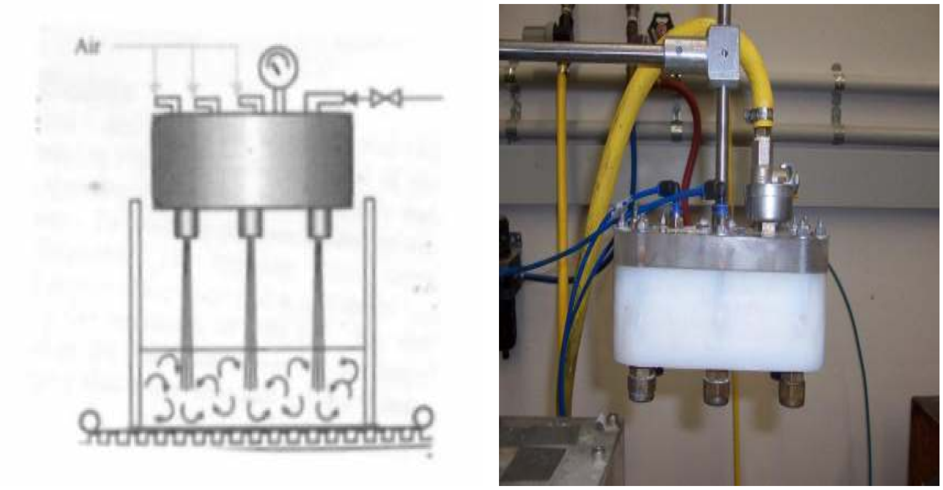

Figure 3. 12: Injector System of the MBSF; (Left)schematic diagram [68], (Right) actual configuration

The researchers investigated the use of ultrasonic agitation but the power requirements were found to be too high. Finally, a novel method was devised whereby very fine jets of water were injected into the stock [68, 70]. The induced turbulence results in thorough mixing of the stock without any unwanted orientation effects. The operation of the agitation head is as follows: The head is initially filled with water (~300 ml) with the help of gravity feed tank. Compressed air at 4 KPa is injected into the head to push the water through the jets with injection ceasing prior to complete evacuation of the head. The current head volume allows for approximately 5 seconds of agitation. The agitation head has proved to be very effective in producing uniform square sheets at near headbox concentrations. At the lowest forming concentration (0.05%) used in the MBSF, the agitation head can produce sheets with formation similar to that produced on a conventional handsheet maker. The moving belt was also modified so that the spacing between the holes was about 10 mm and the lines of the holes were about 40 mm apart. In vacuum dewatering studies it was found that significant rewetting of the sheet can occur after the vacuum has ceased. This rewetting can have a significant effect on the final solids content. The problem was overcome for this instrument by applying suction from above, around the edges of the sheet to remove any water from the surrounding wire. The software and the modifications make the moving belt sheet former a very versatile instrument.

3.5. 3 Sheet making procedure

The handsheets were made at 0.1% consistency initially and then at 0.05% consistency because it was found that the 0.05% consistency sheets showed better formation.

The procedure for making the sheets was as follows:

1. The pulp was taken in a tower with an air agitator at the bottom.
2. Water was added as per calculations to get the mixture to 0.05% consistency.
3. The MBSF was started and the program "Varad" was used.
4. The mat was extended and the forming chamber was placed on it, ensuring that it did not leak.
5. The agitator was filled and the slurry was added into the forming chamber.
6. The pump was started with the agitator in position and the program was then activated.
7. The handsheets were couched off from the forming mat and pressed.

The program "Varad" (Appendix I) was written specifically for these experiments. Changes to the vacuum levels, the stirrer speeds and the belt speeds were made while writing this program. The program has specific codes to activate the switch used for retracting the mat, starting the injector and allied operations. The details of the program can be found in the appendix.

Isotropic sheets were obtained using the MBSF. The sheets were tested using the Instron 5566 (Instron Tensile tester) tensile tester. Samples were conditioned at 23°C and 50% Relative Humidity (R.H.) as they dried and tested [71]. The 30 gsm sheets were tested for their isotropic nature and the results shown in Table 3. 2 confirm that the sheets were isotropic.

Parameter	**Direction 1**	**Direction 2**
Number of tests	15	15
Average Tensile Index	27.7	26.4
95 % Confidence interval for average	1.2	1.3
Standard Deviation	3.2	3.5

Table 3. 2 Results for Isotropic nature of sheet calculations

The MBSF makes sheets from which 26 to 28 samples for tensile testing can be obtained.

All sheets were pressed at “0” MPa twice to get rid of the excess water gently. The “0” MPa step was necessary because the sheets started cracking when directly put under a high pressing pressure. The sheets were then pressed at “0.275” MPa twice and put in special stacks for restrain drying in a conditioned test room set at standard temperature of 23°C and standard humidity of 50%.

3.5. 4 Identification of broken and pulled out fibres

Several ideas were tested about the best way to identify the fraction of broken and pulled out fibres. The first method that was tried was to dye a fraction of the fibres used for sheet making. Pergabase Violet dye from CIBA specialty chemicals was used for this purpose. The idea was that the dyed fibres could be observed under the microscope (Olympus BX 60) (Figure 3. 13) and it could be checked if the fibres were broken or pulled out.

Figure 3. 13: Dyed fibre observed under the Olympus BX 60

Initially a dye concentration of 1% w/w (in solution) was used. 3 grams of fibre were dyed using 2 litres of dye. It was found that at this concentration, the dye seemed to interfere with the bonding. The sheets were weaker when compared with the undyed sheets (Table 3. 3).

Type of Sheet	Number of tests	Average Tensile index (Nm/g)	Standard Deviation	95 % Confidence Interval
Dyed (30 gsm)	14	27.7	2.4	1.3
Undyed (30 gsm)	14	52.8	3.9	2.6

Table 3. 3: 30 gsm dyed-undyed sheets comparison (1% dye concentration)

It can be seen from Table 3. 3 that the tensile index drops by 50% for a sheet dyed at 1% dye concentration.

This difficulty was overcome by reducing the dye concentration to 0.5%. This concentration was found to be optimum because the fibres were dyed well and the dye did not interfere with the strength or the bonding of the sheets (Table 3. 4).

Type of Sheet	Number of tests	Average Tensile index (Nm/g)	Standard Deviation	95 % Confidence Interval
Dyed (30 gsm)	14	51.3	4.4	3.3
Undyed (30 gsm)	14	52.9	3.9	2.6

Table 3. 4: 30 gsm dyed-undyed sheets comparison (0.5% dye concentration)

The dyeing procedure was quite simple and involved putting 2 ml of dye in a water container and diluting it till the desired concentration was obtained. The pulp to be dyed was then put into the container and a simple stirrer running at low speeds was used to stir the dye slurry. After about 10 minutes, the slurry was taken and the pulp was repeatedly washed till all of the excess dye was removed or in other words till the dye stopped bleeding. This stage was very important because any extra dye would have meant interference in the fibre bonding and an undesirable effect on the results. The sheets containing the dyed fibres were tested and it was found that the dye did not affect the strength of the sheets.

The next challenge after the dyeing procedure was to expose the dyed sheets to acid vapours and see if there was any interaction between the dye and the acid. The sheets were exposed to acid and then tested for tensile strength.

A comparison of completely dyed and undyed sheets was made and it showed that the dye did not have any negative effect on the strength of the paper sheet (Table 3. 5).

Type of Sheet	Number of tests	Average Tensile index (Nm/g) after acid exposure	Standard Deviation	95 % Confidence Interval
Dyed (30 gsm)	14	22.8	2.8	1.5
Undyed (30 gsm)	14	24.1	3.7	1.9

Table 3. 5: 30 gsm dyed-undyed sheets after acid exposure [120 mins] (0.5% dye concentration)

How ever, it was found that a conventional microscope (Olympus BX 60) was not able to give a high resolution images (Figure 3. 14) and also the images weren't easily processed using image processing software. Therefore it was concluded that this technique was not suitable for measuring the fractions of broken and pulled out fibres.

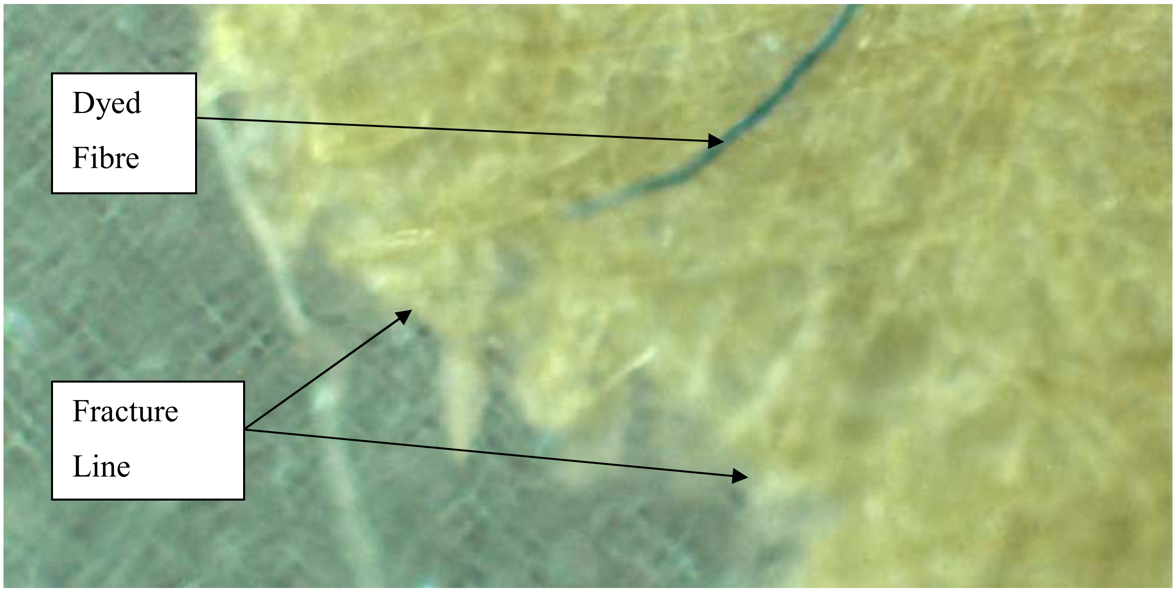

Figure 3. 14: Fracture line and dyed fibre (Conventional microscope)

The confocal microscope was thought to be a more suitable instrument for the job since with the confocal one can directly observe the fracture line in the sample and see if the fibre ends are broken. The use of the confocal meant that there was no need to dye the sheet initially with Pergabase Violet. Instead the plain sheets were made and after tensile testing were dyed with acridine orange dye.

The dyeing procedure was as follows:

1. The sample was put into a beaker containing acridine orange and allowed to soak up the dye for about 10 minutes.
2. The sample was then allowed to dry out on a blotting paper so that the excess dye and water were removed.
3. The sample was then put into a small dish containing oil and this dish was put inside a vacuum chamber.
4. A vacuum was applied and the sample was allowed to be completely impregnated with oil.
5. The impregnated samples were kept for about 24 hours in the dish and were then observed under the confocal microscope.

3. 6 Microscopy Procedures

The Confocal Microscope (Figure 3. 15) is a specialized instrument which makes use of an argon ion laser (λ=480 nm) to generate high resolution images. A confocal microscope (Optiscan F900e with a BH2 optical microscope) was used in this study to look at the fibres after they had undergone treatment. The advantage of using a confocal microscope is that by having a confocal pinhole, the microscope is really efficient at rejecting out of focus fluorescent or reflected light. The practical effect of this is that the image comes from a thin section of the sample. By scanning many thin sections through the sample, one can build up a very clear three-dimensional image of the sample.

Figure 3. 15: Optiscan F900e Confocal Microscope

The working (Figure 3. 16) of the confocal is explained in the following paragraph. The confocal microscope can operate in either florescence or reflectance mode. In reflectance mode, the image is the light that has been reflected from the sample. In fluorescence mode, fluorescence excited by the incident laser beam is detected. To use the fluorescence mode, the sample must either be naturally fluorescent or fluorescent dye must be added.

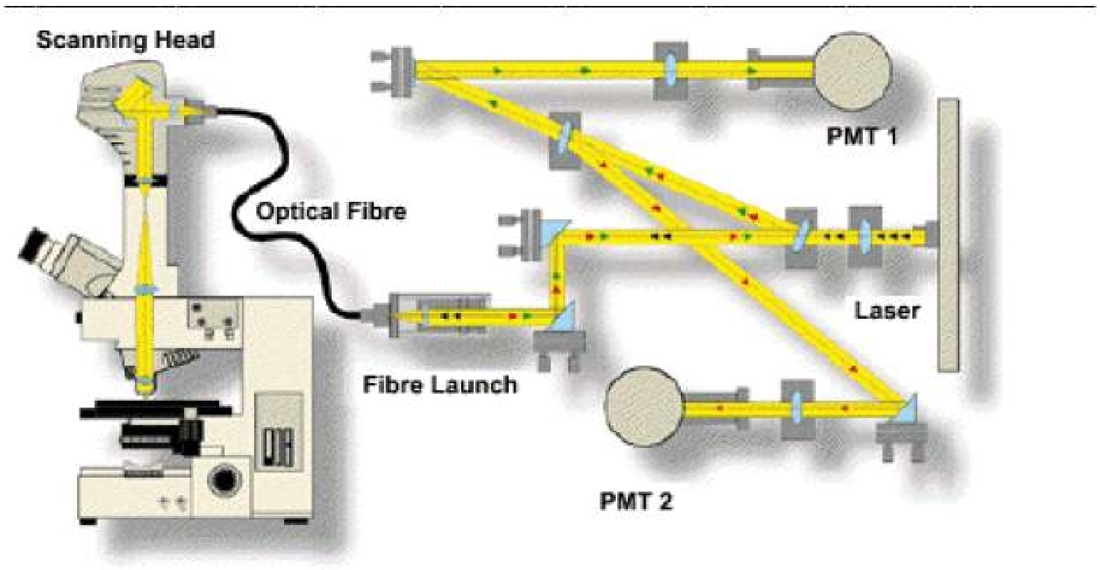

Figure 3. 16: The working of the confocal microscope [72] (from Optiscan Pty. Ltd)

The Optiscan F900e uses an optic fibre to deliver the laser light through the optic system of the microscope and to collect the light signal from the excited fluorescent dye contained in the fibres. The signal from the excited fluorescent dye is passed back through the optical path and through a small aperture, the confocal pinhole, before reaching an electronic detector or photo-multiplier tube (PMT). The PMT converts the light into a digital image displayed on a computer monitor. Because of the confocal pinhole, only light returning from on or very near the focal plane is permitted to pass through to the PMT. Light returning from anywhere other than the optical plane is blocked. This process creates an extremely thin optical section that can be positioned within a specimen to potentially provide a sharp image with a significantly higher resolution than a conventional microscope [72].

