

# **DEVELOPMENT OF BARK-BASED ENVIRONMENTAL-FRIENDLY COMPOSITE PANELS**

by

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A thesis submitted in conformity with the requirement for the degree of  
Master of Science in Forestry  
Faculty of Forestry  
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## **ABSTRACT**

Due to increasing shortage of wood supply and higher environmental concerns with the depletion of forest resources, in recent years, there is a strong interest in using forest and agricultural residues for development of value added products. Bark is a mill-waste residue, available in plenty, having limited uses and causing disposal problems. Bark possesses a large amount of phenolic compounds, which can act as an adhesive in making panels, however only limited research has been done in this area.

The main objective of this project is to develop bark-based environment-friendly panels with and without synthetic resins, using mountain pine beetle infested lodgepole pine barks. Analysis of bark constituents, barkboard development, mechanical properties evaluation, characterization and improvement tests were performed. Various results support the possibility of bark utilization for barkboards production; however, more research is required for further improvements and feasible commercial production process.

**Keywords:** Barkboard, Forest Residue Utilization, Bark.

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## **ACRONYMS, ABBREVIATIONS AND FORMULAE**

ANSI	- American National Standards Institute
ASTM	- American Society for Testing and Materials
CH <sub>2</sub> Cl <sub>2</sub>	- Dichloromethane
CSA	- Canadian Standards Association
DSC	- Differential Scanning Calorimetry
ET	- Ethanol-Toluene
FTIR	- Fourier Transform Infrared Spectroscopy
GC-MS	- Gas Chromatography-Mass Spectroscopy
IB	- Internal Bond
KBr	- Potassium Bromide
LB	- Liquefied Bark
MDF	- Medium Density Fiberboard
MMA	- Methylmethacrylate
MF	- Melamine Formaldehyde
MOE	- Modulus of Elasticity
MOR	- Modulus of Rupture
MPB	- Mountain Pine Beetle
N/mm <sup>2</sup>	- Newton/square millimeter
NaClO <sub>2</sub>	- Sodium Chlorite
NaOH	- Sodium Hydroxide
NH <sub>4</sub> Cl	- Ammonium Chloride
OSB	- Oriented Strand Board
PF	- Phenol Formaldehyde
psi	- pound/square inch
SEM	- Scanning Electron Microscopy
TAPPI	- Technical Association of the Pulp and Paper Industry
TGA	- Thermal Gravimetric Analysis
UF	- Urea Formaldehyde

# **CHAPTER 1: INTRODUCTION**

## **1.1 Background:**

Wood in the form of timber and fuel is one of the most important products derived from forests. Presently, the whole world is facing a huge shortage of wood and similar natural resources and demand is higher than supply. Besides this shortage, increasing global population is also magnifying this gap and responsible for depletion of natural resources. To save our environment, it is necessary to protect our forests, but this results in a shortage of raw materials for various wood based industries. With ever increasing environmental concern over the products made from non-renewable resources, there has been a global trend towards developing new products with less environmental impact from renewable resources. As a result, composite boards that can make use of the various forest and agriculture residues have been gaining strong interest all over the world.

Due to environmental awareness and shortage of wood as raw materials for various wood based industries, there are many efforts towards development of environmental-friendly boards from industrial, forest and agricultural residues. A significant amount of these residues generated annually by the forest industries include a large portion of bark. It is available in plenty and has limited uses like for fuel, which is not recommended in current scenario of environmental & health awareness (WHO, 2006). Further, because of its low calorific value, the burning bark has not supported its use as a raw material for fuel (*Deppe and Hopmann, 1972*). Millions of tons of bark are produced annually all over the world by forest industries. The North American forest industries alone produce more than 50 million tons of bark annually (U.S.F.P.L.). Worldwide, the amount of bark generated as a result of the industrial wood harvesting, is definitely many times higher than this figure. Approximately 50% of the bark is currently burned for energy production while a considerable amount is disposed of in landfills, which raises serious concerns for ground-water pollution. In addition to the normal production of bark by forest industries, the largest outbreak of the mountain pine beetle ever recorded in various

parts of North America also contributes to the availability of tremendous amount of beetle infested bark due to the high mortality rate of pine trees.

In general, bark consists of around 9 to 15 percent of a typical log by volume or sometimes more than this on a dry weight basis (USDA, 1971). This huge volume of bark residue must be continually removed from mill sites for better functioning. Pulp and paper industries also face similar problems, where bark disposal is costly. Further, markets for bark have never been in greater demand due to its futility. Air pollution regulations and high timber prices make a necessity of maximum utilization of this forest product.

During the 1960s and 1970s, the need for improved utilization of bark was acknowledged as a means of reducing volume of waste bark requiring disposal. This led to the development of various new by-products of the forest industry. A review of the literature supports that various efforts of bark incorporation into different types of boards have been made and the opinions of authors on this form of utilization range from highly enthusiastic to mildly doubtful. Positive opinions, behind the thinking of utilization of bark emerged due to its surplus availability, high amount of natural phenolic components, fibrous nature and no requirements of synthetic resins for particle bonding etc., while negative thinking was probably due to variability and complexity of bark and its chemical components and requirement of very high pressing temperature (up to 300°C) during the board pressing. Indeed, the higher extractive content of bark may be an aid in binding the bark particles together.

However various efforts have been made to utilize the bark as raw material for composite boards even though its utilization for value added products is still in a relatively primitive stage. In order to utilize this material to its full potential, it is necessary to conduct comprehensive research in this area. Efficient bark utilization can create a new industry and boost the economy by making a valuable asset out of a costly waste. The opportunities of bark utilization appeal to many wood enthusiasts and conservationists. It is noticeable that many wood processing companies like Kafus Industries Ltd., The CanFibre Group etc. have invested huge sums in the construction of bark processing plants (Business Wire, 1999). The

effective utilization of bark in smarter way will not only solve the environmental issues associated with it, but can also increase an economic gain. So it may be a good idea to convert bark to panel products which can replace the similar wood based products.

