MODELLING OF WOOD RESIN INTERACTION

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ABSTRACT

There are 11 medium density fibreboard (MDF) and 11 particle board (PB) plants in Malaysia. The total production capacity is approx 2.5 million cubic ton per year. Wood based industries constitute fourth biggest export earnings for the country. Thermosetting resin such as Urea Formaldehyde (UF) and Phenol formaldehyde (PF) constitutes near about 50% of the cost of wood composites. Not many studies have been carried out to understand the behaviour of resin on wood fibre. Sometimes manufacturer's spray resin more than required which is a waste of material and some time they spray less, which may cause low internal bonding and low modulus of rupture of wood composite. There is a need to develop better understanding, by means of experimental data and modelling. The present model studies the impact of various factors such as resin surface tension, diameter of wood pores, resin contact angle on the penetration rate of resin on the wood surface. The Matlab software is used for programming and running the simulations. The present model will help the wood composite industries to develop better understanding of wood-resin interaction and to optimize the parameters, to get the better bonding between wood fibres.

ABSTRAK

Terdapat 11 kilang papan serat kepadatan menengah dan 11 kilang papan partikel di Malaysia. Jumlah kapasiti pengeluaran sekitar 2.5 juta tan padu pada setiap tahun. Industri berasaskan kayu merupakan pendapatan eksport keempat terbesar bagi negara. Hampir 50% daripada kos penghasilan komposit kayu adalah kos pelekat termoset seperti Urea Formaldehid (UF) dan Fenol Formaldehid (PF). Tidak banyak kajian dilakukan untuk memahami perilaku pelekat pada serat kayu. Kadang-kadang pengilang menyembur pelekat lebih daripada yang diperlukan yang merupakan pembaziran dan kadang-kadang mereka menyembur pelekat kurang daripada yang diperlukan, yang boleh menyebabkan ikatan dalaman dan modulus pecah kayu komposit yang rendah. Adalah satu keperluan untuk menambah pemahaman yang lebih baik dengan pemodelan dan melakukan eksperimen. Model ini menyelidik tentang kesan daripada pelbagai faktor seperti ketegangan permukaan pelekat, diameter pori-pori kayu, sentuhan sudut pelekat pada permukaan kayu ke atas peringkat penetrasi pelekat. Perisian Matlab digunakan untuk pengaturcaraan dan menjalankan simulasi. Model ini akan membantu industri komposit kayu untuk mengembangkan pemahaman yang lebih baik dalam interaksi pelekat kayu dan untuk mengoptimumkan parameter untuk mendapatkan ikatan yang lebih baik antara serat kayu.

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LIST OF ABBREVIATIONS

BS	-	British Standard
EN	-	European Normalization
IB	-	Internal Bonding
JANS	-	Japan Australia and New Zealand Standard
MDF	-	Medium Density Fibreboard
MOE	-	Modulus of Elasticity
MOR	-	Modulus of Rupture
PB	-	Particleboard
PF	-	Phenol Formaldehyde
SEM	-	Scanning Electron Microscopy
UF	-	Urea Formaldehyde

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CHAPTER 1

INTRODUCTION

1.1 Background

The medium-density fibreboard (MDF) industry currently has fourteen plants with a total annual installed capacity of 2.9 million. For 2008, the export of MDF totalled at RM1.2 billion. Currently, Malaysia is the world's third largest exporter of MDF, after Germany and France. MDF from Malaysia has attained international standards such as British Standards (BS), Asia-Pacific: Japan Australia and New Zealand (JANS), and European Normalization (EN) standards. A number of companies have also ventured into the production of laminated MDF or printed MDF. Medium density fibreboard (MDF) is primarily used for industrial applications such as furniture, building material, and laminate flooring because of its good mechanical and economical aspects – is usually high in strength, easy to machine, and has good weathering properties (Suchsland and Woodson, 1986).

Despite over 40 years of evolution, the MDF process still consumes a great deal of resin when compared with other wood composite processes. At first, resin pre-cure was considered primarily responsible for this waste, but resin penetration into the fiber cell wall can also be an issue. Visualization of the resin on spruce fibers by confocal laser scanning microscopy led to the development of a mathematical model which simulates the resin diffusion process in MDF fibers. An atomic force microscope was also used to measure the wood pore diameter which cannot be observed under a traditional or electron micro-*Cyr eta* scope. We found that the resin not only diffuses through large openings, such as bordered pits, but mostly into very small (nanometer) cracks and fiber microstructure defaults of the wood fibers.