A 20X magnification immersion oil lens was used for observing the samples. The peculiarity of this lens is that it does not require a cover slip during observation. A drop of oil was placed on the slide so as to facilitate better lubrication of the lens. The laser was kept at a medium intensity so as to avoid bleaching of the sample. The confocal microscope penetrates to a depth of about 40 microns only and the sheets used were about 80 microns thick. Thus it was needed to flip the sample over and observe it from the other side and to observe as many samples as possible to ensure that the fibres that were examined were representative of the sheet. For the sake of uniformity, 150 fibres were observed for each data point. It is quite difficult to make out if a sample is well and truly broken but computer software, good quality lenses make the job much simpler.

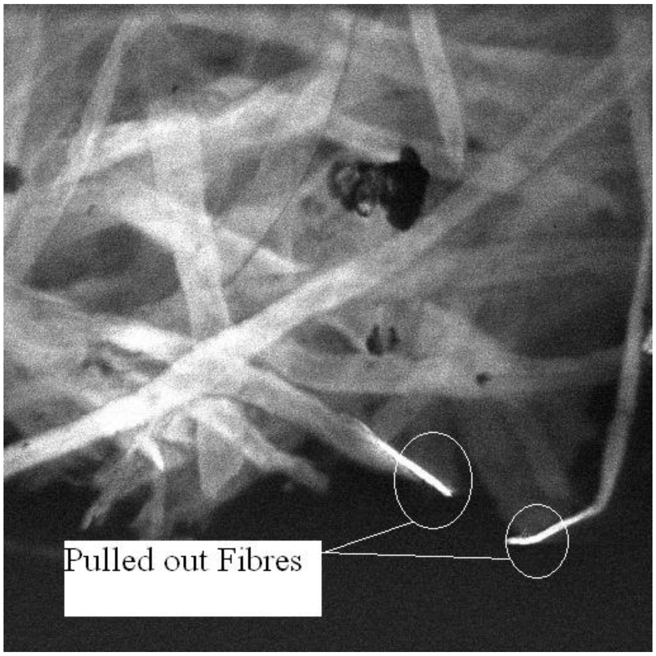

Figure 3. 17: Pulled out fibres along the fracture line of paper (Confocal)

Observe the pulled out fibre ends as appearing in Figure 3. 17. It can be observed that the fibres are extending a fair distance out from the fracture line. The fibre ends have a “tapered end” which is the characteristic feature of the end of a pulled out fibre. The tapered end is the thin elongated part of the fibre where it is broken and is circled in Figure 3. 18.

A clean break at the fibre end indicates that the fibre is broken. This can be observed in Figure 3. 19. The broken fibres do not stick out from the fracture line as much as the pulled out fibres.

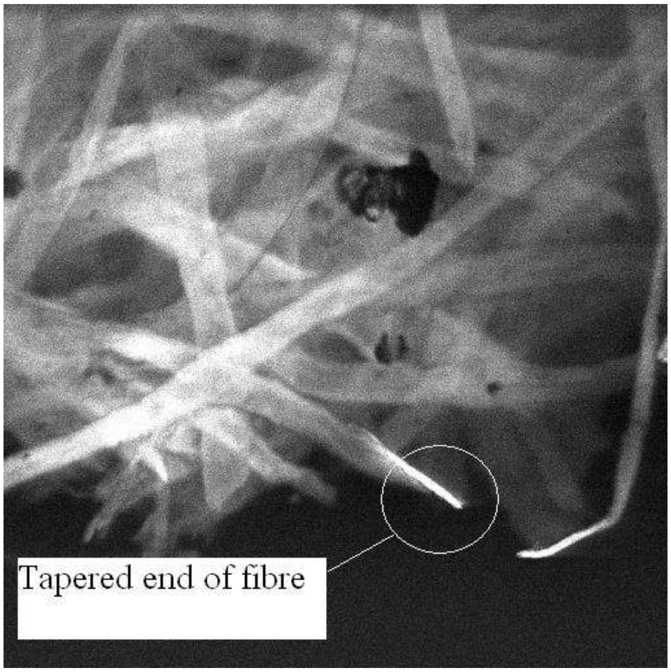

Figure 3. 18: "Tapered end" of a pulled out fibre

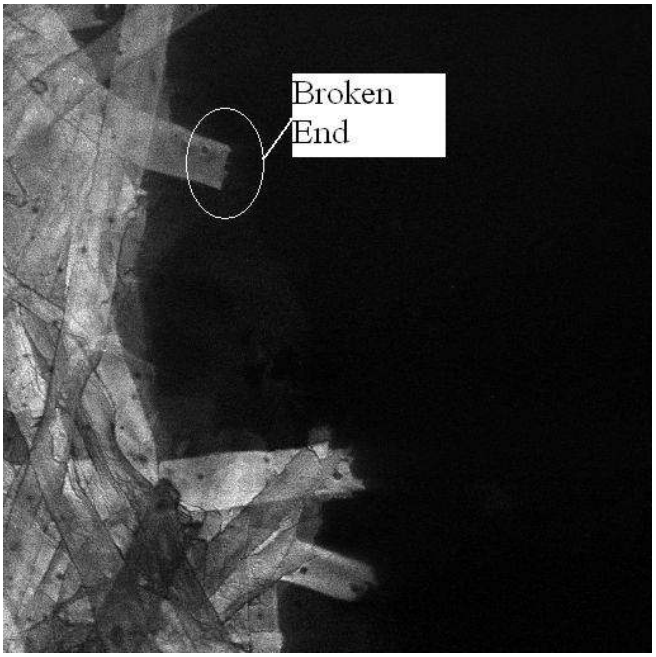

Figure 3. 19: Broken fibres along the fracture line of paper (Confocal)

It was quite difficult to judge which fibre to assess when observed under the confocal microscope. The method used was to include all the fibres along the fracture line which could be identified unambiguously as having a broken or pulled out end so as to not risk biasing the results.

Another important input that was measured using the images from the confocal microscope was the width of the fibre. IMAGE PRO 5 is image analysis software which was used for the purpose of measuring the fibre width. Fibre width was measured from the images using the built in drawing and distance options for converting pixels into distance.

3. 7 Tensile testing Procedures

It has been mentioned (3.5. 3) that the sheets were tensile tested using the Instron Tensile tester. Zero span tests were also conducted on the acid exposed sample sheets using the Pulmac Troubleshooter CT00403K instrument at CSIRO Forestry and Forest products.

The Zero span test was used in preference to testing single fibre strength as single fibre measurements are too tedious and time consuming. Fibre strength needed to be measured and hence the Zero span tests were used to measure the fibre strength.

3.7. 1 Instron Tensile Tester

Similar tensile testers to the Instron Tensile tester 5566 (Figure 3. 20) are found almost in all mechanical testing labs. The machine consists of two jaws (Figure 3. 21). One of the jaws is a fixed jaw and the other one is a moving jaw.

Figure 3. 20: Instron Tensile tester 5566

Figure 3. 21: Jaws of the Instron Tensile tester

The movement of the jaw is in the vertical direction. Horizontally moving high speed testers are also available but the vertical tester is the more common instrument used for the in-plane testing of material. Different types of plastics, films, paper, wood samples etc can be tested using the Instron. The jaws (Figure 3. 21) operate either manually or with the help of a pneumatic system which facilitates their opening and closure. The jaws of the Instron are so designed that they grip the specimen firmly. The jaws can be changed depending upon the type of material and the sample size. The instrument also allows changing the rate of separation of the jaws (mm/min) and also changing the span length for the test. The machine is linked with a computer and appropriate software. The software allows the user to access the machine more easily and helps make the use of the machine easier. The machine and additional computing facilities also allow the direct and easy calculation of the elongation, the maximum load and other data.

For the work in this thesis, tests were done according to ISO 1924-2 and the rate of separation of the jaws was 10 mm/min. The dimensions of the sample were 110 mm x 15mm. Samples were cut using a commercially available sample cutter for tensile test specimen.

3.7. 2 Zero span tensile tester

The Zero span tests have been used as a measure of the strength of individual fibres. However there are a few limitations for using this test, the major ones being:

1. A residual span may exist between the jaws of the tester, meaning that the true span between the jaws could be greater than the separation between the ends of the jaws.
2. Fibre defects like curls, kinks etc are known to have an impact on the zero span strength.

The tester (Figure 3. 22) has two jaws (Figure 3. 23) which clamp the sample horizontally and then move apart rapidly. The tester allows a zero span test and also tests at different distances between the jaws; e.g.: 0.05 mm, 0.01 mm, 0.15 mm, 0.2 mm, 0.3 mm, 0.4 mm and 0.6 mm. We used only the zero span tests where the jaws are touching each other and thus the span is effectively almost zero. Samples were prepared as per ISO 15361.

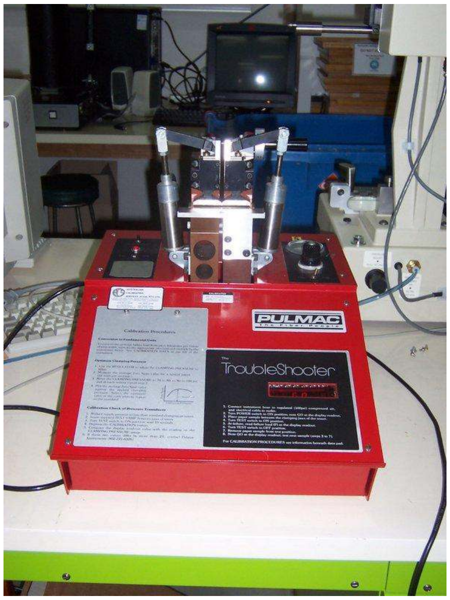

Figure 3. 22: Zero Span Tensile Tester

The sample is inserted between the two jaws which are almost touching each other and the machine is started. The jaws clamp down firmly on the sample firmly and hold the sample in place for a second, before starting to move outwards. The pneumatic cylinders help the firm clamping of the jaws.

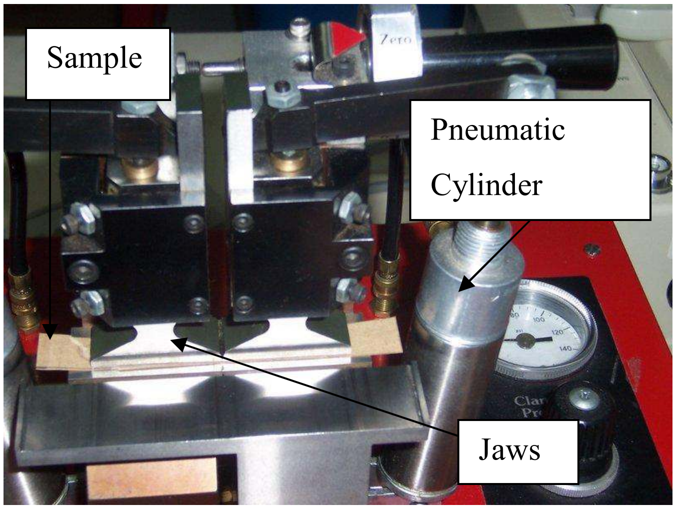

Figure 3. 23: Jaws of the Zero span tensile tester

The clamping pressure used was 0.41 MPa (60 psi). This was selected as the most appropriate value for the test because it is the clamping pressure at which the fibres are gripped firmly and yet not crushed. Clamping pressures of 0.48 MPa (70psi) and 0.55 MPa (80 psi) were also used and from the larger variations in the zero span test values, it is seen that these were not the optimum values for the clamping pressure (Table 3. 6).

Clamping pressures	**Number of tests**	**Average Zero Span Tensile index (Nm/g)**	**Standard Deviation**	**95% confidence interval**
0.41 MPa (60 psi)	12	30.5	2.5	1.2
0.48 MPa (70 psi)	12	30.6	3.1	1.4
0.55 MPa (80 psi)	12	31.9	3.7	2.1

Table 3. 6 Data for choosing optimum pressure (120 minutes acid exposed, 60 gsm sheets)

60 gsm sheets were chosen for the optimum clamping pressure experiments because they minimized the chances of formation effects biasing the zero span results which is observed in low grammage sheets.