This research project is an attempt to develop and improve the environmental-friendly boards from bark. It includes chemical and thermal characterization of raw material, study of self-bonding and temperature and particle sizes influence, investigation of role of bark composition and extractives in auto-adhesion, possibilities of internal bond improvement by the use of catalyst, bark liquefaction products, comparison with boards produced using synthetic resins and board characterization.

## **1.2 Problem Statement:**

Although some efforts have been made to utilize the bark for making of barkboards or bark particleboard during the last four decades, this research is still in the preliminary phase and comprehensive study in many areas is still lacking. Few researchers tried to improve the auto-adhesion and the practical feasibility of process parameters. There is a need to develop better and improved production techniques and there is a large scope to investigate various phenomena associated with the manufacturing of barkboards.

The most important problem in commercialization or industrial production of barkboard is the requirement of high temperature and long pressing time. Furthermore, a high amount of moisture is released while pressing of boards due to condensation and polymerization reactions which cause blowing of boards and high core gas pressure during pressing. As a raw material, bark is very complex in chemical nature and highly variable. Its low thermal conductivity also causes trouble in heat transfer to core layers during pressing. Poor mechanical properties like internal bond, MOE, MOR etc. are also issues to be addressed. The inferior quality related to physical properties like color and surface quality are additional hindrances in success of this product in the marketplace. Very little or no work has

been done to investigate chemical reactions during pressing which are responsible for auto-adhesion of bark particles. In-depth study is also required to explain many other issues related to barkboard characterization and process parameters.

### **1.3 Hypothesis:**

It is the hypotheses of this thesis that:

1. Mountain pine beetle infested lodgepole pine barks can be utilized for making barkboards without any synthetic resin due to the polymerization reactions of its phenolic compounds and polymer softening at the higher temperature;
2. Various conditions of pressing (temperature) and raw materials (particle sizes) have an effect on the barkboard manufacturing;
3. The board's properties can be improved by the use of bark liquefaction products.

### **1.4 Objectives:**

The main goals of this project are to investigate self-bonding mechanism, with special emphasis on the role of bark components involved in this mechanism, effects of temperature and particle size on boards properties, optimization of process parameters, study of chemical, thermal and anatomical properties of bark and board characterization. Barkboard requires a high temperature during pressing, which is the main obstacle in its production on a commercial scale, so related studies will definitely be helpful in better understanding of thermal reactions and further improvements of the boards.

The core objectives of this research project are:

1. Chemical analysis of green and beetle infested lodgepole pine bark and their comparison.
2. Comparison of thermal behavior (softening and degradation) of green and beetle infested lodgepole pine bark with and without extractives and with different amounts of catalyst concentrations and their comparison.
3. Study of barkboards manufacturing process at laboratory scale and trials to improve the board properties by adaptation of appropriate techniques.
4. Evaluation of the effects of temperature, pressing conditions, particle size and additives on boards properties.
5. Comprehensive study of self-bonding mechanism and efforts to determine the specific role of different bark components in this process.
6. Study of the chemical and thermal reactions, heat transfer from surface to core, bond curing and cross-linking during board pressing.
7. Investigation of the role of bark liquefaction products as additives to improve the bond strength and properties of barkboards.
8. Evaluation and comparison of mechanical & physical properties of produced boards.
9. Characterization of produced boards and study of chemical changes under different conditions.

Systematic study should be helpful to initiate a clear direction of further research in the area of bark utilization for making of composite products.

## **1.5 Significance of Project:**

It is interesting to clarify the usability of bark in production of quality composite boards. Such systematic investigation can promote better bark utilization. Production of improved quality barkboards not only can overcome the problem of bark disposal but can also replace the similar products made from wood and contribute positively to address some environmental issues. It can be claimed on the basis of previous studies that certain properties of barkboards, such as high resistance to water, make it ideal for floor underlay, door stock, shingles and decking; its low production cost makes it a competitive alternative to wood and non-wood siding. Barkboard is also environmentally friendly, as it is manufactured without the use of added chemical resins. The process uses bark's natural phenolic compounds as a binder through heating and pressing, eliminating the need for industrial adhesives.

Expected outcomes from this project are:

1. An improved knowledge in using lodgepole pine bark as the raw material for board manufacturing.
2. A better understanding of the role of bark components in self-bonding of the barkboards.
3. A better insight into the curing process and chemical & thermal reactions in self-bonding of bark particles.
4. A clearer understanding of the feasibility of mountain pine beetle infested bark for barkboard manufacturing will be evaluated.

Furthermore, there are many significant professional benefits expected from the proposed research project. The results will be beneficial in the development of better and advanced environmental-friendly barkboards. Experimental results

should contribute scientifically to improvement in the existing barkboards production and forest waste utilization techniques. Additional indirect benefits associated with this project are socio-economic benefits and contribution in conservation of valuable natural resources.

## **1.6 Structure of the Thesis:**

This thesis is comprised of eight chapters. Each chapter is divided into various topics and subtopics and contains introduction, experimental methodology, results & discussion, conclusion etc.

The first or introductory chapter describes the background of the research and basics related to barkboards. The second chapter consists of a detailed review of literature related to bark and barkboards. The third chapter is focused on chemical and thermal analysis of bark materials. Chapter four discusses the developmental procedure of barkboards that including various problems encountered in the research. Chapter five contains the observed effects of temperature and particle size on barkboards. Chapter six includes trials of barkboards improvement with liquefied bark and comparison of results with boards made with commercial PF resin. Chapter seven is devoted to characterization of barkboards and their comparison. The eighth and final chapter summarizes the entire research and discusses the conclusions from the experimental work, recommendations, and considerations for the future research.