The term resin has been applied to a group of substances obtained as gums from trees or manufactured synthetically. Resins are used as adhesive in wood bonding. This is in making medium density fiberboard (MDF), particleboard and hardboard. The recorded history of bonded wood dates back at least 3000 years to the Egyptians (Skiest and Miron 1990, River 1994a), and adhesive bonding goes back to early mankind (Keimel 2003). Certain of the fundamental aspects are not fully known even though wood bonding is the largest applications for adhesives.

Thermosetting resin is a resin which polymerizes to a permanently solid and infusible state upon the application of heat. Thermosetting resins form a highly diverse, versatile, and useful class of polymeric materials. They are used in such applications as moldings, lamination, foams, textile finishing, coatings, sealants, and adhesives. The thermosetting resins are dominated by phenolics, polyesters, polyurethanes and amino resins. There are several factors such as resin type, pH, temperature and pressure that exacted in pressing the fiberboard, surface tension and kind of resin spray that affects the internal bonding properties of wood composite.

Carvalho (1999) obtained the kinetic model for the Urea Formaldehyde (UF) resin polycondensation reaction by using Raman spectroscopy. He concluded that the evolution of the bands attributed to methylene groups follows first order kinetics. Although the cross linking is mainly obtained by the formation of methylene bridges, other reactions, such as the formation of cyclic structures are also involved. However, as a good approximation, Carvalho *et al.* (2003) considers the kinetics of the formation of methylene bridges [B] representative of the polycondensation kinetics. So the rate of the polycondensation reaction of UF resin (in s^{-1}) can be calculated by:

$$(-r) = \frac{1}{A_o}\frac{d[B]}{dt} = \frac{1}{2}k\exp(-kt) \qquad (1.10)$$

Where :

$\left(-r\right)$: Reaction rate for resin polycondensation (s^{-1});

A_0 : Initial concentration of methylol groups (mol kg^{-1});

k : Rate constant calculated using the Arrhenius equation with $k_0 = 71.597 s^{-1}$ and E_{act} = 33 (kJ mol^{-1});

t: Time (s).

The water production by the polycondensation reaction was calculated, keeping in mind that for each methylene bridge formed a water molecule is released. We can calculate the water production in kilograms of water per kilogram of resin per second using the following the expression:

$$\left(-r'\right) = \frac{d\left[-H_2O\right]}{dt} = \frac{1}{2} A_0 k \exp\left(-kt\right) MM_w \tag{1.11}$$

Where :

MM_w : Water molecular weight (kg mol^{-1});

ΔH_r : Resin polycondensation enthalpy (J kg^{-1});

Previous studies have shown that a uniform surface resin distribution is a necessary prerequisite for the production of MDF with satisfactory quality and physical properties at low cost (Chapman 1998; Deng 2004; Xing et al. 2004, 2005). Application of resin by blow line method eliminates resin spotting on the surfaces of medium density fibreboard (MDF). This process, however, results in lower resin efficiency than the mechanical blending to achieve comparable board properties. There are four main factors, which cause low UF resin efficiency: resin pre-cure, resin distribution or resin coverage, resin loss and resin penetration. For good adhesive bonding, a moderate amount of penetration is desirable (Xing et al. 2005). However, excessive penetration will waste adhesive and lead to a starved bond line with insufficient adhesive left at the interface (Gindl et al. 2005). High level of defect on the fibre surface or higher natural porosity in the fibre tends to increase resin consumption as a result of filling the pores. The present modelling work is to develop better understanding on the penetration rate of resin.

1.2 Problem statement

Not many studies have been carried out to understand the behavior of resin on wood fiber. Same like Malaysian, no one have been carried out any research in understanding the behavior of the resins. Therefore, there is a need to understand it by means of experimental data and modeling. Most of the overseas studies were done on different wood species, which are not used by Malaysian manufacturers. As we know, medium density fiberboard is one of important thing in making furniture and buildings in Malaysia. Therefore, it is important to study the behavior of resin on wood fibers from Malaysia. This is because; in Malaysia the major raw material is rubber wood and other tropical species. Bonding of thermosetting adhesives plays an important role within wood-based composites. During hot pressing, there is a continuously changing state of factors such as temperature, moisture content and vapor pressure within the mattress, which affects the process of adhesion and the development of bond strength. This affects the properties of the final product, the required hot-pressing time and energy consumption (Humphrey PE 1982).

As due to lack of information, manufacturers do not have information about the right percentage of resin. Sometimes they spray more than required which are a waste of material and some time they spray less, which may cause low internal bonding and low modulus of rupture of wood composite. Resin constitutes nearly half the cost of raw material. Therefore, it is important that we need to understand the behavior of resin on wood fiber in order to produce good quality of MDF and in helping to reduce the cost of the production of MDF.