The value for the maximum pressure, at failure is displayed on a small screen on the front panel of the machine. This is converted to kg-f/15 mm using the calibration given by the manufacturers. This was then converted to the zero span tensile Index

30 gsm, 45 gsm and 60 gsm hand sheets were made. Different grammages were used because the Zero span strengths tend to show an upward trend with reducing grammages (Figure 3. 24). It has been argued that the true zero span tensile index can then be calculated by extrapolating the graph to 0 gsm [14].

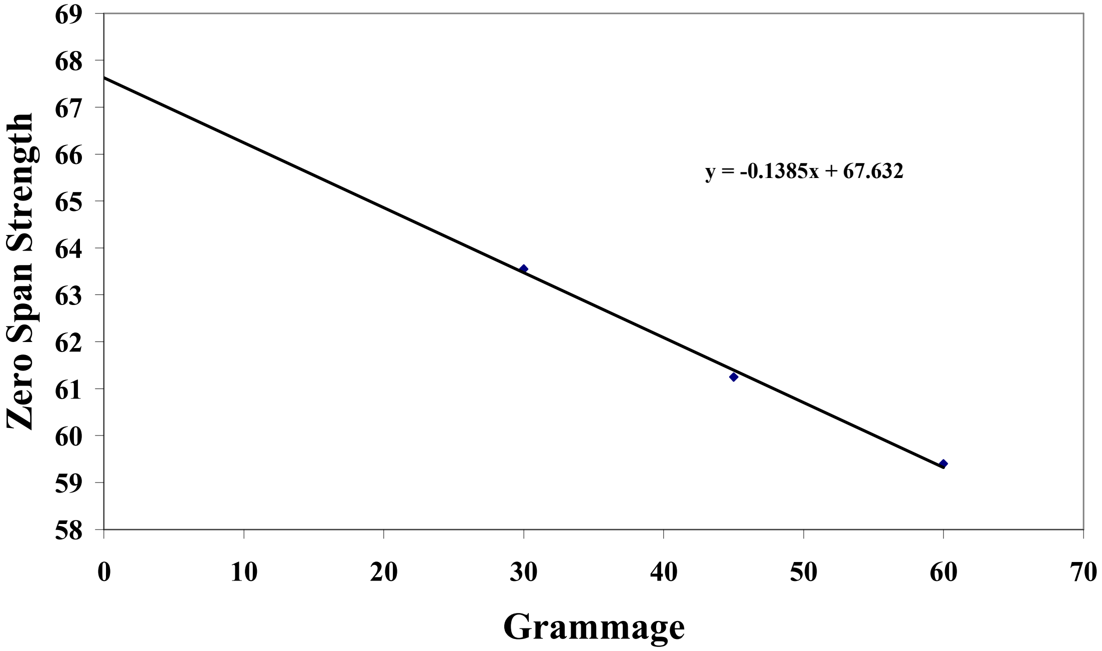

Figure 3. 24: Zero span strength vs. Grammages for never dried pulp

3. 8 Stepwise description of the experimental procedure

The complete final stepwise experimental procedure for the never dried pulp can be summarized as follows:

1. Never dried Radiata Pine Pulp, 60% yield was refined and shives and fines were removed using multi-stage screening operations (3.5. 1).
2. The pulp was dewatered (3.5. 1).
3. 30, 45, 60 gsm handsheets were made at 0.05% consistency (3.5. 1)
4. The sheets made in step 3 were restraint dried and conditioned at 23°C and 50% R.H.
5. The 60 gsm samples were exposed to the acid gas. Exposure times were 50, 60, 70, 80, 90, 100, 105, 110, 115,120,125 and 130 minutes (3. 4).

6. The acid exposed sheets were tensile tested and observed under a conventional microscope (3. 6).
7. The samples were dyed using acridine orange dye and observed under the confocal microscope (3. 6).
8. 150 fibres were counted manually to determine the fraction of fibres that had broken for each exposure time and the optimum acid exposure time was determined. The optimum acid exposure time was the smallest acid exposure time at which all the fibres across the fracture line failed. The procedure for fitting the data to determine the optimum exposure time is described in (4.2. 6)
9. Zero span tensile tests were conducted only at the optimum exposure time for the 30, 45 and 60 gsm samples.

The zero span strength was used to calculate the shear bond strength as described (4.2. 8).

3. 9 Drying Experiments

The first set of experiments was done using never dried fibres. Two more sets of experiments were performed to investigate the effect of drying.

The once dried handsheet experiments can be considered as step 4(a) in the procedure described (3. 8). The sheets were made as described in steps 1, 2, 3 and 4. The dried sheets were then put into the disintegrator and re-slushed. The operation was carried out by soaking the sheets for 4 hours in distilled water and then re-slushing them at 15,000 revolutions. The slurry was then used to make handsheets following steps 1, 2, 3 and 4. The further experiments were carried out as described step 5 onwards. The Shear bond strength was calculated and compared with the previous results.

The third set of experiments was to study the effect of heat on the shear bond strength. This can be considered as step 4(b) in the procedure described (3. 8). This experiment follows the procedures up to step 4. The dried sheets were then put into the disintegrator and re-slushed. The operation was carried out by soaking the sheets for 4 hours in distilled water and then re-slushing them at 15,000 revolutions. The slurry was then used to make handsheets following steps 1, 2 and 3 which were restrain dried at high temperatures of about 105 °C for 1 hour by keeping the stacks in a temperature controlled oven. The sheets were conditioned at 23°C and 50% R.H. Further experiments were as described step 5 onwards. The Shear bond strength was calculated and compared with the other two results.

Chapter 4: Results and Discussion

4. 1 Introduction

In the last chapter it was seen how the experiments were designed and what all steps were taken to be sure that the methodology was free of faults. In this chapter the results obtained from the experiments will be seen and discussed. The results will also be compared with the literature data discussed in Chapter 2.

4. 2 Data and Results

This part of the chapter displays the results obtained in the final experiments after the initial tests were done and the feasibility of the experimental technique was established. As discussed earlier, the acid exposure of the sheets was one of the critical parts of the entire experiment. The design of the chamber was such that the sheets were evenly exposed to acid (3.4. 1).

4.2. 1 Tensile Strength Measurements

The graphs of Tensile Index vs. Acid exposure time for the never dried fibres, once dried fibres and high temperature dried fibres are shown in Figure 4. 1, Figure 4. 2 and Figure 4. 3. The y-direction error bars indicate the 95% confidence intervals for the tensile index data.

It can be seen that the strength decreases with increasing exposure times. The data also seems to indicate that at a given exposure time the never dried fibres are stronger than the once dried fibres, which in turn are stronger than the high temperature dried fibres.

Transition points for the tensile strength can be observed on fitting the data. E.g.: For the never dried fibres, a first transition can be seen at 85 minutes of acid exposure.

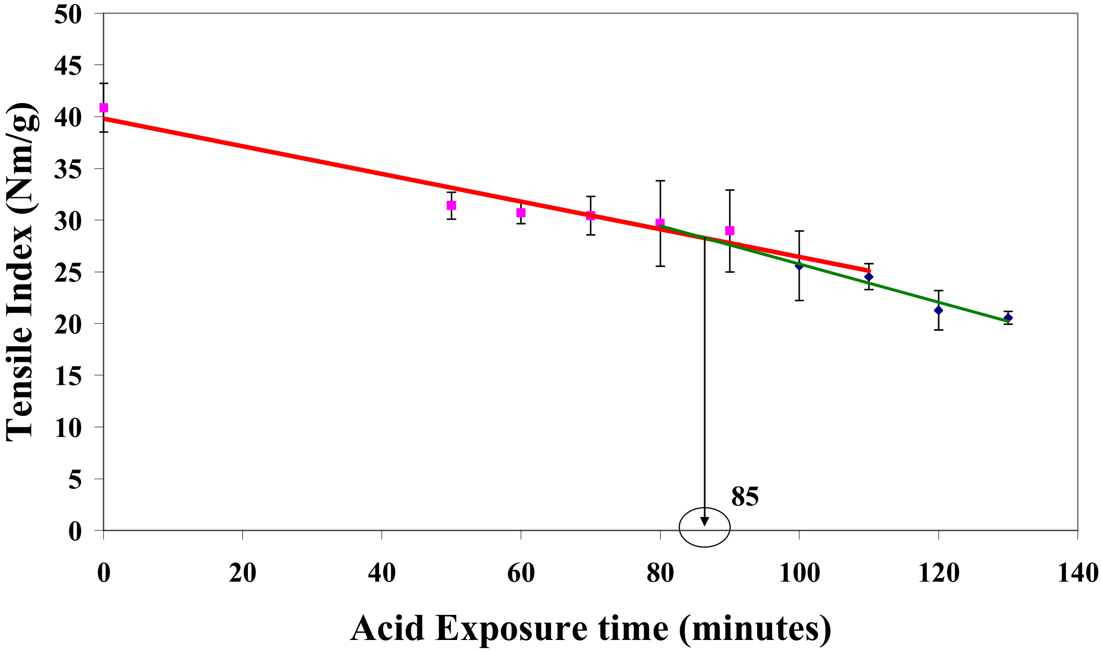

Figure 4. 1: Tensile Index vs. Acid exposure times for never dried sheets

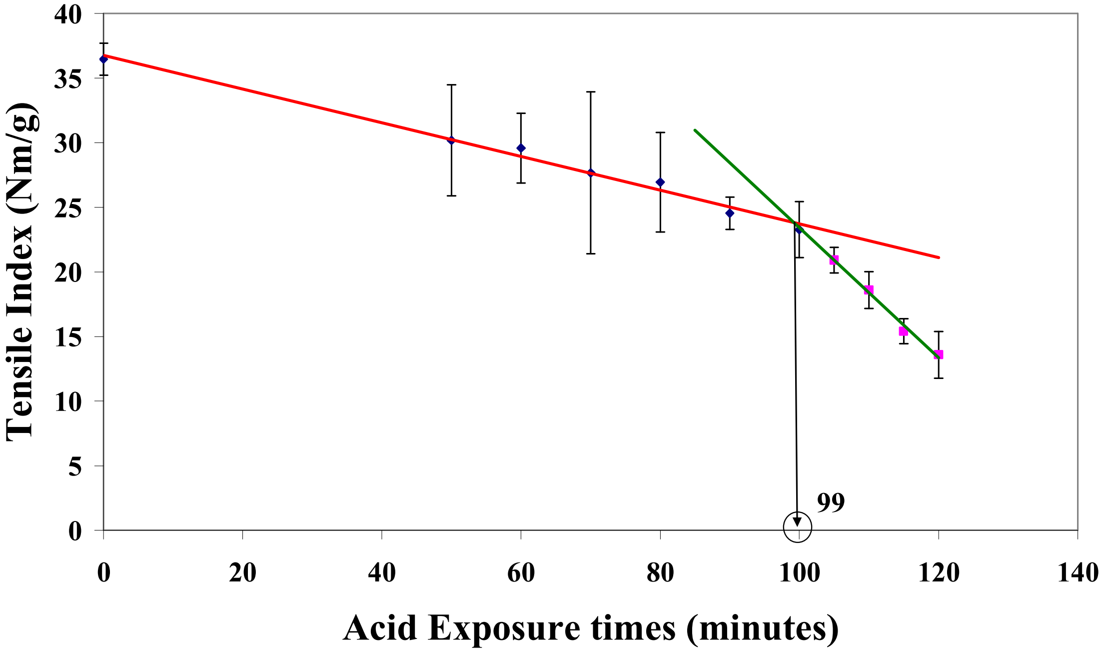

Figure 4. 2: Tensile Index vs. Acid Exposure times for once dried sheets

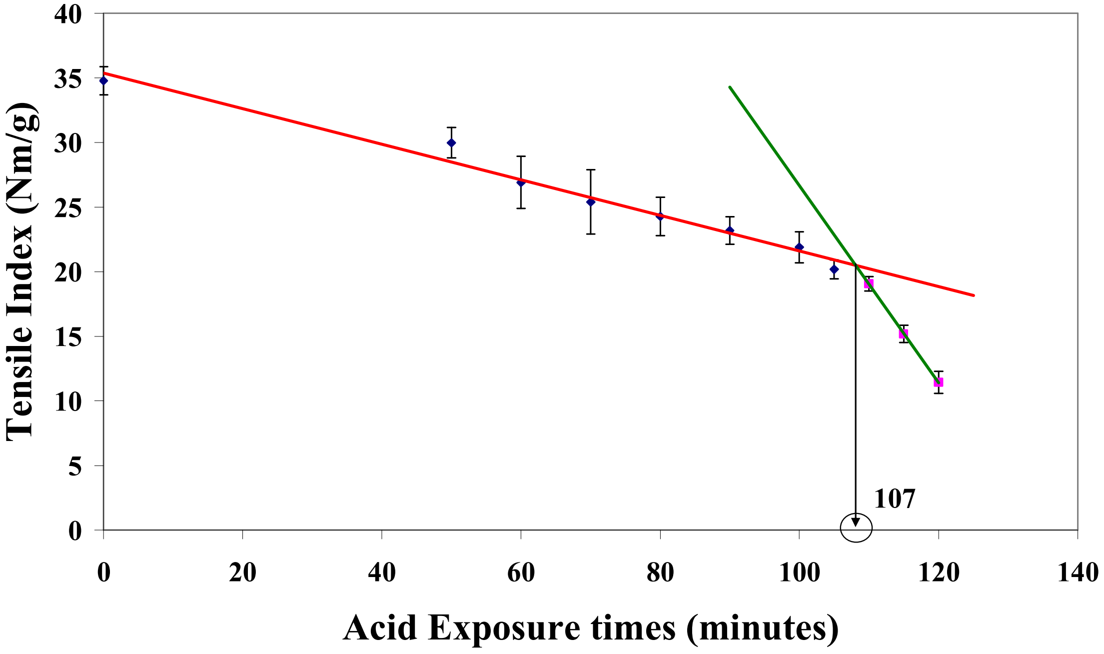

Figure 4. 3: Tensile Index vs. Acid Exposure times for High temperature dried sheets

Similarly, transition point at 99 minutes and 107 minutes can be observed for the once dried fibres and the high temperature dried fibres, respectively. Sheet fracture usually is a mixture of fibre break and fibre pull out. It could be that at the transition point the fracture mode changes from that of the mixture of fibre breaking and pull out to fibre breaking alone. In other words the transition point could be related to the optimum exposure point where the fibre strength is equal to the strength of one bond. This transition point will be compared with the optimum exposure point in (4.2. 6).