For quick identification, an overall list of figures, tables and abbreviations is provided at the beginning of this thesis. References are listed in alphabetical order of name of authors at the end of the thesis.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 Introduction to Bark Anatomy:**

Bark is the outermost layer of a tree trunk. It is the protective skin for wood that consists of three layers, from outer to inside known as cork, phloem, and the vascular cambium. Generally bark amounts to about 9-15% of a stem depending upon the species and other conditions. Proportion of bark in the entire tree is highest for branches and tops at around 20-35%; while its portion for the stump and the roots is also higher than that of the stem (*Chang 1954, Harkin and Rowe 1971*).

In comparison to wood, barks have lower swelling behavior, less anisotropic, have slightly lower heat transfer coefficients and are considerably weaker in all mechanical properties due to their anatomical features and chemical compositions (*Fengel and Wegener 1983*).

The structure and elements of the bark are also different from the wood of the same species. Phloem is mainly composed of sieve cells or sieve tubes, companion cells, parenchyma cells in the rays and the phloem parenchyma, phloem fibers and sclereids. Sieve tubes perform the function of transportation of water and sap while Parenchyma cells and fibers are responsible for accumulation of nutrients and support respectively. Elements of inner and outer bark are also quite different in their structure. Inner bark or secondary phloem is made up of sieve tube elements, fibres, sclereids, vertical parenchyma, ray parenchyma and companion cells etc. while outer bark or rhytidome is composed of old phloem and periderm, which is again divided into phellogen, phellem or cork, phelloderm (*Patel 1974, Bowyer, Shmulsky and Haygreen, 2003*).

## 2.2 Bark Chemistry:

Various textbooks (Forest Products and Wood Science, Wood; chemistry, ultra-structure and reactions etc.) provide general information on bark chemistry. The chemical composition of bark determines the properties which are important for its utilization.

Like other bio-materials, chief elements in the organic portion of bark are carbon, oxygen and hydrogen. These are combined to form the organic polymer substances or bulk of bark. These polymers can be divided into two main groups, carbohydrates (also called polysaccharides and made up of chains of sugar molecules) and polyphenolics. Bark contains very small amounts of nitrogen. Considerable amounts of mineral elements are also present in bark and remain in the form of ash after burning of bark. The polymeric phenolic part of bark is mostly composed of lignin. Hardwood bark lignins are mainly composed of syringyl, guaiacyl and small amounts of p-hydroxyphenyl nuclei while softwood bark lignins have quite similar composition of syringyl-guaiacyl ratio but differ in higher proportion of p-hydroxyphenyl units (*Koch P.* 1972, 1985; *Fengel and Wegener* 1984).

The general chemical composition of wood and bark of hardwoods and softwoods is given in Table 2.1:

Table 2.1: General chemical composition of wood and bark of hardwoods and softwoods (According to Forest Research Note-091, Forest Products Laboratory, U.S. D.A., 1971).

Constituents	Hardwoods		Softwoods	
	Wood	Bark	Wood	Bark
Lignin	18-25	40-50	25-30	40-55
Polysaccharides	74-80	32-45	66-72	30-48
Extractives	2-5	5-10	2-9	2-25
Ash	0.2-0.6	Up to 20	0.2-0.6	Up to 20

Other than polymeric compounds, many low molecular weight extractives which are soluble in neutral organic solvents and water are also found in barks. The amount of extractives is much higher in bark than in wood. Their amount varies according to bark species, but solvents used for their extraction also affect their values. With the help of sequential extraction yields it is possible to characterize their composition and this composition may vary highly even in the same genus (*Fengel and Wegener 1984*).

Bark contains both polar and non-polar extractives. Usually, polar materials (e.g. tannins, polyphenols, glycosides) are three to five times as abundant as non-polar constituents (e.g. fats, waxes, terpenes, steroids). In general important extractives which are present in the bark include polyphenols, di-, tri- and oligo-flavanoids, monomeric flavanes and flavones i.e. catechin, gallic acid, myricetin, quercetin, taxifolin, cyanidin etc., Sterols, resin acids (diterpenes), tannins, suberins, gallic and allelic acids, and stilbenes (*Rowell 2007, Sjostrom 1993, Weissmann 1983*).

In brief, in its chemical composition, bark is much richer in quantity and complexity of organic chemicals than wood of the same species. It differs from wood by the presence of polyphenols and suberin, by the lower percentage of polysaccharides and higher percentage of extractives (as shown in table 2.4). Bark is also more acidic than wood and has higher amounts of minerals e.g., Ca, K, Mg etc. (*Fengel and Wegener 1984*).

### **2.3 Bark Thermal Properties:**

Bark differs greatly from wood in morphological and chemical structures. Due to the amorphous nature of extractives and crystallinity of cellulose, the structural components of bark is supposed to more sensitive to temperature and pressure than the wood. Bark extractives are mostly in solid form at room temperature, but heating under pressure may cause them to soften or flow. This thermal property of bark is important in the ultimate utilization of bark in panel production.

In recent years, studies of the thermal behavior of the bark have been performed by various researchers (*Chow and Pickles 1971, Hengst and Dawson, Place and Maloney 1975, Demirbas 2005*). Many workers isolated lignin, hemicellulose and cellulose to study their thermal softening temperatures separately. Thermal properties like specific heat, heat transmissivity (thermal conductivity & thermal diffusivity), heat of combustion etc. of barks are significant in its utilization.

When bark is exposed to elevated temperatures, changes can occur in its chemical structure and morphological features. These changes affect its performance. Temperature level and the length of time under exposure conditions are the key factors affecting changes. At lower temperatures, the changes in chemical structure may be apparent only as reduced strength, and hygroscopic water and volatile oil weight loss while higher temperature may cause very drastic chemical changes which may result in reduced strength and considerable carbohydrate weight loss. At the same time carbon content increases, an indication of chemical conversion of bark constituents (*Chow and Pickles 1971, Koch 1985*).