1.3 Scope of research work

This study will be focus on urea formaldehyde resins. This is because, urea formaldehyde resins are the most important type of adhesive resins for the production of wood based panels. They convince by their high reactivity and good performance in the production by their low price, however they lack in water resistance of the hardened resin owing to the reversibility of the aminomethylene link and hence the susceptibility to hydrolysis (M.Dunky 1997).

Hence, in this research the properties of the current wood resin and also wood fiber that is used in industry which is urea formaldehyde resin and also mixed tropical wood fibre were studied. The properties that have been studied are, pore diameter on wood fibres, resin surface tension, resin contact angle and also resin viscosity. These studies have been done in Universiti Malaysia Pahang (UMP), and also in Forest Research Institute Malaysia (FRIM) under my supervision of my supervisor. In FRIM, I have succeeded in making six fiberboards with different resin content. I have tried improved a mathematical model in Matlab of resin wood interaction and curing of resin and also the experimental part of wood resin interaction on MDF.

1.4 Significance of study

The present research work will help in developing better understanding of wood fiber and resin interaction; subsequently it will help in reducing the amount of resin required for proper bonding and in helping reducing the cost of production.

1.5 Objective

The objectives of this study are;

1. To improve the interaction of wood resin interaction.
2. To reduce the amount of resin used in making wood composites.
3. To reduce the cost of production.

CHAPTER 2

LITERATURE REVIEW

2.1 Manufacturing of Medium Density Fiberboard

MDF is an engineered wood product formed by combining wood fibers with wax and a resin binder, and forming panels by applying high temperature and pressure. The general steps in production of MDF are shown in Figure 2.1. The first process in production of MDF is debarking of suitable logs to convert it into small chips. After that, the chips will pass through the screen to make sure that, there no have sand, dust and other unwanted materials mix with the chips. Then, the chips will go to the refiner to convert into thin fibres. Thermosetting resin such as Urea-formaldehyde (UF) or Phenol-formaldehyde (PF) will be sprayed to the fibres. After that, the mixture of resin and fibres are first dried. The moisture content of the dried resonated fibres is about 6% to 12%. After that, the resonated fibres will go through the mat former area to form a thick mat. The next step is, the mat will pass through the hot press in a few minutes. In hot press area, the mats will be gave some pressure and heat to form it as MDF board. Then, the next steps in production MDF are cooling process, trimming and sanding. Finally MDF boards are ready for selling to the market.