4.2. 2 Image Analysis

Observe Figure 4. 4. It shows the pulled out fibres and the broken fibres clearly. Pulled out fibres seem to have a tapered end and can stick out at a fair distance from the fracture line. The broken fibres on the other hand do not stick out that much and haven't got a tapered end, but a clearly broken end. The identification of pulled out and broken fibres has been discussed previously in (3.5. 4).

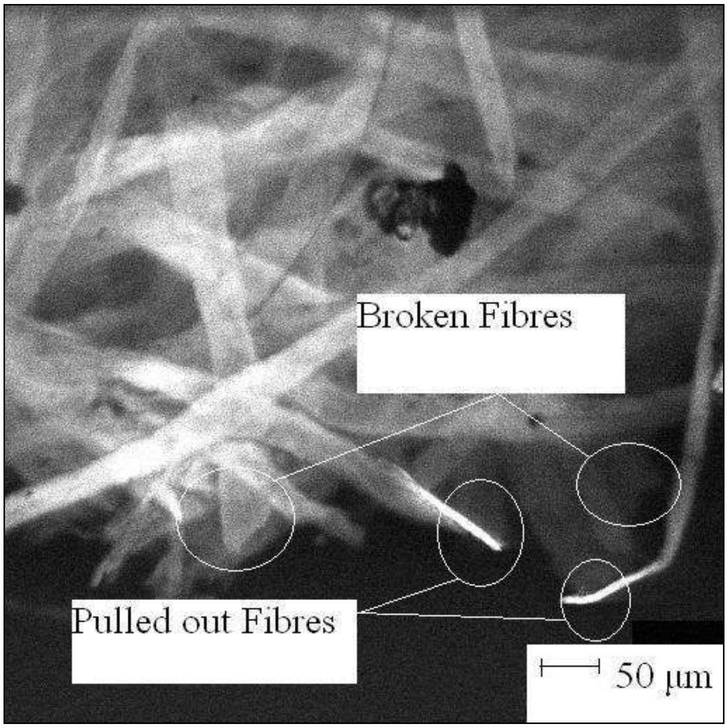

Figure 4. 4: Appearance of Broken and Pulled out fibres

Fibre width was measured using the in-built options of IMAGE PRO 5 software and the fibre widths were slightly different in case of each of the type of fibres. Fibre width was measured only at the optimum point. Table 4. 1 shows the measured fibre widths.

Type of Fibre	Fibre width (microns)
Never dried fibres	40 ± 1
Once dried fibres	42 ± 1
High Temperature dried fibres	44 ± 1

Table 4. 1: Measured fibre widths

4.2. 3 Never dried fibres

Figure 4. 5 to Figure 4. 11 show the appearance of the never dried fibres along different points on the fracture line at different levels of acid exposure.

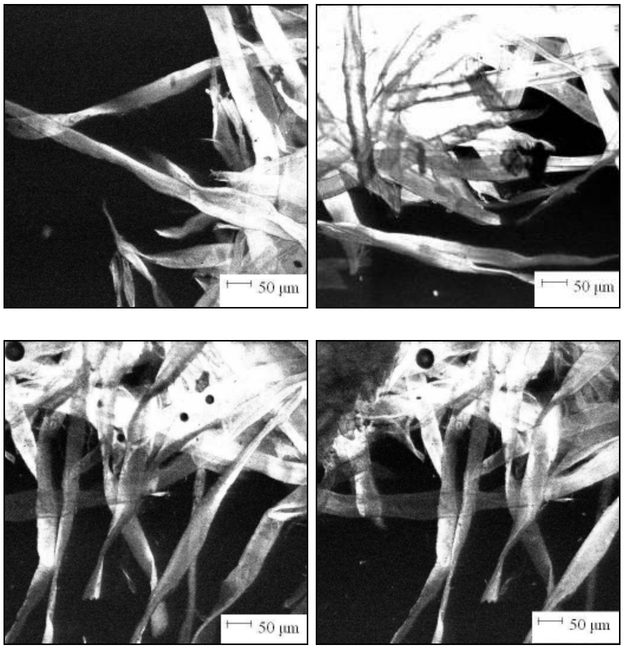

Figure 4. 5: Fracture line-never dried fibres (50 minutes)

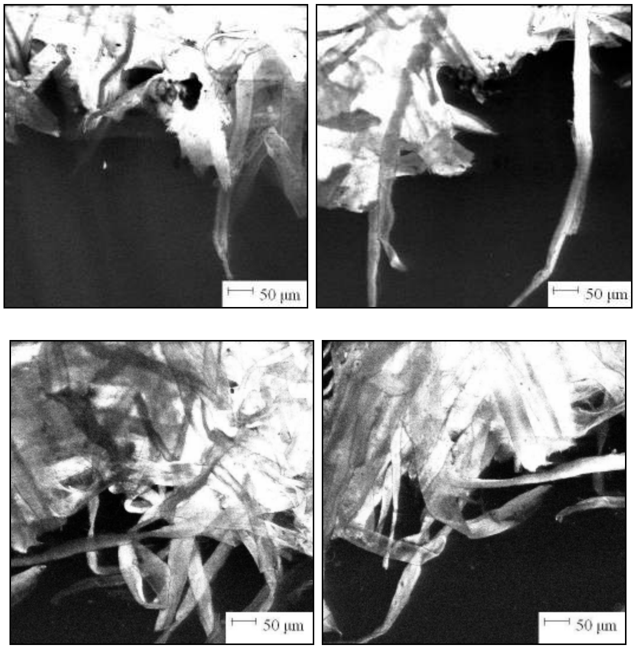

Figure 4. 6: Fracture line-never dried fibres (80 minutes)

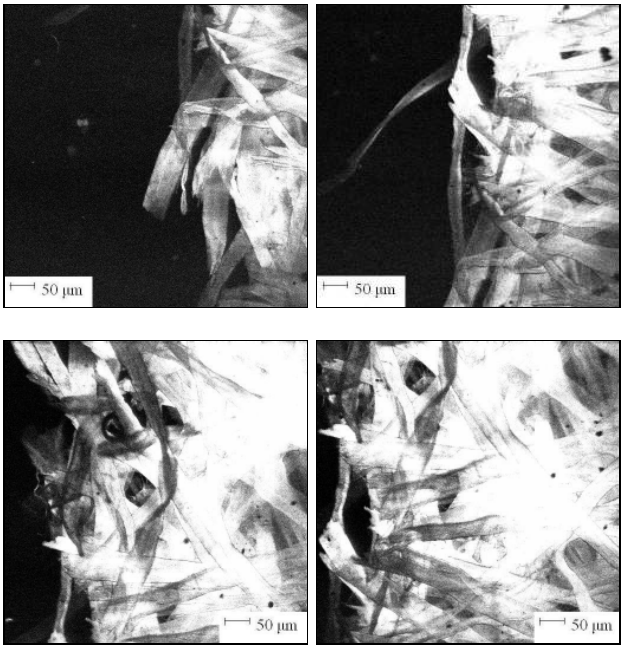

Figure 4. 7: Fracture line-never dried fibres (100 minutes)

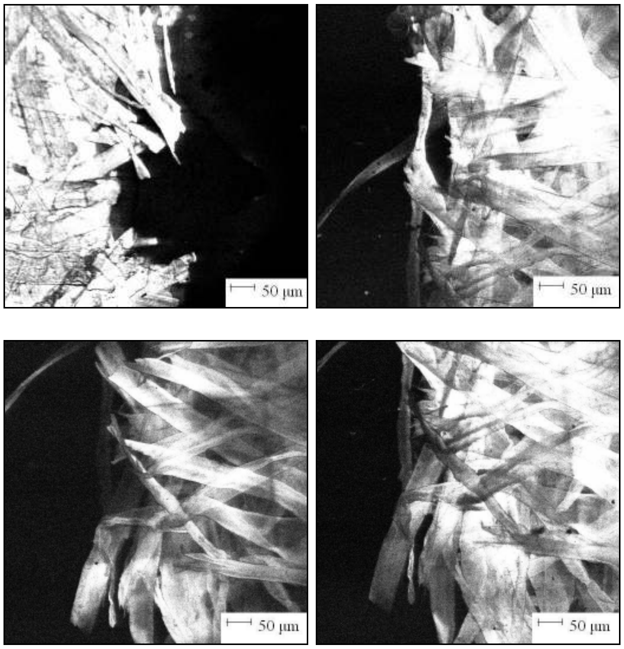

Figure 4. 8: Fracture line-never dried fibres (105 minutes)

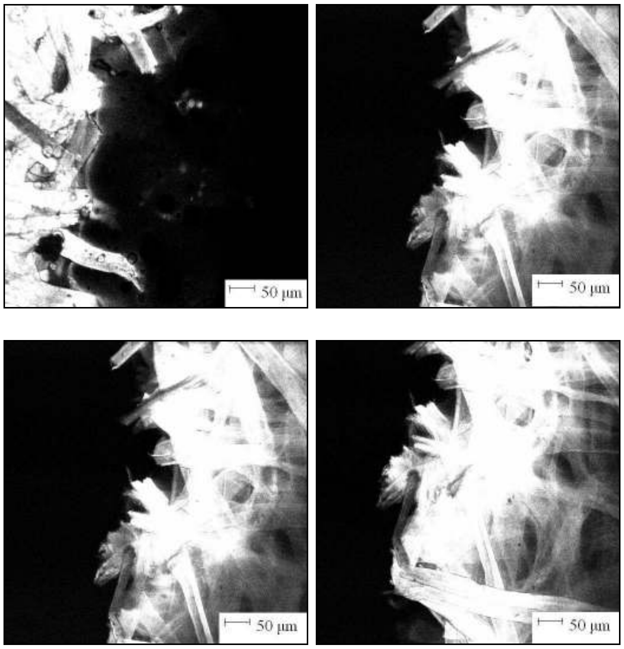

Figure 4. 9: Fracture line-never dried fibres (110 minutes)

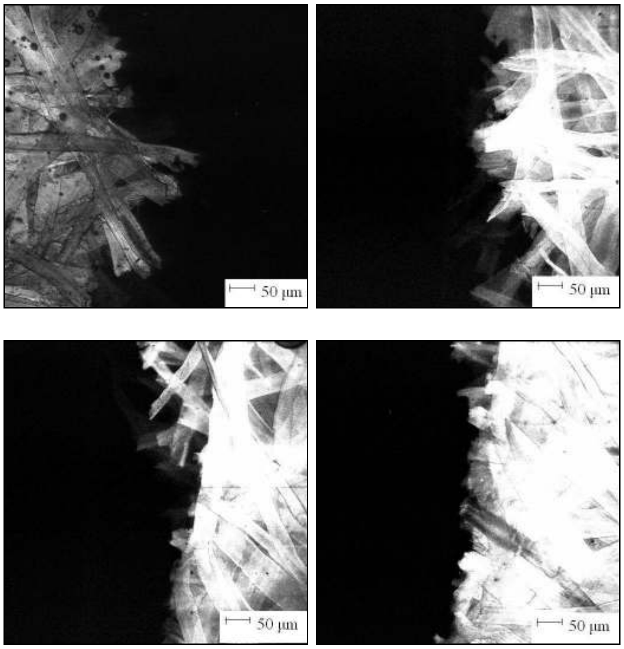

Figure 4. 10: Fracture line-never dried fibres (115 minutes)

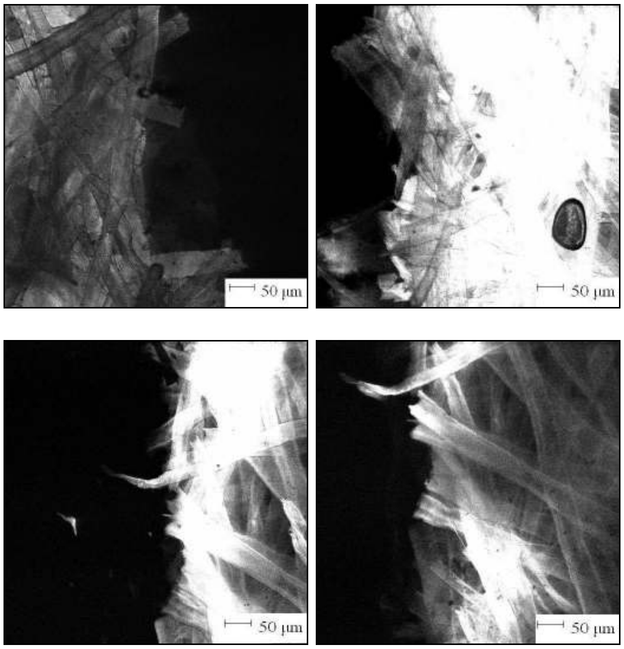

Figure 4. 11: Fracture line-never dried fibres (120 minutes)

4.2. 4 Once dried Fibres

Figure 4. 12-Figure 4. 15 show the appearance of the once dried fibres along different points on the fracture line at different levels of acid exposure.