In a thermal softening experiment of bark *Chow and Pickles (1971)*, observed that below 180°C to 200°C, the thermal softening of bark in the presence of moisture was accredited to plasticization by water and no chemical bonding occurred at this time. After this temperature, the bark was highly sensitive to chemical degradation and polymerization reactions. Due to the polymerization of phenolic extractives and lignin components of bark, adhesion occurred among bark particles. It is obvious that at the same time cellulosic compounds should degrade which may cause negative effects on strength properties of boards.

In chapter 12 of their textbook titled “Wood: Chemistry, Ultra-structure, Reactions” *Fengel and Wegener* described the influence of temperature on woody materials. They mention that softwoods and hardwoods soften near 180°C with a maximum at 380°C and this softening is greater in the presence of moisture. Temperatures above 200°C resulted in structural changes, conversion of components, occurrence of gaseous degradation products etc. If the temperature is more than 270°C, pyrolysis of wood started. Further increase in temperature causes

an increase of gaseous products and temperature above 500°C led to gasification of wood. With regard to chemical components, it is mentioned that polyoses start to degrade at 180°C and converted into methanol, acetic acid and volatile heterocyclic compounds like furan, valerolacton etc. while for cellulose, after 200°C cleavage of molecular chains, dehydration and oxidation occurred and volatile substances like levoglucosan, anhydroglucoses, furan and furan derivatives are formed. Other than hemicellulose and cellulose, lignin showed most thermal stability with a softening temperature of 160-200°C. Its alkyl-aryl ether linkages are broken up to 270°C and an attack on C-C linkage begins at 230-300°C.

## **2.4 Beetle Infested Lodgepole Pine (*Pinus contorta*) Bark:**

The species of primary interest of this research is lodgepole pine. The beetle infested bark was used for the purpose of making of boards.

### **2.4.1 Bark Structure:**

In the coastal region, bark of lodgepole pine is thicker (may be up to 2.5 cm near stump) with deep furrows. This bark has reddish-brown color. In contrast, trees grown away from the coast have much thinner barks (around 0.5 cm thick) and have light yellowish-brown color with small scales. Usually, outer bark of lodgepole pine shows narrow rhytidome layers with narrow and thin periderm. It has fine texture and light colored secondary phloem (*Koch 1985*).

The mountain lodgepole pine has rather characteristic bark. It is yellowish-brown in color and has very narrow secondary phloem in both inner and outer bark. It also has many large resin canals and sporadically distributed phloem parenchyma (*Koch 1985*).

#### **2.4.2 Chemical Changes due to Infestation:**

It is interesting to know about the chemical changes in bark of lodgepole pine due to the attack of mountain pine beetle. Very limited data are available in the literature on beetle infested lodgepole pine bark's chemistry; however few researchers (*Hartley and Pasca 2006, Safranyik and Wilson 2006*) describe the chemical nature of beetle infested wood so it can be assumed that bark chemistry is also affected, more or less, in a similar manner.

*Ophiostoma lavigerum, O. montium, O. minus* and *O. ips* are the common species of stain fungi, which are associated with mountain pine beetle (*Dendroctonus ponderosae* Hopk. Coleoptera: Scolytidae) infection. Cumulative effects of the fungi and beetle lead to chemical changes in wood and bark (*Safranyik and Wilson 2006* report).

Researchers demonstrated that holocellulose (cellulose and hemicellulose) content in beetle infested lodgepole pine bark is slightly higher than normal. In contrast, content of lignin decreases. It is also found that infested barks have a higher proportion of fatty and resin acids, and a lower proportion of sterols, steryl esters and triglycerides compared to sound bark. This difference occurs due to the defense mechanism; beetle infested lodgepole pine bark secretes oleoresin which is a mixture of resins and monoterpenes (*Safranyik and Wilson 2006* report).

#### **2.5 Barkboard:**

Barkboard is a panel product, moderately similar to particleboard. Technically this term is used for boards, which are exclusively made from bark particles and without any synthetic resin, using heat and pressure to utilize the bark's natural chemicals as a binder rather than adding resin. Polymerization of phenolic compounds and plasticization of lignin probably play major roles in binding bark particles together. Overall, about 30 percent of bark reacts as a phenol adhesive (*Chow, 1975*).

According to Forintek Canada, the following are the suggested uses of barkboards (on the basis of performance tests):

1. Roof insulation of panel homes.
2. Heat and sound insulation under wooden floors.
3. Middle layers of crosspieces of sandwich constructions.
4. Vertical and horizontal insulating elements in industrial and agricultural buildings.
5. Other general uses if laminated by veneer, plastic, melamine etc.

Various research attempts have been made previously to study bark as a raw material for manufacturing of composite boards. Other than traditional uses, other uses for bark can be as building insulation boards, hardboards, fiberboards, and particleboards, and many publications have dealt with this possibility.

On the basis of a literature review of previous research work, which utilized the bark as raw material for making of panels, two different approaches can be recognized. Researchers like *Burrows* (1960), *Chow* (1972, 1975), *Wellons* and *Krahmer* (1973), *Troughton* (1997) etc tried to make boards without any resin and used self-bonding of bark particles due to lignin plasticization and extractives polymerization of bark components. In this case temperature played a key role.

In the second approach, *Alvang* and *Johanson* 1965, *Blankenhorn* 1977, *Deppe* and *Hoffmann* 1972; *Dost* 1971; *Place* and *Maloney* 1977; *Wisherd* and *Wilson* 1979; *Muszynski* and *McNatt* (1984); *Blanchet*, *Cloutier* and *Riedl* 2000, 2008 etc. used synthetic resin to bond bark particles together. Here the intention was to use bark particles for their physical properties only and the role of bark chemicals as for the first approach, was ignored.