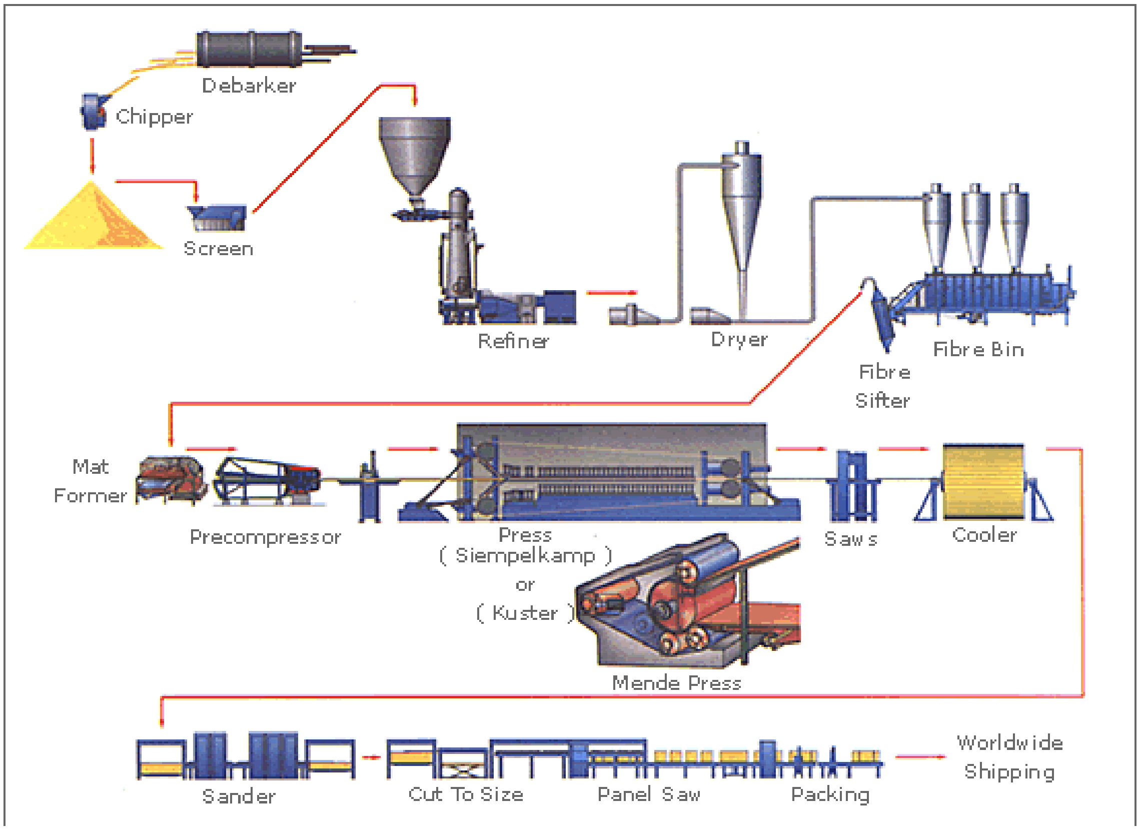

Figure 2.1 General Production of MDF board (Gupta A. 2007)

2.2 Resin Interaction

In wood bonding, once an adhesive is applied to wood the adhesive needs to set to form a product with strength. The term set is mean to convert an adhesive into a fixed or hardened state by chemical or physical action; such as condensation, polymerization, oxidation, vulcanization, gelation, hydration or evaporation of volatile solvent. Water-borne adhesives often contain some organic solvent to help in the wetting of wood surface. For certain of polymeric adhesives, the loss of solvent sets the adhesive. For formaldehyde-cured adhesives, the set involves both the loss of water and polymerization to form the bond between wood fiber and the adhesives. The original wood adhesives were either hot-melt or water-borne natural polymers (Keimel 2003).

In resins interaction, phenol formaldehyde and urea formaldehyde are the common adhesives used in wood interaction. Both of these resins are synthetic resin. In order to select the method of application is depends on the adhesive form, whether liquid, paste, powder, film or hot melt. Other factors influencing the choice of application method are the size and shape of the adhesive to be applied and production volume and rate (Sina Ebnesajjad 2008). After application of adhesive, the adhesive must be mated as quickly as possible in order to prevent the contamination of the bond surface. All the substrates are held together under pressure and also heated until the curing process are achieved.

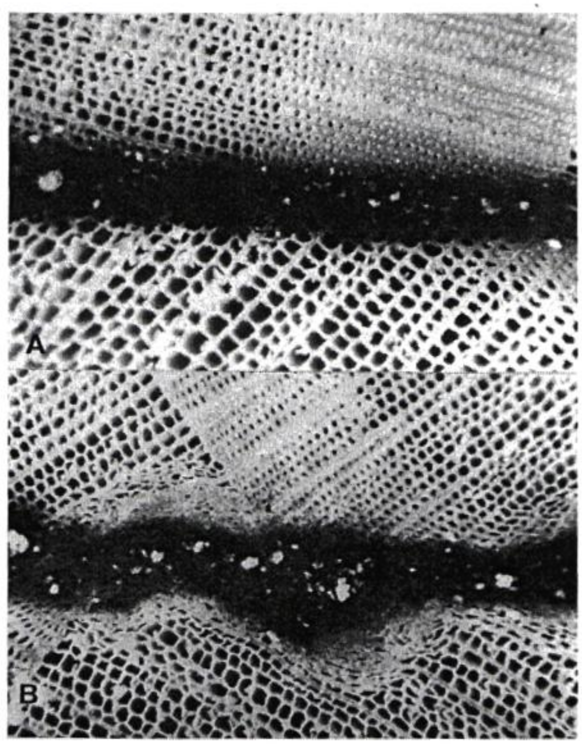

Figure 2.2 Bond lines show good adhesive penetration for (a) a sound wood surface, but not for (b) a crushed and matted wood surface.