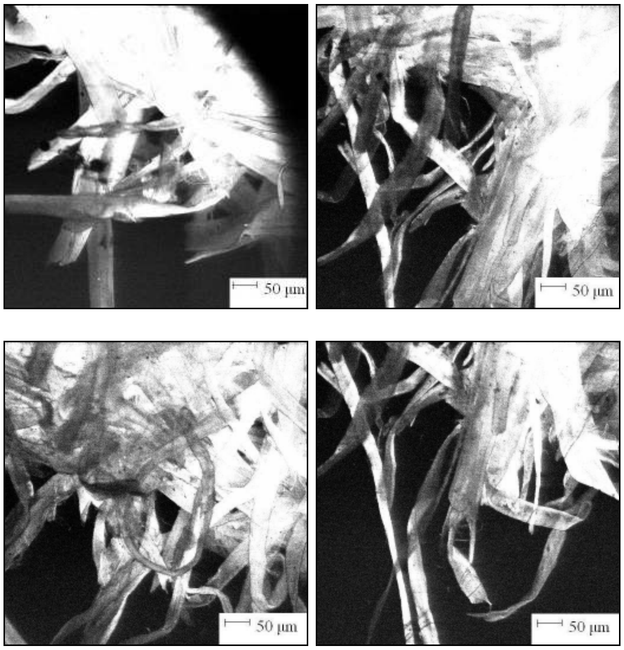

Figure 4. 12: Fracture line-once dried fibres (80 minutes)

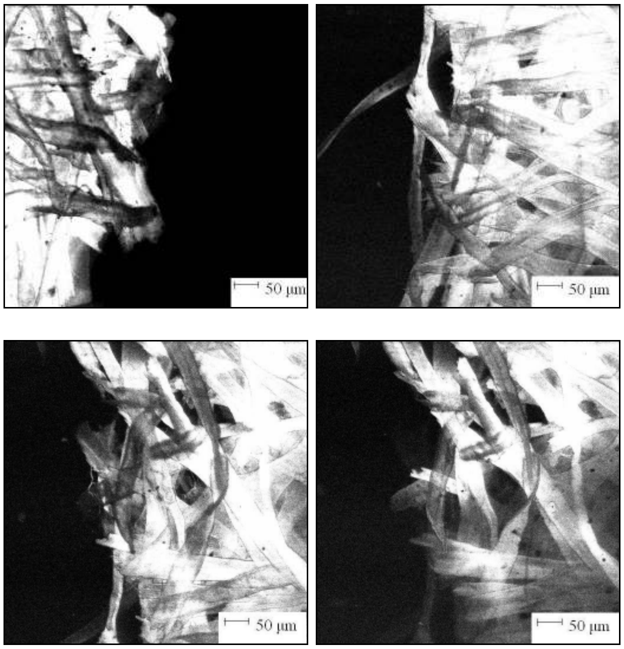

Figure 4. 13: Fracture line-once dried fibres (100 minutes)

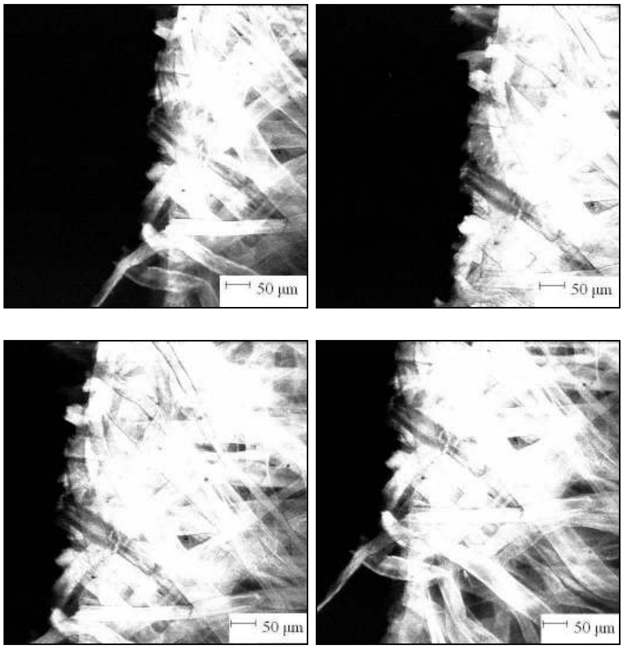

Figure 4. 14: Fracture line-once dried fibres (105 minutes)

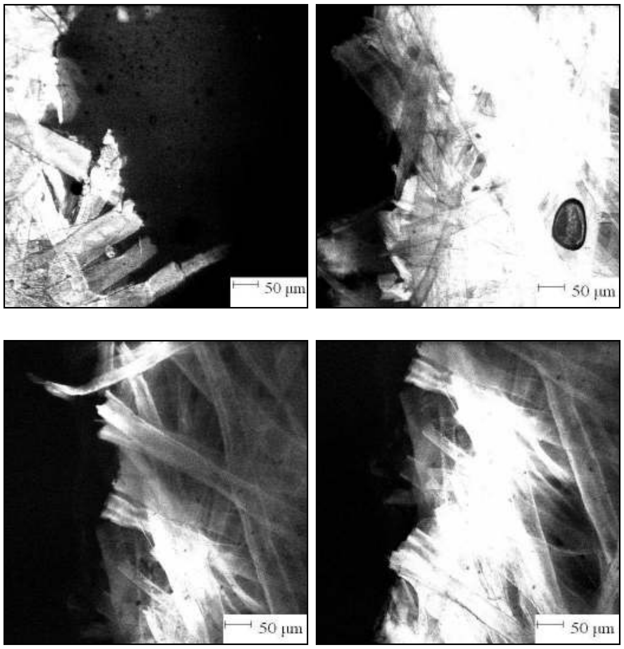

Figure 4. 15: Fracture line-once dried fibres (110 minutes)

4.2. 5 High Temperature dried fibres

Figure 4. 16-Figure 4. 19 show the appearance of high temperature dried fibres along different points on the fracture line at different levels of acid exposure.

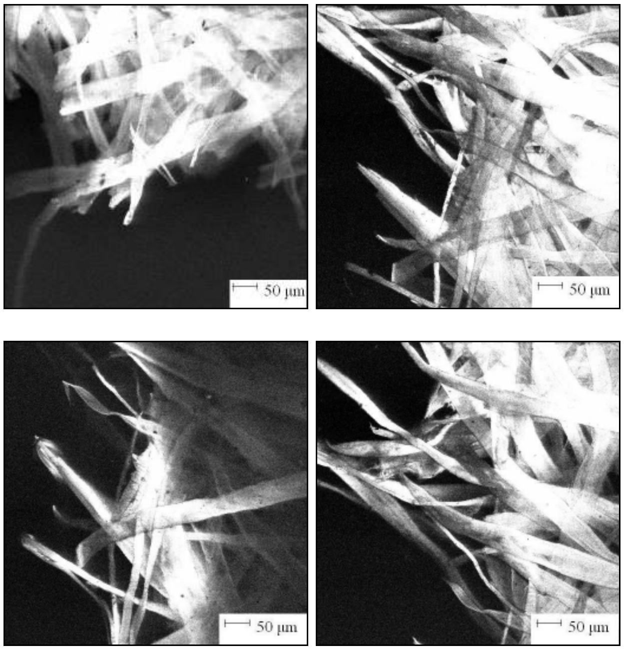

Figure 4. 16: Fracture line-high temperature dried fibres (80 minutes)

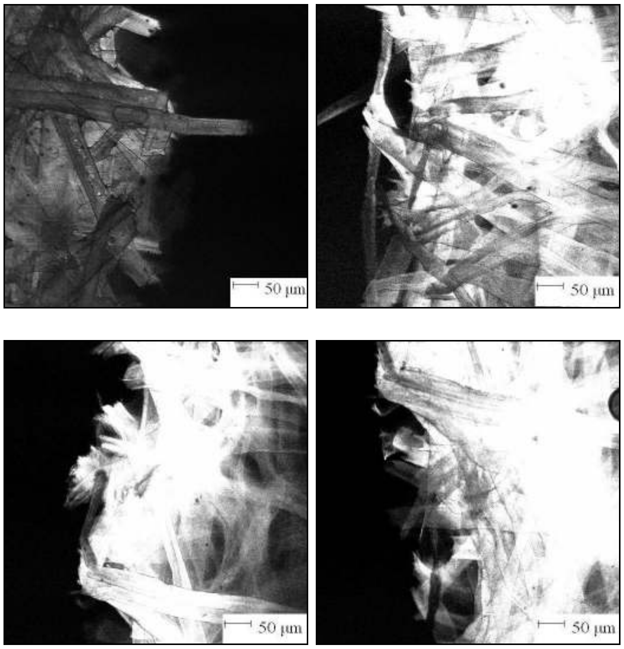

Figure 4. 17: Fracture line-high temperature dried fibres (100 minutes)

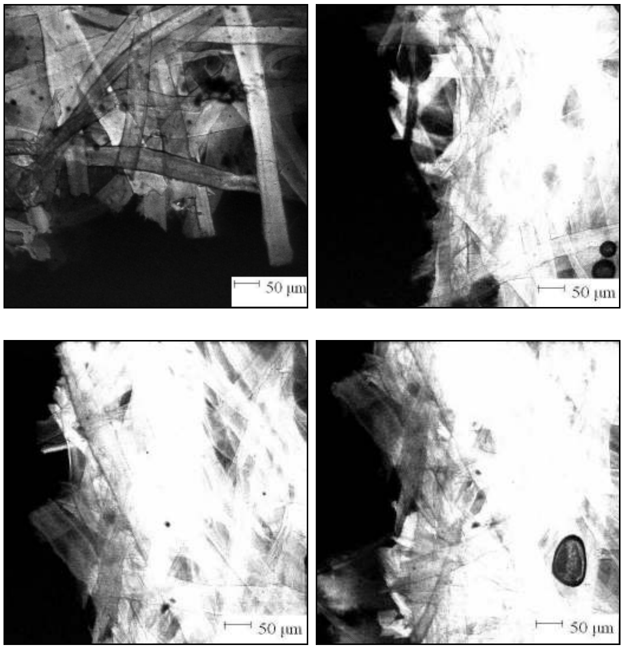

Figure 4. 18: Fracture line-high temperature dried fibres (105 minutes)

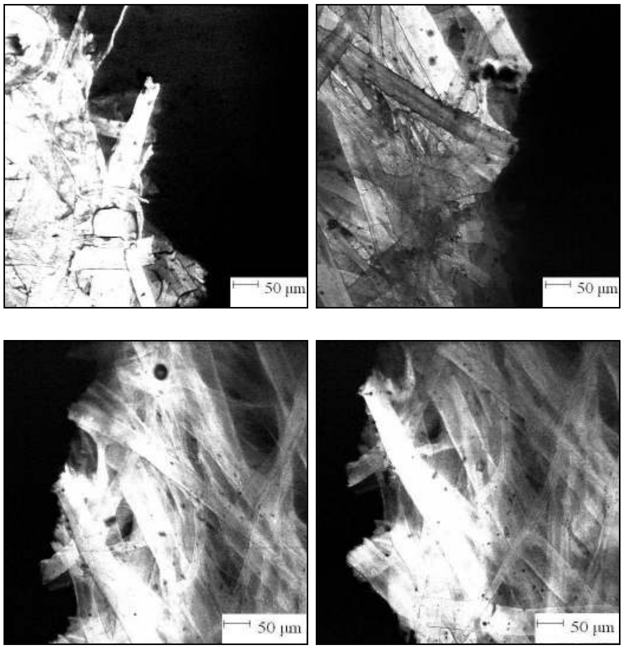

Figure 4. 19: Fracture line-high temperature dried fibres (110 minutes)

The image analysis was used to count the number of broken ends and number of pulled out ends along the fracture line for samples at different acid exposure times. This was then plotted against the acid exposure time and used to estimate the optimum exposure time as elaborated in the next section.