Both approaches are described below in section 2.6 and 2.7 in detail.

## **2.6 Self-bonded Barkboard (Without Synthetic Resin):**

Research on barkboards without addition of synthetic adhesives was pioneered by *Heritage* (1956) and *Burrows* (1960). *Heritage* worked on thermal plasticization principle for pressing barks containing cork into particleboard at press temperature below 210°C while *Burrows* reported a plasticization technique by using moisture to plasticize lignin by varying amount (2 to 20%) of moisture content (MC).

In 1972, *Chow* reported on a kinetic study of Douglas-fir and red alder bark. He pointed out that the phenolic substances of these barks can be polymerized by high-temperature heating. On the basis of thermal studies he proposed that the moistened wood and bark softened at temperatures below 200°C, due to physical rather than chemical factors attributed to plasticization by water. At higher temperatures (greater than 180°C), the thermal reaction of bark was attributed to the polymerization and degradation of bark components. These thermal reactions are important in barkboard's manufacturing and its process parameters settings.

*Wellons* and *Krahmer* (1973) explained the mechanism for the cohesive bonding of Douglas-fir bark without adhesive to assess the different hypotheses about self-adhesion. They selectively prevented bonds from forming and broke bonds once formed by organic vapors. They concluded that below 205°C, self-bonding in Douglas-fir bark boards resulted primary due to thermoplastic flow and physical consolidation of bark particles. There was no evident of chemical bonding at this temperature.

Major work in the area of barkboard was carried out by *S. Chow*. He reported his research findings in a paper titled "Barkboards without synthetic resins" published in the *Forest Products Journal* in 1975. In this paper he utilized the principle of bark extractive-lignin polymerization at high temperature. He found the most effective pressing temperature in the range of 250°C to 300°C for barkboards manufacturing. The important properties like dimensional stability, moisture absorption and strength of such barkboard were found similar to or better than barkboards made with 4-7% urea-formaldehyde and phenol-formaldehyde resins

using a pressing schedule similar to commercial particleboard production. As per Canadian Standard Association 0188-1968 standard requirements, these barkboards were close to type I (exterior) grade particleboard, in their properties.

*Chow* reported that at 200°C temperature and up to 120 minutes of pressing time, oven-dry bark particles released 2 to 9 percent of moisture. This release of moisture linearly increased the Internal Bond strength of the resultant barkboards, about 18 psi for every 1 percent of moisture release. According to *Chow* this moisture release was most likely due to the chemical condensation and dehydration of the bark chemical components. This is the reason that barkboards are more susceptible to blow and moisture blisters when pressed at higher temperature. *Chow* developed a vacuum-platen system to reduce the possibility of blisters due to released moisture during pressing.

*Chow* also established the pressing parameters required to manufacture Douglas-fir bark particleboards. He found improved board properties at 280°C (for 20 minutes) and at 300°C (for 5 minutes). He also discussed and compared the different mechanical properties of boards under different pressing conditions. *Chow* tried to explain the sharp contrast between the results of 200°C and other temperatures by assuming that the board formation in 200°C consists mainly of a plasticization effect with little or no lignin/extractive polymerization. At the higher temperature ranges (up to 300°C), the thermal polymerization becomes the dominant factor.

In recent years, *Chow's* work has been continued by *Troughton*. He obtained self-bonded barkboards at different conditions of pressure and temperature. He also produced different kinds of barkboards by lamination with veneer and lumber. *Troughton* et al (2000) patented their work in U.S. patent nos. 6,120,914 and 5,725,818. In these patents they described their invention and commercial method of making barkboard without any synthetic resin. They used hog-fuel as a raw material for making of boards and also avoided using a vacuum press (as in case of *Chow*) by the use of interwoven stainless steel wire mesh screen. In the testing results, *Troughton* found that boards met the minimum

requirement as per CSA 3-0188.1-M-78 standard (Interior mat formed wood particleboard). Other than these exciting results, the process was still not of much commercial interest because of requirement of high temperature during pressing.

As a partial solution for the above problem, *Troughton* described an improved method for manufacturing of hog fuel board by using a catalyst in another patent US 6,544,649B1 (2003). He explained that the presence of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) as a catalyst, uniformly distributed through the hog fuel mat significantly lowers the temperature required at the heating press platens to form a board which also has improved properties. He found that boards with 3% ammonium chloride pressed at  $260^\circ\text{C}$  are better than those of the non-catalyzed control boards pressed at  $300^\circ\text{C}$ .

In a recent experiment, *Geng, X et al.*(2006) treated black spruce bark by 1% NaOH for the manufacture of binder-less fiberboard. In their experiment they characterize black spruce bark for its chemical components and suitability for the manufacture of fiberboard. According to the authors, alkaline extractives of the bark contributed in self-bonding ability. The bark was treated with 1% NaOH solution, pre-heated with steam, and then refined to produce fibers by steam-pressure. For comparison, pre-heating and refinement of the untreated bark was also performed. They used FTIR Spectroscopy and Differential Scanning Calorimetry (DSC) for characterization of bark fibers. The alkaline-treated bark fiberboards showed lighter color, higher internal bonding strength, higher MOR, and higher MOE in comparison with the untreated panels.

To study the self-bonding mechanism of barkboards it is also important to study the bark extractives and research on development of adhesives from these extractives. Many researchers have worked on bark extractives, their extraction techniques, chemical analysis, thermal behavior and adhesion properties. *A. Pizzi, Y. Yazaki, P.J. Collins, P. Labosky, G. Weissman, E. Masson, C.T. Liu, C. Ayla, L.K. Dalton* etc. are a few key researchers.