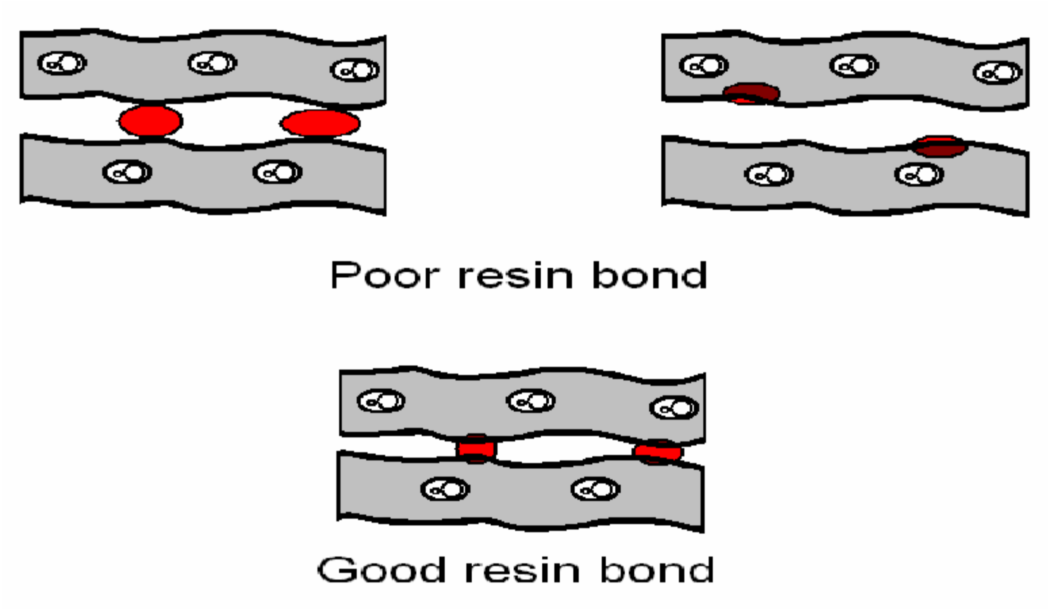

Figure 2.3 Examples of poor and good resin bonds

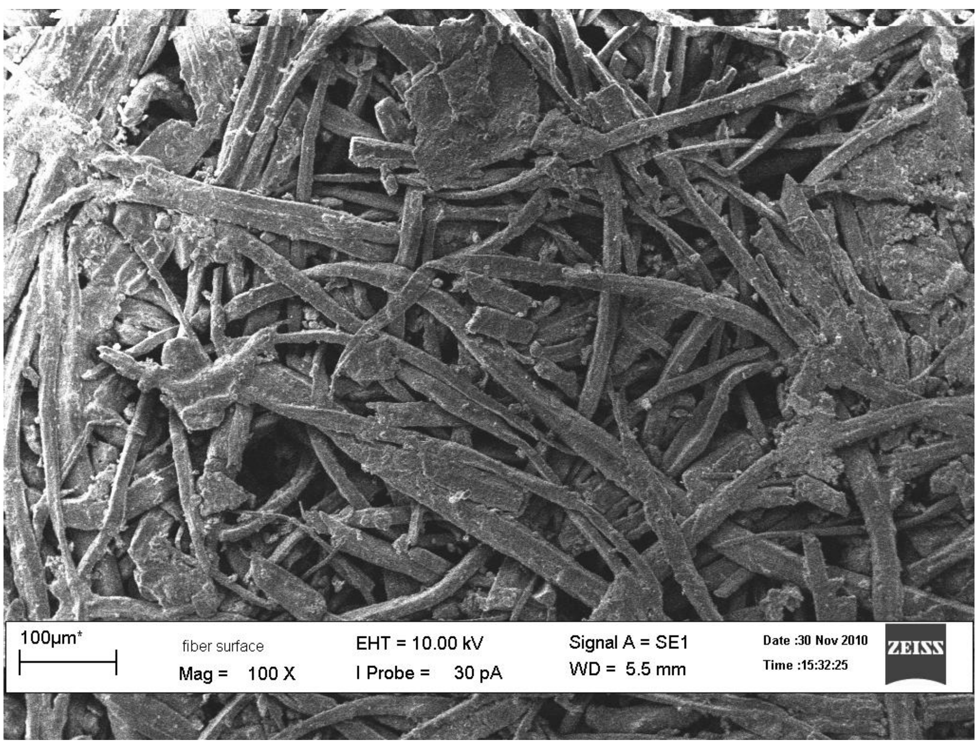

Figure 2.4 MDF surface with 100X magnification

2.3 Urea Formaldehyde Adhesive

Approximately 1 million metric tons of urea-formaldehyde resins are produced annually. More than 70% of this urea-formaldehyde resin is used by the forest products industry for a variety of purposes (White 1995). Urea formaldehyde adhesives are commonly called urea glues (I. Skiest 1990). Urea-formaldehyde resins are formed by the reaction of urea and formaldehyde. The overall reaction of urea with formaldehyde is quite complex and, although initially studied early in this century, is not completely understood at the present time (Pizzi and Marcel 1983). The chemistry of the urea formaldehyde adhesives involve several steps, with the first being the addition of the formaldehyde to the urea under neutral or basic conditions (Pizzi 2003e, Updegall 1990).

In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups. This reaction is in reality a series of reactions that lead to the formation of mono-, di-, and trimethylolureas. Tetramethylolurea is apparently not produced, at least not in a detectable quantity. The addition of formaldehyde to urea takes place over the entire pH range. The reaction rate is dependent on the pH. The rate for the addition of formaldehyde to successively form one, two, and three methylol groups has been estimated to be in the ratio of 9:3:1, respectively (Pizzi and Marcel 1983).