4.2. 6 Determination of Optimum exposure point

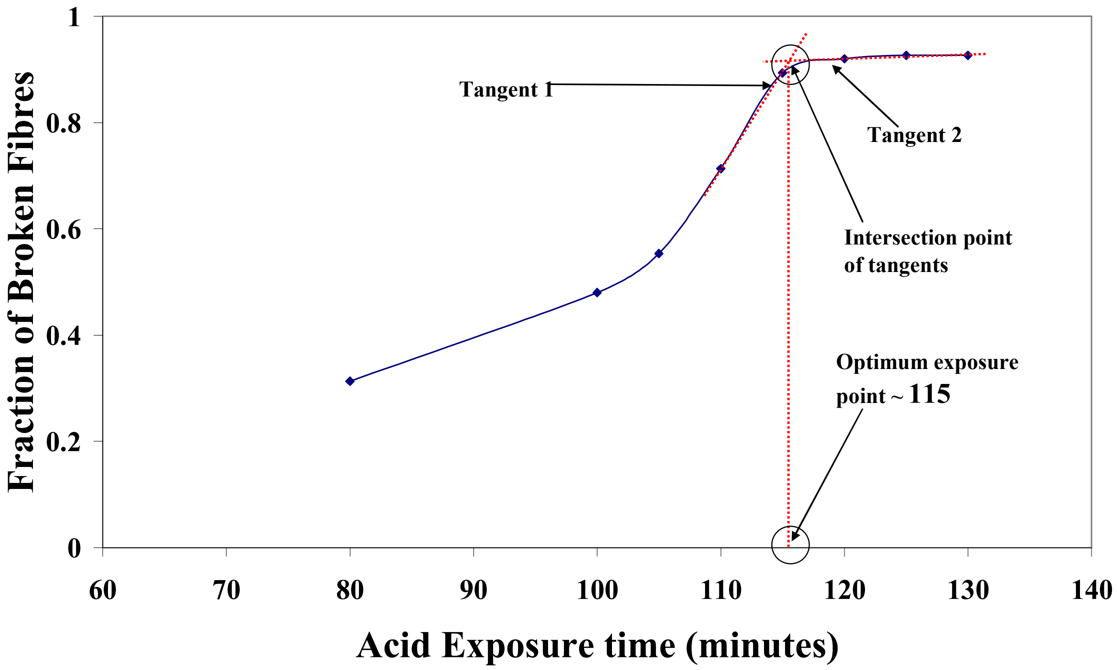

Figure 4. 20: Illustrating the optimum exposure point determination (never dried sheets)

The graph of Fraction of broken fibres vs. Acid exposure times (Figure 4. 20) shows how the optimum exposure time was determined. The graph shows that the number of broken fibres increases with increasing acid exposure time, reaching a plateau region at high exposure times. It can be seen (Figure 4. 20) that if tangents are drawn along the region where the graph changes its shape, then the tangents would intersect and give the optimum exposure time. The graphs change shape at two places as can be seen. The upper part of the "S-Shape" is the region where the tangents should be drawn as this is the region where all the fibres, except the ones bonded on one side only are broken. The optimum exposure time for never dried sheets is 115 minutes (Figure 4. 20). The optimum exposure times for the once dried and high temperature dried fibres was estimated in a similar manner and found to be 110 minutes and 105 minutes respectively.

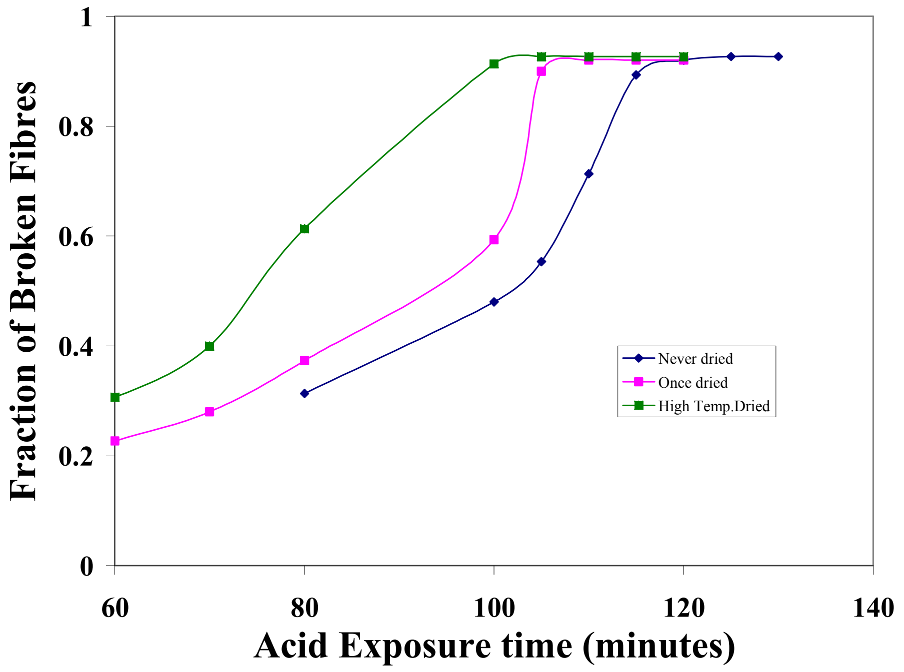

Figure 4. 21 Fraction of Broken Fibres vs. Acid Exposure time for never dried, once dried and high temperature dried fibres

Figure 4. 21 shows the data for the Fraction of broken fibres vs. Acid exposure times for never dried, once dried and high temperature dried fibres. The optimum points obtained from this analysis and the previous ones from the tensile index data are compared in Table 4. 2

Type of fibres	Optimum Exposure point	Optimum point (Tensile Index data)
Never dried	115	85
Once dried	110	99
High temperature dried	105	107

Table 4. 2: Comparison of optimum points

If the optimum exposure times obtained from the Tensile Index vs. Acid Exposure time and Fraction of Broken fibres vs. Acid Exposure time are compared then we notice that they are in fact quite different and thus tensile index data cannot be used directly to calculate the optimum exposure time.

4.2. 7 Tensile data at optimum exposure point

Table 4. 3, Table 4. 4, Table 4. 5 show the tensile index data at the optimum exposure time for the never dried, once dried and high temperature dried fibres. The tensile test refers to the values obtained from the Instron tensile tests and the Zero span values come from the zero span test.

Grammages		**Tensile Test (Nm/g)**	**Zero Span (Nm/g)**
30	**Average T.I.**	24.8	63.6
	S.D.	3.2	2.9
	95% C.I.	2.4	1.6
45	**Average T.I.**	21.3	61.2
	S.D.	1.2	3.9
	95% C.I.	0.7	2.2
60	**Average T.I.**	22.6	59.4
	S.D.	3.3	3
	95% C.I.	1.9	1.8

Table 4. 3: Tensile Index data for never dried pulp

Grammages		**Tensile Test (Nm/g)**	**Zero Span (Nm/g)**
30	**Average T.I.**	22	57
	S.D.	1.2	2.7
	95% C.I.	0.7	1.5
45	**Average T.I.**	18.4	59.9
	S.D.	1.1	1.8
	95% C.I.	0.6	1
60	**Average T.I.**	19.8	51.7
	S.D.	0.5	2.1
	95% C.I.	0.3	1.1

Table 4. 4: Tensile index data for once dried pulp

Grammages		**Tensile Test (Nm/g)**	**Zero Span (Nm/g)**
30	**Average T.I.**	19.3	50.5
	S.D.	2	3.6
	95% C.I.	1.1	2
45	**Average T.I.**	20.2	48.3
	S.D.	2.2	3.4
	95% C.I.	1.2	1.8
60	**Average T.I.**	21	46.2
	S.D.	1.4	2.5
	95% C.I.	1.4	0.8

Table 4. 5: Tensile index data for high temperature dried pulp

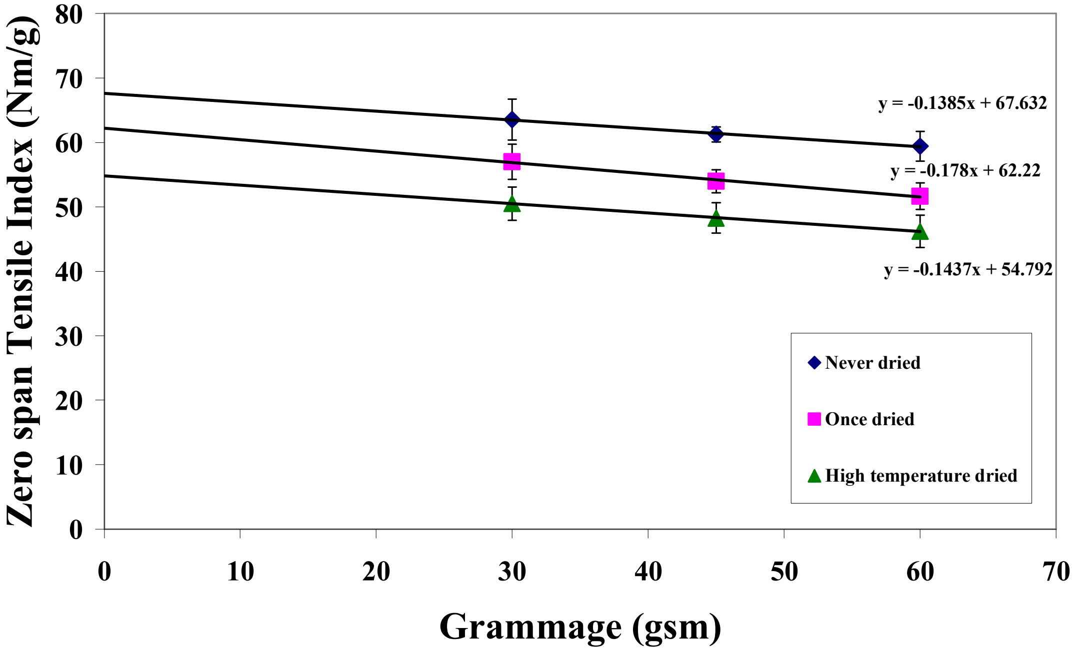

Figure 4. 22: Zero span Tensile Index vs. Grammage for different experiments

It is seen (Figure 4. 22) that the Zero span Tensile Index show an upward trend as the grammage is reduced. Never dried fibres appear stronger than once dried fibres which in turn appear stronger than the high temperature dried fibres. The upward trend seen for the Zero span tensile index as the grammage is reduced supports the idea by Batchelor et al [14] that the measured Zero span strength is always less than the intrinsic zero span strength and for best results the grammage of material should be minimized to obtain a value closer to the intrinsic true value at 0 gsm.

The values for the intrinsic zero span strength were obtained from the y-axis intercepts and are shown in Table 4. 6

Type of fibre	Intrinsic Zero span strength (Nm/g)
Never dried	54.7 ± 3.2
Once dried	62.2 ± 2.2
High temperature dried	67.6 ± 3.1

Table 4. 6: Intrinsic zero span strength values

Observing the Zero span tensile indices for the 60 gsm sheets only could be a way to speed up the measurements. However, it is cautioned that there are bound to be differences between the intrinsic zero span value and the zero span value at 60 gsm. There needs to be a correction, if this approach is pursued. An error of 12 % for the never dried sheets, 18 % for once dried sheets and 13 % for high temperature dried sheets is observed. It would be fair to assume that an average error of 15 % should be accounted for if the measurements are carried out for the 60 gsm sheets only, i.e.: partial measurement approach.

$$\boxed{\therefore \mathbf{Z}_{\mathrm{i}} = 1.15 \times \mathbf{Z}_{60}}$$

Where,

$\mathbf{Z}_{\mathrm{i}}$ = Zero span strength at 0 gsm or the intrinsic zero span strength.

$\mathbf{Z}_{60}$ = Zero span strength at 60 gsm.

4.2. 8 Bond strength Calculations

The core idea of the project was to weaken the fibres independently of the bonds in a sheet of paper, using acid hydrolysis until all fibres break across the fracture line, except the ones which are bonded on only one side of the fracture line. The bond strength was then calculated from the fibre strength as measured by the zero span test at the point where the fibres first are weakened such that they all break, which has been called the optimum point.

The shear bond strength is given as:

$$\boldsymbol{\sigma}_{\mathbf{s}} = \frac{\boldsymbol{\sigma}_{\mathbf{opt}} \times \mathbf{C}_{\mathbf{s}}}{\mathbf{A}} \text{ .....Equation 1}$$

Where,

σ_s = Shear Bond strength

σ_{opt} = Fibre strength at the optimum point

C_s = Cross sectional area of one fibre wall

A = Area of the bond

The Zero span test has been used to calculate the fibre strength. If it is assumed that in a zero span test, failure is entirely through fibre fracture, it can be written in general that:

$$\boldsymbol{\sigma}_{\mathbf{opt}} = \frac{\mathbf{F}_{\mathbf{total}}}{\mathbf{A}_{\mathbf{cs}}} \text{ .....Equation 2}$$

Where,

F_{total} = Total force on the optimum exposed sample at fracture

A_{cs} = Total cross sectional area of all fibres

The breaking force on the sample in the zero span test is given by:

$$\mathbf{F}_{\mathbf{total}} = \mathbf{F} \times \mathbf{w} \text{ .....Equation 3}$$

Where,

$\mathbf{F}$ = The breaking force for a random sheet per unit width

$\mathbf{w}$ = width of the sample sheet

Van den Akker [34] found that the zero span breaking force for a random sheet is 3/8 the zero span breaking force for a sheet in which all the fibres are oriented in the direction of the stress.

$$\therefore \frac{3}{8}\mathbf{F} = \mathbf{F_o} \text{.....Equation 4}$$

Where,

$\mathbf{F_o}$ = breaking force for an oriented sheet

Therefore the breaking force for a random sheet is given by:

$$\mathbf{F} = \frac{8}{3} \times \mathbf{Z} \times \mathbf{M} \text{.....Equation 5}$$

Where,

$\mathbf{Z}$ = Zero span tensile index

$\mathbf{M}$ = Mass per unit area of the sheet (i.e.: grammage)

The mass per unit area of the sheet, i.e.: grammage is given by:

$$\mathbf{M} = \boldsymbol{\rho} \times \mathbf{t} \text{.....Equation 6}$$

Where,

$\boldsymbol{\rho}$ = Fibre wall density assumed to be 1500 kg/m^3

$\mathbf{t}$ = thickness of sheet if it was compressed to a solid mass of fibres

Multiplying both sides of Equation 6 by **w**, we get:

$$\mathbf{w} \times \mathbf{M} = \boldsymbol{\rho} \times \mathbf{t} \times \mathbf{w} \text{.....Equation 7}$$