## **2.7 Bark Particleboard (With Synthetic Resin):**

According to the second approach which was discussed in section 2.5, various researchers have tried to utilize bark particles for making of particleboard with the use of a variety of resins as binding agents. Key studies are discussed below:

*Dost* (1971) studied effects of wood bark fibers on properties of particleboard. He prepared three layer particleboards from redwood particles using 0, 10, 20 and 30% redwood bark fibers with three different resin contents. He reported that most of the mechanical properties and board performance became poorer as bark fiber content increased.

*Deppe and Hoffman* (1972) performed particleboard experiments and utilized softwood bark residues. They used machine-debarked spruce and pine bark obtained from a sawmill. Phenolic and isocyanate resins were used for spruce and for pine bark respectively. They applied different ratios of wood and bark chips in surface and core layers. As expected, they noticed that bending strength decreased with increased bark content in the surface layers. Decreasing strength of boards with core layers of wood and bark particles followed the same pattern.

*Deppe and Hoffman* also tried to utilize the self-gluing ability of the bark by test with ammonia-disintegrated spruce bark. It was mentioned that when disintegrating spruce bark in ammonia solution followed by adding moisture and heat, a ligno-sulfate complex is formed with irreversible characteristics. They used a swivel-mounted pressure tank with 80°C temperature and 1.5 atm pressure for this process. A preliminary test was performed on 750 gram bark with 4 liters of 25% ammonia solution. Leaching time was set to 24 hours. Researchers didn't found satisfactory results with this procedure.

*Maloney* (1973) performed various experiments on barkboards from west coast softwood species. He conducted his preliminary research on western larch, Douglas-fir, ponderosa pine and western red cedar bark for making of single

layer particleboards at 7.5 and 10 percent UF resin contents. He found that western red cedar boards had good bonding strength, while its internal bond was not found suitable. The other three species showed comparatively lower bending strengths, but better internal bond than red cedar. These differences were attributed to the blocky particle geometries of Douglas-fir and ponderosa pine, and the flaky particle geometry of larch. He made combinations of red cedar and Douglas-fir bark on the faces and in the core respectively which resulted in better bending and internal bond strengths. These three layer boards also showed very low linear expansion values in contrast to the board of larch, pine and Douglas-fir, which showed very high linear expansions.

*Anderson, Wu and Wong (1974)* studied the suitability of ponderosa pine bark extract as a bonding agent for particleboard. They used bark as core furnish in a three layer particleboard. The average extractive content of ponderosa pine bark was around 25% of the OD weight of bark with a tannin content of about 8%. Paraformaldehyde with concentrated bark extract was sprayed on the board particles which were then processed into board. The intention behind this was to initiate a reaction between released formaldehyde during the hot-press cycle with polyphenolic compounds present in the extract to form a waterproof bonding agent. The core of three-layer board was produced from bark with a small amount of paraformaldehyde while bark extract was used as a bonding agent for the outer wood particle or surface layers. Results showed satisfactory and comparable properties with some synthetic phenol exterior type particleboards. The economic feasibility also supports the use of bark extract as bonding agent and bark as core in a three layer particleboard.

In continuation of Maloney's previous work, *Place and Maloney (1975)* manufactured three layer particleboards from combinations of wood and bark. They produced surface layers from western white pine wood particles and bonded it with 5% phenol formaldehyde (PF) resin. The core layer was made with Douglas fir bark particles bonded with 6, 8 and 10% PF resin. Three different press closing times (30, 120 and 210 seconds) were used which resulted in three board densities (550, 700 and 850 kg/m<sup>3</sup>). Their investigation evaluated the role of specific gravity and press

closing time on the mechanical properties of the board. They also obtained thermal conductivity of boards by guarded hot plate apparatus and found that thermal conductivity of wood-bark composite board was generally less than that of particleboard at a given average density.

*Place and Maloney (1977)* studied a variety of three-layer composite boards which were made by using two bark species for the core and varying the pressing conditions. The IB strength of grand fir bark cores was greater than that of Douglas-fir bark cores. Further they also found that water absorption and thickness swell of the grand fir bark boards were higher than those of the Douglas-fir bark boards.

*Blankenhorn et al (1977)* investigated some of the compressive and flexural properties of the barkboard and polymer impregnated barkboard. The objective of their study was to compare the properties of non-impregnated barkboard with barkboard impregnated with epoxy and methylmethacrylate. The maximum crushing strength of the MMA-impregnated barkboard was nearly four times higher and the epoxy-impregnated board about eight times higher than the un-impregnated controls. In the same way, MMA-impregnation resulted in a compressive MOE about two times higher and epoxy impregnation gave an MOE about five times higher than the controls.

*K. D. Wisherd and J. B. Wilson (1979)* also studied the effects of bark as a supplement to wood furnish in production of particleboard. They substituted the wood particles by bark particle from 5, 10 to 20 percent (OD weight). They used three types of bark (Douglas-fir, ponderosa pine and red alder) for individual substitution. The boards were bonded with urea-formaldehyde (UF) resin and phenol-formaldehyde (PF) resin. All boards were compared with each other and with control boards (100% wood furnish bonded with either resin) for differences in properties. Results showed that red alder bark with PF resin improved IB strength almost 2.5 times while adding ponderosa pine bark with PF resin improved linear expansion and thickness swelling. Douglas-fir bark with 5% PF resin didn't show any change in strength properties. It is also important to mention that the three barks

performed similarly when bark substitution increased, with a linear decrease in strength properties, but with little effect on dimensional stability. On average, 5 to 20% increase in the rate of bark substitution, resulted in MOR decrease from 7 to 24%, MOE decrease from 4 to 17% and IB decrease from 5 to 20%.