The next stage of urea-formaldehyde resin synthesis consists of the condensation of the methylolureas to low molecular weight polymers. Figure 2.3 shows how the rate at which these condensation reactions occur is very dependent on the pH and for all practical purposes, occurs only at acidic pHs (Jong 1953).

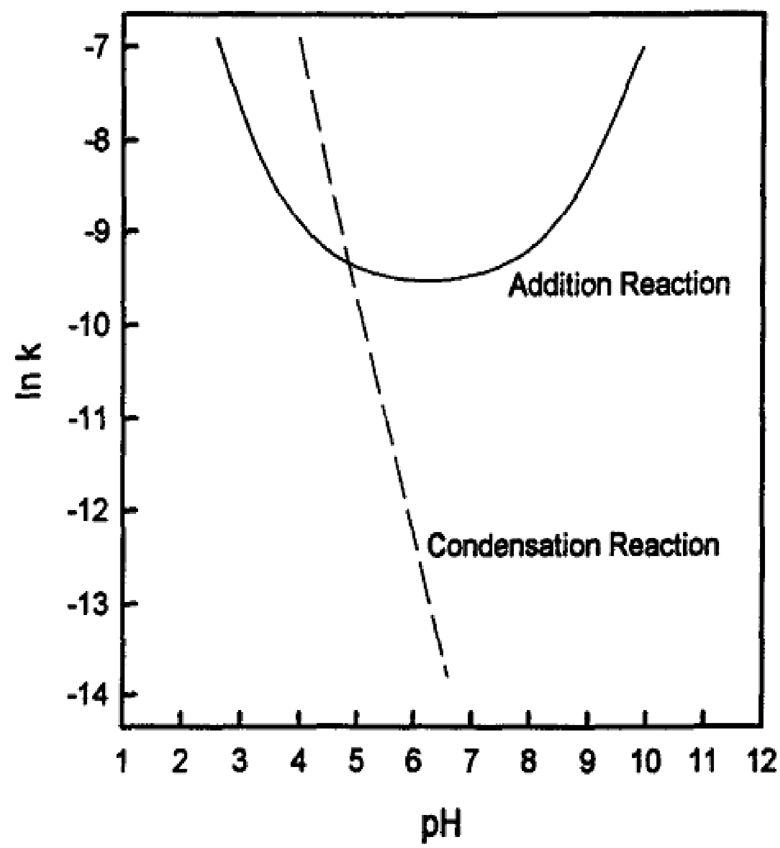

Figure 2.5 Influence of pH on the rate constant (k) for addition and condensation reactions of urea and formaldehyde (Jong 1953)

Urea-formaldehyde resins are the most prominent examples of the class of thermosetting resins usually referred to as amino resins (William and Updegraff 1991). Urea formaldehyde adhesives have very low cost, non-flammable, very rapid cure rate and a light color. However, urea formaldehyde also has the bonds which are not water-resistant. Urea glues are not as durable as other types, but are suitable for wide range of service applications. Thick glue lines craze and weaken the resins interaction unless special modifiers are incorporated; such as furfural alcohol resin. Besides, the other disadvantage of urea formaldehyde adhesives compared with other thermosetting wood adhesives, such as phenol-formaldehyde is the lack of resistance to moist conditions, especially in combination with heat. These conditions lead to a reversal of the bond-forming reactions and the release of formaldehyde. For this reason, these adhesives are not suitable for outdoor application or extreme temperatures (C.A. Harper 2000). However, even when used for interior purposes, the slow release of formaldehyde (a suspected carcinogen) from products bonded with urea formaldehyde adhesives is a major concern that has come under close scrutiny by state and Federal regulatory agencies.Urea-formaldehyde (UF) resins are the main binders for wood composite boards, such as particleboards, fibreboards, or hardwood plywood (Dunky and Pizzi 2002).