The cross sectional area of fibre wall material in a sheet of paper is

$\mathbf{A_{cs}} = \mathbf{t} \times \mathbf{w}$ .....Equation 8

$\therefore \mathbf{A_{cs}} = \mathbf{w} \times \frac{\mathbf{M}}{\rho}$ .....Equation 9

Thus we may write

$\sigma_{\mathbf{opt}} = \frac{8}{3} \times \mathbf{Z_i} \times \rho$ .....Equation 10

where,

$\mathbf{Z_i}$ **=** Intrinsic zero span strength at optimum point

To determine the area of contact, let us consider one fibre-fibre bond as shown in (Figure 4. 23)

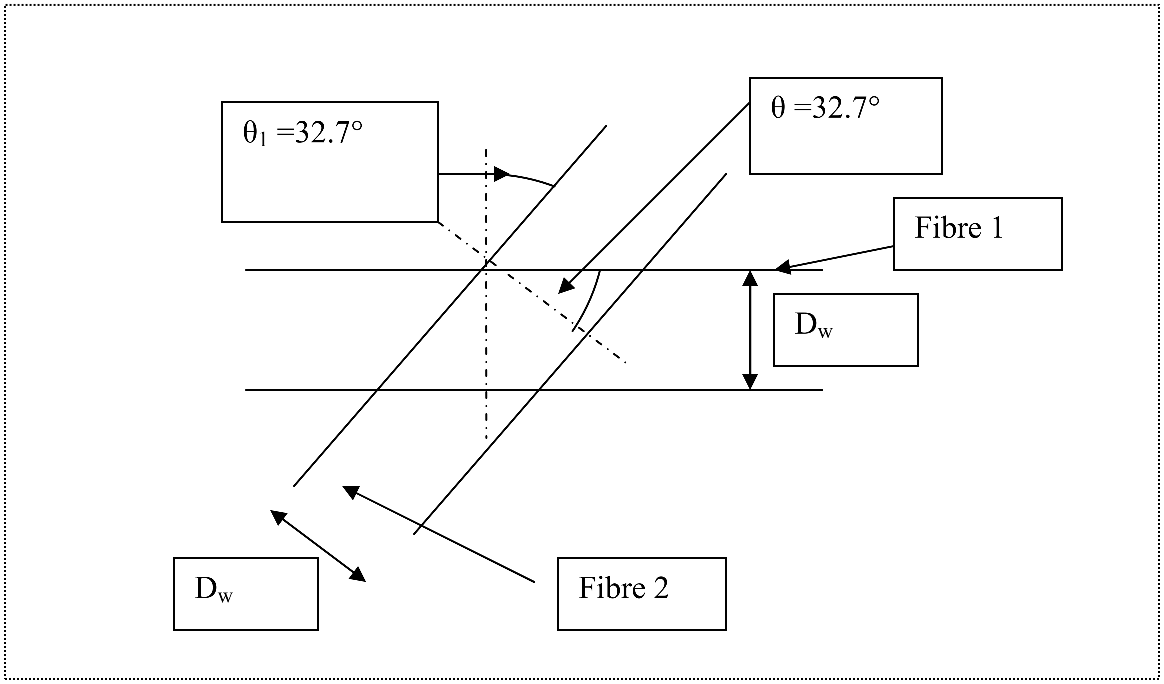

Figure 4. 23: Schematic diagram of one fibre-fibre bond

Figure 4. 23 shows two fibres (width = $\mathbf{D_w}$) crossing each other at an angle ($\boldsymbol{\theta}_{\mathbf{avg}}$) of 32.7°.This is the average crossing angle of fibres [17].

The area of contact is a rhombus having height $\mathbf{D_w}$ and the length of sides unknown. From trigonometric principles we can say that the base (**b**) is given as:

$$\frac{\mathbf{D_w}}{\cos\boldsymbol{\theta}_{\mathbf{avg}}} = \mathbf{b} \text{ .....Equation 11}$$

The area of the rhombus is given as

$$\mathbf{A} = \mathbf{b} \times \mathbf{h} = \frac{\mathbf{D_w}^2}{\cos\boldsymbol{\theta}_{\mathbf{avg}}} \text{.....Equation 12}$$

Where,

A = Area of one bond

$\boldsymbol{\theta}_{\mathbf{avg}}$ = Average crossing angle of fibres, which has been derived to be 32.7° [17]

$\mathbf{D_w}$ = Width of the fibre (microns)

It is worth noting that using the assumed fibre wall density of 1500 kg/m^3, Equation 10 simplifies to:

$$\boldsymbol{\sigma}_{\mathbf{opt}}\,(\text{MPa}) = 4\mathbf{Z_i}\,(\text{kNm/kg})\textbf{.....}\text{Equation 13}$$

Substituting Equation 10, 11, 12 and the values of $\boldsymbol{\theta}_{\mathbf{avg}}$ into Equation 1 we get the complete expression for the shear bond strength as:

$$\boldsymbol{\sigma}_{\mathbf{s}}\,(\mathbf{MPa}) = \frac{\frac{8}{3} \times \mathbf{Z_i} \times \boldsymbol{\rho} \times \mathbf{C_s}}{\frac{\mathbf{D_w^2}}{\cos\boldsymbol{\theta}_{\mathbf{avg}}}} \text{.....Equation 14}$$

The relevant variables for the calculation of bond strength are summarized in Table 4. 7

Variables	**Value**			
		Never dried Fibres	Once dried Fibres	High Temperature dried Fibres
Zero span tensile index (Nm/g)		54.7 ± 3.2	62.2 ± 2.2	67.6 ± 3.1
C_s [72] (square microns)		236 ± 10	236 ± 10	236 ± 10
ρ (kg/m^3)		1500	1500	1500
R [17]		1.35	1.35	1.35
D_w (microns)		40 ± 1	42 ± 1	44 ± 1

Table 4. 7: Summary table of relevant variables to calculate bond strength

Using Equation 15, the values of bond strength obtained for the three sets of experiments are as follows:

Type of Fibres	**Bond strength Value (MPa)**
Never dried fibres	29.6 ± 3.3
Once dried fibres	24.7 ± 2.8
High temperature dried fibres	19.7 ± 2.4

Table 4. 8: Calculated Bond strength values

4. 3 Discussion

The previously published values of the shear bond strength are shown in Table 4. 9. All the values obtained from the data, except that by Gurnagul et al [27] and Torgnysdotter and Wagberg [58] is based on direct measurements of bond strength. Gurnagul et al [27] data is based on indirect measurement techniques.

Researchers	**Year of Publication**	**(≈) Bond Strength Value (MPa)**
McIntosh and Leopold [50]	1962	2.7 to 7.1
Schniewind et al. [52]	1964	1.9 to 3.7
Russell et al. [51]	1964	3
Jones [59]	1972	7.1 to 9.3
Button [53]	1975	8.9 to 13.9
Thorpe et al. [54]	1976	4 to 8.2
Stratton and Colson [55]	1990	2.1 to 9.3
N.Gurnagul et al [27]	2001	2 to 5.6
Torgnysdotter and Wagberg [58]	2006	1.4 to 2.1

Table 4. 9: Summary of previously published bond strength values

The bond strength values obtained by previous researchers seem to have a lower value than the ones obtained in the studies carried out for this thesis.

4.3. 1 Direct measurements

This section will look at the direct bond strength measurement techniques employed by previous researchers.

McIntosh and Leopold studied the bonding of loblolly pine and Kraft fibres [49]. Their procedures are stated in detail in the Literature review. A drop of water was used to form the bond. Polarized light was used to measure the bonded area. This does not necessarily provide a true estimate of the bonded area because the wavelength of the light is such that it can penetrate only to a certain depth and if the gap between the fibres is less than the space required for the light to pass, then that gap will also be considered as a bonded area which in reality is far from the truth. Observing the assembly as a whole, it can be seen that the fibre will slide across the shives and will tear a part of the shives because of the fashion in which the bond is prepared. McIntosh [49] in later work also commented that the surface chemistry of fibres, the lignin content of pulps and in general the non-uniformity of chemical makeup from fibre to fibre could have a significant effect on the strength of the bonds. It was also observed that there was a difference in strength between summerwood and springwood fibres, indicating that the bond strength could also be associated with the polymer chain interactions in the fibres which are pressed against each other during the bonding process.

Schniewind et al. [52] tried to establish a reliable method for shear bond strength measurement. They observed a large variation in the results obtained because 50% of their assemblies were damaged during handling and some of the others had to be discarded due to misalignments. They also mention that the calculated values of bond strength should be higher for improved techniques.

Russell and co workers studied the influence of wet strength resins [51]. They state clearly that theirs is a wet strength procedure and cannot be applied to dry strength studies. The force they applied to separate the bonded fibres are purely translational (even as per their opinion) and do not consider the rotational forces which are generally present at the contacts for real paper. Thus they state that their value could well be in direct proportion to the true value of the bond strength as it does not consider the rotational forces. It is also possible that the area obtained by Page's light scattering technique could have had an influence on the values they obtained.

Thorpe et al. [54] commented that lignin content was an important contributor to the bond strength as the lignin is capable of adhesion to cellulose or cohesion to adjacent lignin surfaces thus making the bond strong. Bonded area was measured using Zeiss Universal microscope and adhesives were used to glue the fibre to the manila folder assembly which could have had an effect on the bond strength values obtained.

Stratton and Colson [55] tried to reinvestigate the work done by Russell et al [51] and found that the design of the assemblies used has been such that peeling could dominate the shearing action during testing of single bonds. They also expected a greater degree of peeling to lower the breaking load and thus affect the calculations of bond strength.

Calculations of Bond strength assume that the stress distribution is uniform along the area of contact. Consider all the single fibre bond strength measurement assemblies: they fail to consider the rotational forces acting on the fibre. In actual paper networks the fibres wrap around the other fibres while forming the network. If a strain is applied to such a network then part of the force applied to the fibre actually acts in a direction normal to the direction of the force (Figure 4. 24).

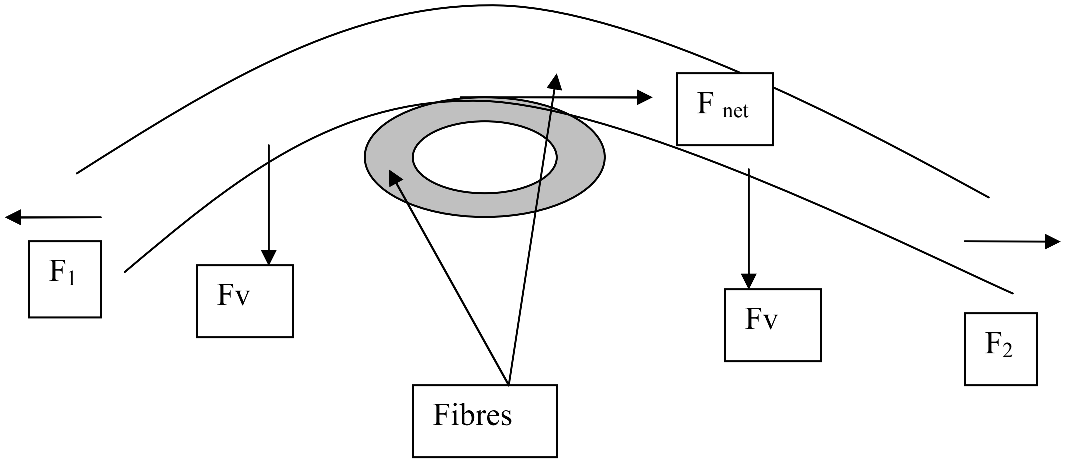

Figure 4. 24: Schematic diagram of fibre wrapping in networks and acting forces

F = Force acting on the fibre in direction of stress

Fv = Component of force acting on fibre pushing it down and helping it wrap around the other fibre.

Also when a single fibre crossing (Figure 4. 24) is strained, the frictional and rotational forces act at certain points on the fibre thus producing a stress concentration and a non uniform stress field leading to rupture of the bond at the weakest point. The rotation depends upon how firmly the bottom fibre is held at the base.