*Muszynski and McNatt (1984)* made single layer wood particleboards from Scots pine with addition of Norway spruce bark in a proportion ranging from 0 to 100 percent of the furnish in 10 percent increments. They used 12 percent of urea-formaldehyde (UF) resin for bonding. The wood and 30 percent spruce bark combination performed best. They also found the following parameters are suitable for pressing of boards: pressing time 8 minutes, pressing temperature 180°C and pressure 22 kg/cm<sup>2</sup>. Their preliminary test also indicated that the best strength properties were obtained with a bark particle size of 3 to 8 mm. All boards met the particleboard requirements according to the Polish Standard PN-72/D-97004 recommended for use in furniture-making industries.

*Blanchet et al. (1998)* studied particleboard, made from hammer milled black spruce bark residues. The objective of their study was to determine the technical feasibility of particleboard production from black spruce bark residues bonded with urea-formaldehyde resin that meet the indoor performance requirements for wood particleboards. In their experiments, dried black spruce bark particles were generated from a hammer mill and sieved. Fine particles were used in the surface layers and coarse particles were used in the core layer. Particleboards of 540X560X16 mm were produced using 200°C temperature for 5 minutes. A factorial design with two manufacturing variables at three different levels resulted in 9 different combinations plus 3 replicates for a total of 27 boards. Observations showed that the wood particles content in the surface layers affected the heating kinetics (heat transfer from surface to core). Mechanical properties of all boards were also evaluated according to ANSI which showed that technically it is possible to make particleboard from bark residues. 50 percent wood content (50 percent bark content) and 14 percent resin content in the surface layers, was found suitable for mechanical properties but linear expansion values were not satisfactory. It was also

observed that a higher wood particles proportion in the surface layers improves the heat transfer from surface to core.

In another paper “Bark particleboard: pressing time, particle geometry and melamine overlay” (2008) *Blanchet et al* discussed the effects of pressing time, particle geometry and melamine overlay on bark particleboard properties. The objective of that study was to determine the possibility of making black spruce bark particleboards with a short curing time and to assess the effect of bark particle geometry on the mechanical and physical properties of bark particleboards. Effects of melamine films were also reviewed. Mechanical and physical properties were evaluated for all combinations. Their work shows that it is feasible to press bark particleboards with a short curing time for a 16-mm thick particleboard. A four minute curing time, which was 18% shorter pressing schedule than what was shown in previous work (*Blanchet et al. 2000*), was found good for most of the mechanical properties while use of wood fibers instead of wood particles reduced the linear expansion. Use of hammer-milled bark particles or refined bark particles had no effect on flexural properties of boards. White melamine overlay affected the color while no difference was observed with black film by colorimeter.

## **2.8 Conclusions of Literature Review:**

The detailed literature survey presented in this chapter provided the previous and ongoing research efforts related to barkboard and similar products made with partial or full use of bark or bark products with and without resin. Anatomy, chemistry and properties of bark including mountain pine beetle infested lodgepole pine bark were also discussed. On the basis of the above literature survey many conclusions can be drawn, which are helpful in understanding the past efforts and can provide the future direction of research needs in omitted areas.

The anatomical structure and chemical composition of bark has not shown any hindrance in utilization as raw materials for panel production. High extractive and lignin contents of barks have make it suitable for self-bonded barkboards. Mountain pine beetle infested lodgepole pine bark has possibility of

chemical changes in its composition; however its application for panel products was not discussed in any research literature.

Various researches concluded with the feasibility of full or partial use of bark as a raw material for particleboard production, but the end products lack many desired properties and have not attracted much research due to mixed results. Most of the barkboards or particleboards made from bark have low to moderate mechanical & physical properties which can be improved by further research efforts; therefore an elaborate research is required to improve its properties and possibilities of its use at commercial level. Possibility of chemical modifications, strength improvement and better production techniques may be issues which need more emphasis.

Barkboards do not require any synthetic resin for bonding. Self-adhesion occurs as a result of thermal and chemical reactions by lignin plasticization and polymerization of phenolic compounds. There are many advantages associated with barkboards. Further, it is environmental-friendly & no there are no formaldehyde emissions, as it is pressed without the use of added chemical resins.

Significant work of key researchers in the development of self-bonded barkboards was concentrated around the alteration of temperature in binding of particles, since thermal reactions plays a major role in auto-adhesion and mechanical properties of barkboards. Even after various efforts, elimination of the high temperature requirement for making of boards cannot be done satisfactorily. Further, the basic issues like effects of particle size, optimization of process parameters, exact knowledge of thermal and chemical reactions, bark and barkboard characterization, application of environmental-friendly adhesives like liquefied bark for improvement in binding and mechanical properties improvement are still need to be explored more and require significant scientific contribution in these areas. This thesis aims to explore most of these issues and develop barkboards from beetle infested lodgepole pine bark.

## **CHAPTER 3: BARK CHEMICAL & THERMAL ANALYSIS**

### **3.1 Introduction:**

Knowledge of chemical and thermal properties of any raw material is very important in its ultimate use in fabrication of value added products. Its chemical and thermal evaluation data can be used to analyze its suitability for end uses. Bark is a complex and highly variable material. A substantial amount of information can be traced in the literature for chemical constituents and thermal behavior of barks but similar to other bio-materials, bark shows huge variation in its properties even from the same species. These variations are due to factors, such as the location of tree, part of bark selected, age of tree, environmental condition of area etc. Thus published data, even for a particular species, cannot provide accurate information about specific bark. Therefore, in this part of the project, chemical and thermal analysis of the bark, used throughout the project, was performed.

Extraction is one of the important steps in chemical analysis of barks. Analyses have been made of several barks, but their comparison is restricted because of the different extraction steps and types of solvent used in extraction. It is quite possible that the same bark gives different results if extracted with different solvents. With regards to other chemical components like holocellulose and lignin, there is more possibility to get standard results but they can be influenced by pre-extraction procedure used for determination of the extractive content.

For determination of thermal behavior of lignocellulosic materials, the most common methods are Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The advantage of these methods is the accuracy and speed with which data can be obtained and the small sample size required.