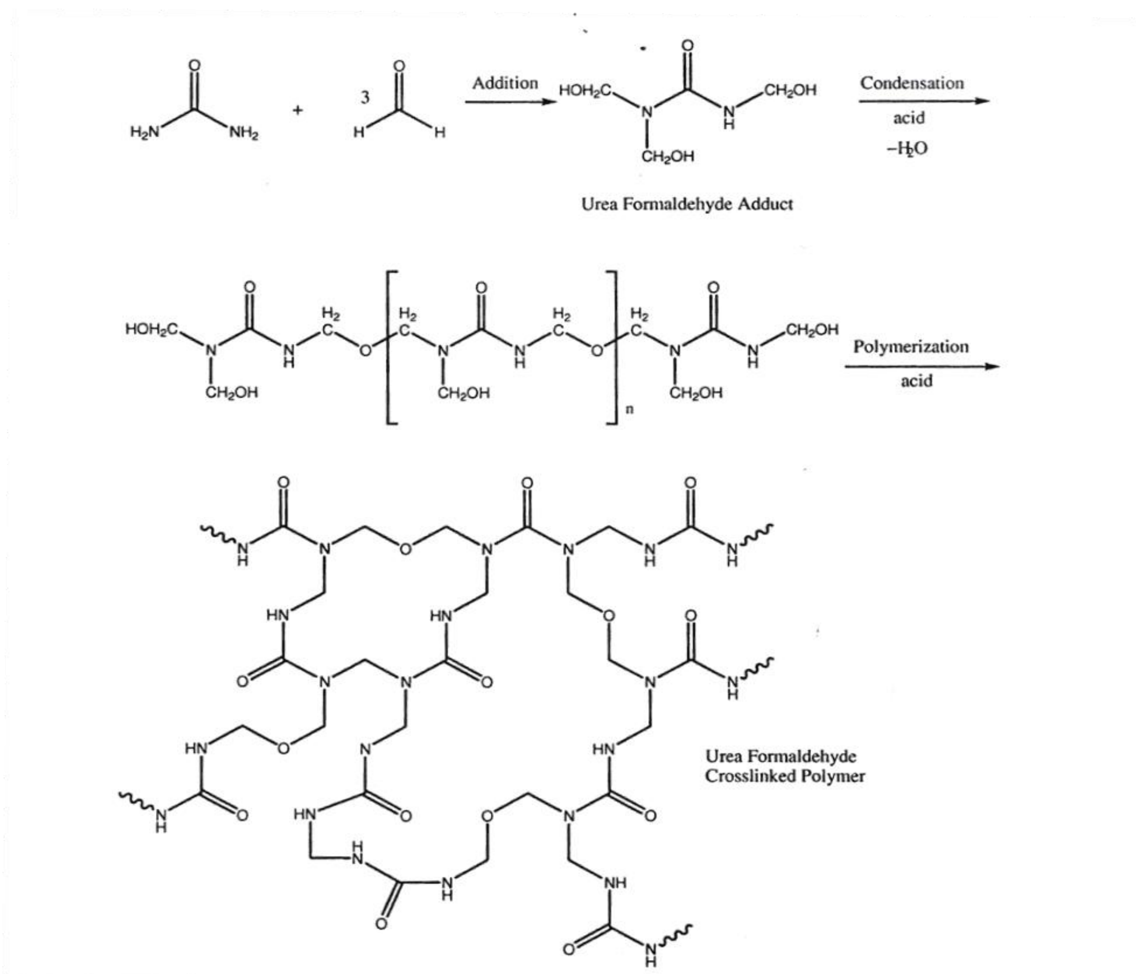

Figure 2.6 Urea-formaldehyde polymerization goes through an addition reaction and then condensation to give an oligomer that is applied to the wood. After application, the polymerization is completed to give crosslink network

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2.4 Bending Test

The bending strength determines the load limit value of an MDF board and the modulus of elasticity the stiffness and therefore the degree of deformation at load. In bend test, it measures ductility, the ability of a material to change form under pressure and keep that form permanently. By using bend test, can be see which side of the material breaks first to see what type of strength the material has. It also lets them know what kinds of pressure it holds up against and what kinds it does not. Ductility describes how well a material, usually metal, can be stretched and keeps its new shape.

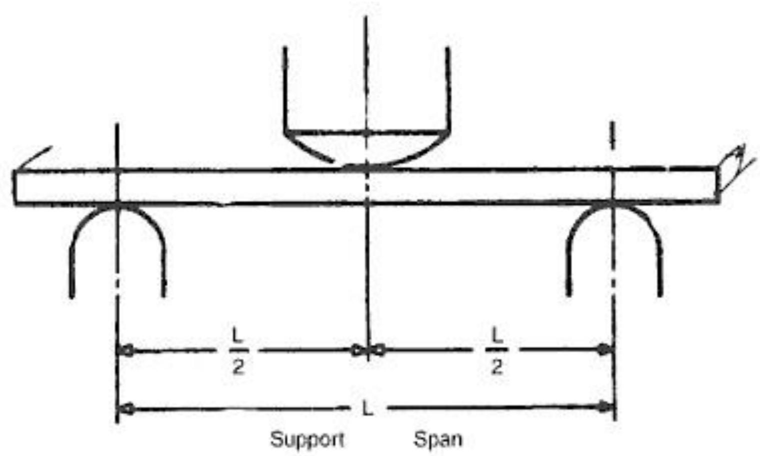

Figure 2.7 Three-point loading schematic diagram for bending test (Klyosov, 2007).

2.4.1 Modulus of Elasticity

Modulus of elasticity (MOE) quantifies that, deformations produced by low stress are completely recoverable after loads are removed. When loaded to higher stress levels, plastic deformation or failure occurs (David W, Jerrold E and David E 1999).