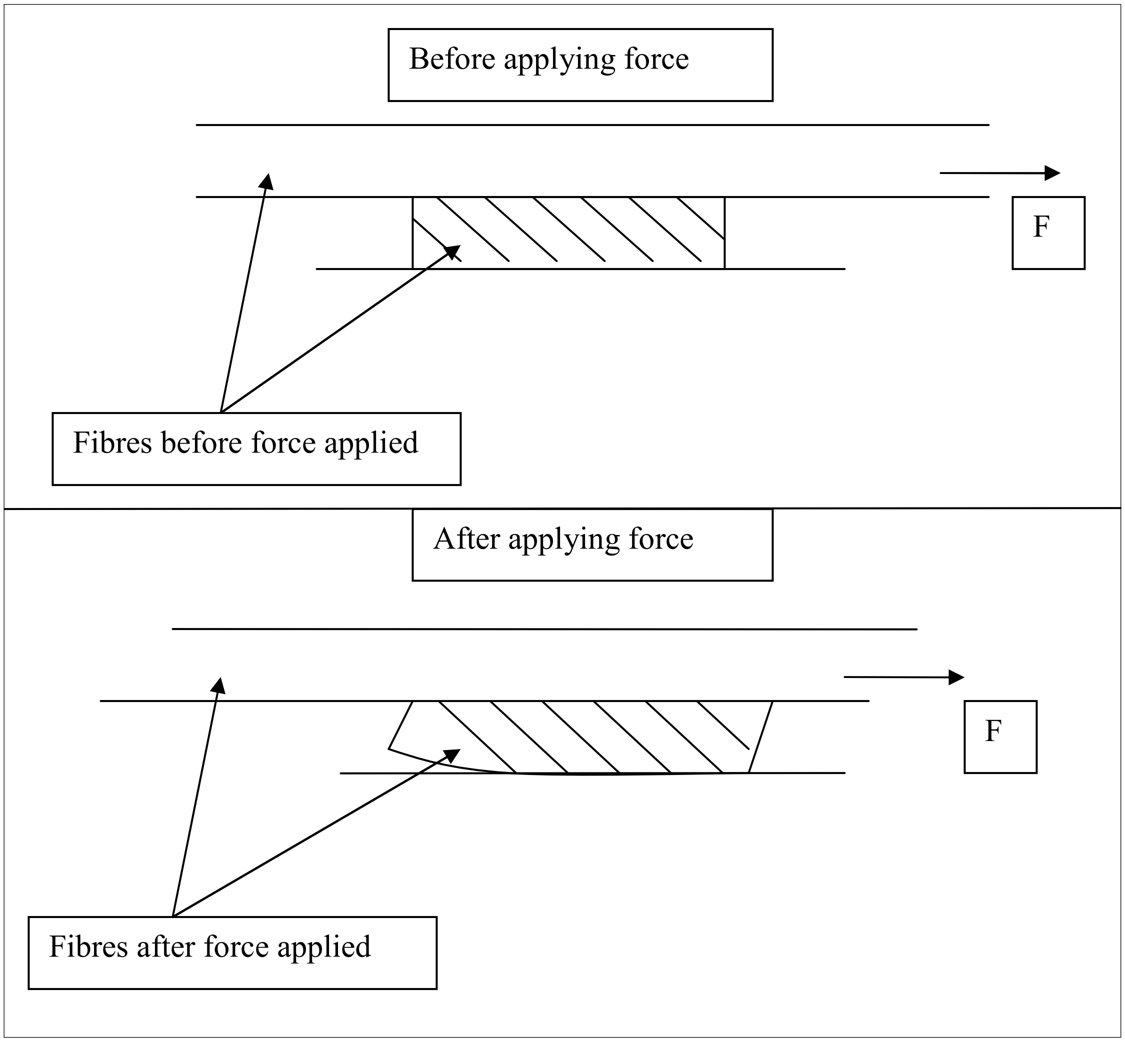

Figure 4. 25: Schematic diagram showing effect of force on fibres

This contradicts the basic assumption of uniform stress along the area under the bond. Fibres also shrink as they dry. The bonds formed during the drying will be affected by these drying stresses. The only way to ensure that the bond dries under the same stress as it would in a sheet is to actually form the bonds in the sheets. Most of the single fibre assemblies neglect the drying stresses and their possible effect on the bond strength.

4.3. 2 Indirect measurement techniques

This section will look at the indirect bond strength measurement techniques employed by previous researchers.

Jones [59] made handsheets and tested them for obtaining the zero span strength. The area of bonding was measured using nitrogen adsorption method. The shear bond strength was calculated using Page's equation. It should be noted that the Page equation has never been fully verified.

Gurnagul et al. [27] found significant losses in fibre swelling after drying operations and any loss in tensile strength is on account of reduction in the bonding strength. This supports the nature of the results obtained during the studies conducted here for the never dried and recycled fibres.

4.3. 3 Why is the new technique better?

Different researchers used different fibres, different bond preparation techniques and different testing methods to determine the bond strength. However the values of the Bond strength calculated here would be considered more realistic because of the way in which the bonds are formed. It is very difficult to replicate the state of a bond in a sheet using individual fibre crossings. It is easier to do the measurements in the sheet itself. The new method employs in-sheet measurements. The main measurements are overall average sheet properties which makes the measurements statistically more correct. The drying experiments at 110°C are more representative of the commercially produced sheets.

4.3. 4 Potential Weakness

The technique used during the experiments is a new and simple method to measure the Shear bond strength; however it could be criticized on the grounds that the zero span measurements are still average measurements. There also might be the question of what happens if the bonds are weakened due to HCl. HCl seems to cause polymer chain scission and no reports have been found which indicate that HCl actually affects the surface bonding. Hence it is assumed that HCl doesn’t affect the bonds. In addition, the bonded areas of the paper are the least accessible areas, thus least prone to being affected by HCl. However, if it is assumed that HCl does affect the bonds then the measured values would be considered too low and even further away from most previously measured values.

Paper is a variable structure due to the non uniform nature of the raw material and the non uniform pulping process. One may question the utility of a technique which gives a single value of bond strength. Mechanical properties of paper are directly related to the bond strength and the Shear bond strength was the last unmeasured variable required to validate and develop models and theories for paper mechanical properties. Shear bond strength has been measured in terms of in-plane tensile strength and zero span tensile strength as a network parameter. Other factors that influence tensile strength are formation, pressing pressure, types of fibre used, pulping techniques, quantity of fines etc. The experiments performed here illustrate that if all the other variables are known then this new technique can be used to measure the shear bond strength directly.

4.3. 5 Reasons for strength loss in Recycled fibres

The terms Hornification and shrinkage have been used extensively in the literature pertaining to the behaviour of fibres after recycling. Once fibres have been dried, their dimensions change. This change is irreversible. Drying causes an irreversible physical contraction of the fibre cell walls and thus the hornified cell walls are less swollen and less flexible compared to the initial state. Researchers have found that the loss in strength properties on recycling is related more with physical changes in the fibre rather than the small chemical changes [21].

Surface changes at fibrillar level or molecular level could be responsible for losses in strength after recycling. Gurnagul et al [27] used the diffusion theory which states that adhesion between plasticized polymeric materials will occur as a result of significant diffusion-intermingling of molecular segments from both sides of interface. As a result of the loss of swelling upon drying, the mobility of surface molecules is reduced, in turn decreasing the intermolecular interaction between two fibres interfaces resulting in a decrease in fibre-fibre bond strength. This theory seems to be acceptable. This theory is also applicable to the results obtained here because like the experiments by Gurnagul et al [27], the fines have been eliminated in the present set of experiments and thus their influence on the bond strength and overall sheet strength is not significant

The fibres after undergoing a drying operation have collapsed to an extent during the drying and pressing operations. It is not possible for the fibres to revert back to their original shape even after a re-wetting cycle. It is still not clear why drying the fibres once causes irreversible changes to their structure and bonding capability. The slightly collapsed fibres do not bond that readily with other fibres and thus the level of bonding decreases to a certain extent. As the level of bonding decreases, the strength of the sheet is affected and hence the lower values of tensile index are observed. Values of tensile index are known to drop within the range of 10% to 30 % after a single drying operation. The values obtained from the experiments fall within this range. The third experiment used a high temperature along with a pressing cycle to investigate the effect that high temperature would have on the drying of fibres and what changes take place. It is suspected that the drying out of the fibres due to high temperatures causes the fibres to dehydrate rapidly and thus grow hard, brittle and collapse. It is also suspected that the fibres might shrink due to the heat treatment. On re-wetting, the fibres do not regain their original shape. The fibres would also have lost their flexibility and thus their ability to form bonds would be hampered. This explains why there is a decrease in tensile strength and the bond strength.

More recently Torgnysdotter and Wagberg tried to tailor fibre-fibre joints. In their studies [58] they tried to investigate the opportunities to modify the contact-zone properties of dried Kraft pulp. The data they generated during their experiments can be used to calculate the Shear bond strength (Table 4. 10).

Type of fibre used	Yield (%)	Shear Bond strength (MPa)
Never Dried	60	2.1
	52.1	1.5
	40.9	1.6
Once Dried	60	1.8
	52.1	1.5
	40.9	1.4

Table 4. 10: Torgnysdotter and Wagberg's values of Shear Bond strength

The behaviour of the fibres, i.e.: decrease in tensile strength after recycling agrees with the theoretical results summarized by Garg and Singh [73].

Once the fibres are dried, they loose most of the water they hold and collapse. This collapse is not a completely reversible phenomenon and thus after re-slushing, the fibres will continue to be more flat than a virgin fibre. This state of the fibre causes problems in bonding and thus it would be expected that the strength of the re-slushed sheet is less than the virgin fibre sheet. High temperature drying is a further extension of the drying process in which the sheets are initially dried at high temperatures in an oven and later re-slushed to make sheets. The heat further accelerates the dehydration of the fibres and takes the drying process a step further in intensity. It would be expected that the sheets made from such fibres will further decrease in strength. The values of bond strength calculated during the experiments show that there is indeed almost a loss of strength by 17% when comparing the never dried and the once dried bonds. The loss of strength is 34% when we compare the never dried and high temperature dried sheets.

Chapter 5: Conclusions & recommendation for future work

5. 1 Conclusions

The Shear bond strength value at zero gsm for sheets made from never dried Radiata pine pulp, 60% yield is found to be 29.6 ± 3.3 MPa. The Shear Bond strength value at zero gsm for sheets made from once dried Radiata pine pulp, 60% yield is found to be 24.7 ± 2.8 MPa. The once dried sheets are the sheets initially made from never dried Radiata pine pulp, restrain dried, re-slushed in a disintegrator and made into sheets again. The shear Bond strength value at zero gsm for sheets made from High temperature dried sheets is 19.7 ± 2.4 MPa. The high temperature treatment involved making handsheets from never dried pulp, restrain drying them, re-slushing them and remade into handsheets which were then dried at 105°C for one hour.

It can be concluded that the shear bond strength values decrease with recycling operations. A re-slushing and drying operation reduced the shear bond strength by 17% and a high temperature drying operation reduced the strength by 34%. High temperature drying thus seems to be more detrimental to the shear bond strength than a plain drying operation. Heat and rapid removal of moisture have a negative effect upon the fibre properties and thus reduce their bonding abilities, resulting in reduction of the shear bond strength.

A new and simple method for measuring the Shear Bond strength has thus been developed.

5. 2 Recommendations for Future work

5.2. 1 Different types of pulps

This study has been done using a 60% yield unbleached Radiata Pine pulp. Yield and pulping process are known to affect the paper properties. The bond strength measurements should also investigate:

1. Effect of Pulps of different yields (low yield and high yield)
2. Effect of bleaching on the bond strength (bleached and unbleached pulp)
3. Effect of pulping process, i.e.: comparing TMP and chemical pulps

Earlywood and latewood fibres also show a marked difference in the bond strength as observed in the literature review. The bond strengths should also be calculated for earlywood and latewood fibres and the difference in strengths should be verified.

5.2. 2 Effect of Fines and shives

The fines and shives were screened and removed in the course of this study. However they may influence the bonding process significantly and thus influence the Shear Bond strength considerably. Also to be noted is the fact that some of the earlier studies on single fibre bonds were carried out using shives and fibres bonded together. Thus the further studies could investigate how the bonding strength changes for different levels (percentage) of fines and shive addition.

5.2. 3 Commercial Recycling treatments

Two types of drying and recycling treatments have been used in this study. However a process closer to the commercial recycling process could be designed and used for studying bond strength. Till now there were no means to actually measure the bond strength, but now with this study the bond strength can be measured and recycling can be made more effective. A commercial recycling process will thus take one more step forward in the direction of applying this process to get better recycled paper.

5.2. 4 Hypothesis testing

It is believed that when the relationship between fibre strength and sheet strength is examined, then two regimes can be identified. Weak fibres will have strength less than the bond strength of any individual bond and sheet strength will be linearly proportional to fibre strength. As the fibres get stronger, a point of transition will be reached where some bonds will fail before the fibres themselves fail; which is where the relationship between fibre and sheet strength becomes non-linear. The non linear part of this hypothesis hasn't been completely tested and needs to be examined.

5.2. 5 Refining

The effect of refining on the shear bond strength needs to be tested. It needs to be verified if refining can actually help restore the Shear bond strength lost due to Hornification.

5.2. 6 Additives

Studies also need to be carried to see if wet strength or dry strength additives have a significant effect on the Shear bond strength.

5. 3 Concluding comments

The Shear bond strength measurements are a part of an ongoing paper mechanical properties and strength studies. The Shear bond strength and the restoration of Shear bond strength in papermaking fibres is of commercial interest. Once the ways and means of restoring the Shear bond strength have been established, the paper industry would be able to manufacture better quality recycled paper with environmental benefits.

APPENDIX I

The program VARAD was written for the MBSF. The values in the columns can be changed and the program can be modified as per requirement.

Stirrer Speed	Vacuum Level (Bars)	Belt speed (m/s)	Magnetic Valve Control code	Comments
0	0	0	0	
0	0	0	239	Stirrer Down
0	0	0	248	Water jet starts
0	0	0	248	
0	0	0	248	
0	0	0	248	
0	0	0	248	
0	0	0	248	
0	1	0.1	247	Stirrer off, belt starts
0	1	0.1	223	Draw plastic
0	1	0.1	255	Low vacuum starts, air injectors on
0	1	0.1	255	
0	1	0.1	255	
0	1	0.1	255	
0	1	0.1	191	High vacuum
0	1	0.1	191	
0	1	0.1	191	
0	0	0	255	Belt stops
0	0	0	255	
0	0	0	255	
0	0	0	255	

The MBSF used to have a mechanical stirrer due to which the first column of stirrer speed is present. With the new stirrer system, this column is redundant and the values are zero throughout.

The second column is used to control the vacuum level (in bars) used by the machine. The values can be modified to a maximum of 4 bars. The third column is used to control the belt speed. A maximum speed of 6 m/s can be used. The fourth column has program specific codes used to activate controls such as the actions in column 5 are performed as per the input in column 4.

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