2.4.2 Modulus of Rupture

Modulus of rupture (MOR) reflects the maximum load carrying capacity of a member in bending and is proportional to maximum moment borne by the specimen. Modulus of rupture is an accepted criterion of strength, although it is not a true stress because the formula by which it is computed is valid only to the elastic limit (Andreas 2007)

2.5 Internal Bonding

In internal bond (IB) strength, one of the important mechanical properties is the strength perpendicular to the plane of the board. IB strength testing on board provides direct information on the adhesion of the wood particles. The IB strength is also related to evaluation of the adhesive condition within the board. In medium density fibreboard, the internal failure mechanism generally involves the size of the particles, the change in moisture content and how well the fibres and resin mixed. The machine used in testing the IB strength is Universal testing machine. The force capacity 10 kN (1000 kgf, 2250 lbf). It used internal bond fixture clamp. The fixture consists of a self-aligning upper grip and a rotatable lower grip. Tensile loading is applied to the specimen via blocks bonded to the specimen itself. The upper grip contains an integral self-aligning connection which ensures uniform distribution of the tensile load. A rotatable lower grip makes loading the specimen easy and minimises any torsional misalignment. It is compliance to ASTM D1037-99, BS5669-1979, JIS A5905-1994, JIS A5906-1993, JIS A5908-1994 Standard (Instron Corp., 2007).

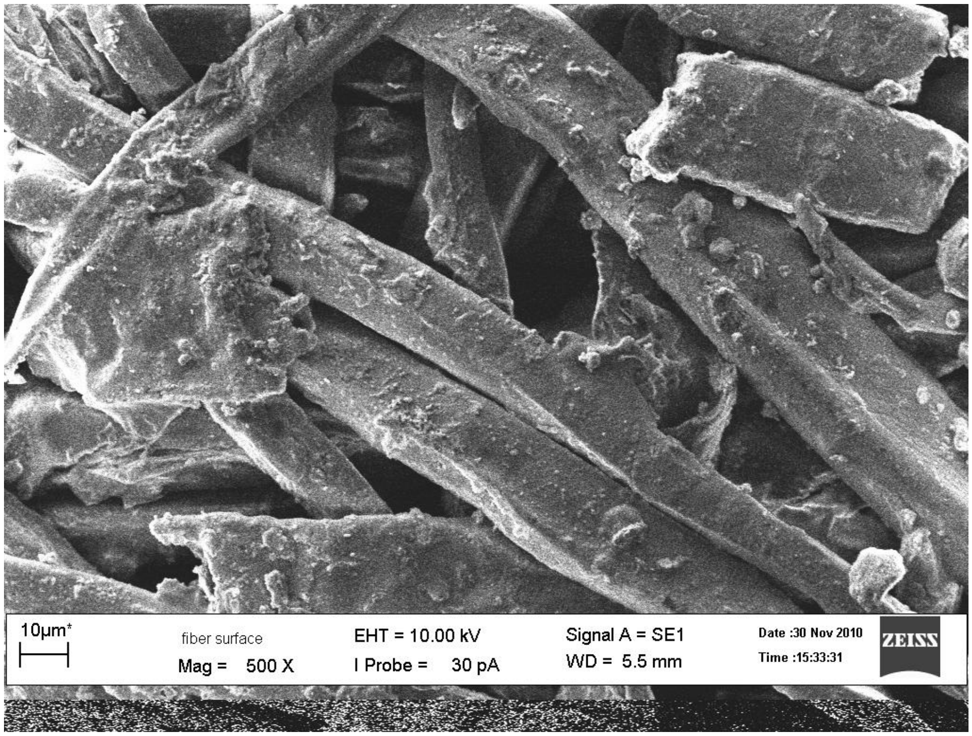

Figure 2.8 MDF rupture point with 500X magnification

2.6 Scanning Electron Microscopy (SEM)

In 1926, Busch studied the trajectories of charged particles in axially symmetric electric and magnetic fields, and showed that such fields could act as particle lenses, laying the foundations of geometrical electron optics (Oatley, 1982). Then, the French physicist de Broglie introduced the concept of corpuscule waves. A frequency and hence a wavelength was associated with charged particles: wave electron optics began (Hawkes, 2004). Both discoveries are the idea of the electron microscopy began to develop (Bogner et al., 2007).

In 1942, the first SEM, as we understand it today, was built by Y. Zworykln at RCA (Zworklyn et al., 1942). SEM use electrons instead of light to form an image. The SEM allows researchers to examine a much bigger variety of specimens. The SEM permits the observation of materials in macro and submicron ranges. The instrument is capable of generating three-dimensional images for analysis of topographic features.