The main objective of this chapter is to conduct chemical and thermal analysis of beetle infested lodgepole pine bark to help with manufacturing of the barkboards. It is believed that various extractives and lignin play a major role in the

formation of self-bonded barkboards; their chemical analysis is therefore important. Furthermore, thermal analysis of bark under different extractive free conditions and with various amounts of catalyst also gives an idea about the probable response of the material during hot pressing and conversion to composite boards.

### **3.2 Analysis of Bark Chemical Composition:**

These experiments investigate the chemical constituents of green pine and beetle infested lodgepole pine bark and their comparison. Other than cellulose, hemicellulose and lignin, there are many extraneous materials associated with bark. The beetle infested lodgepole pine bark is expected to differ in its chemical structure due to decay by fungi associated with beetle infestation from its sound counterpart. The difference in the chemical composition can potentially alter the properties of the boards.

#### **3.2.1 Experimental:**

The procedure for determination of the chemical constituents was according to TAPPI Standards T264 om-82 and T204 os-76. Following are the steps in the experimental procedure:

- I. Determination of Extractives Content
- II. Determination of Holocellulose
- III. Determination of Alpha-cellulose
- IV. Determination of Klason and soluble lignin

##### **3.2.1.1 Extraction:**

The main objective of the extraction work was to perform quantitative analysis of extractives present in these barks and to obtain extractive free barks of green and beetle infested lodgepole pine for comparative studies of thermal properties in next part of research.

Extraction of all samples was performed in a Soxhlet extractor by the standard sequential extraction techniques according to ASTM D1107-96, D1108-96, D1109-84, and D1110-84. Extractive-free bark was prepared according to ASTM D1105-96. Hydrophilic and lipophilic compounds were extracted by use of hot water and ethanol-toluene solvents respectively. 1% Sodium Hydroxide (NaOH) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solubility was also carried out for all samples.

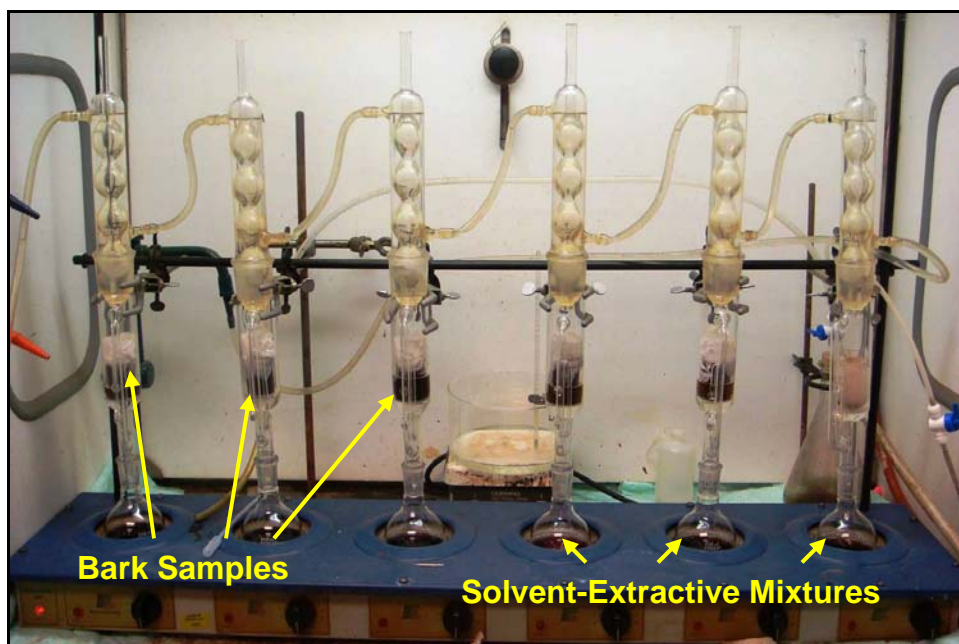


Figure 3.1: Soxhlet extractor arrangement for bark extraction.

### **Materials:**

Green lodgepole pine bark and beetle infested lodgepole pine bark obtained from Forintek were used for the chemical analysis. Dried bark specimens were passed through a Wiley mill and then screened through a 35 mesh screen. These screened and dried bark samples were used for the different steps in the procedure.

Solvents used for sequential extraction were ethanol-toluene (1:2 by volume), hot water, 1% NaOH and CH<sub>2</sub>Cl<sub>2</sub>.

### **Equipment:**

Soxhlet apparatus, condenser, 500 ml round bottom flask, 2000 ml beaker, funnel, Buchner funnel, rotary evaporator, 25 ml flask etc. were used in this experiment.

### **Method:**

After drying the material in a vacuum desiccator to 2-3% moisture content, around 2 g of bark was placed in paper crucibles (3 replicates for each type of bark), which are then positioned in Soxhlet assembly for extraction. First non-polar solvent extraction was performed with ethanol-toluene (1:2 by volume) for 6 hours. The temperature was kept to liquid boiling so that siphoning from the Soxhlet occurred at least 4 times per hour. On the completion of extraction, solvent containing the extract mixture in the round bottom flask was cooled down. The extracts were then dried in the rotary evaporator under suction. Finally, extracts were weighed to determine the amount of extractives.

After the extraction of lipophilic compounds, the paper crucibles with bark samples were left in oven at 60°C for two days to dry completely and the same were then again placed in the Soxhlet apparatus for extraction of hydrophilic compounds with hot water. The procedure described for lipophilic compounds was repeated for this extraction.

### **3.2.1.2 Holocellulose determination:**

After the extraction of bark samples in the 1<sup>st</sup> step, the substances that remained were composed of holocellulose and lignin; the 2<sup>nd</sup> step of chemical characterization of bark was carried out for determination of holocellulose.

#### **Materials:**

The extractive free bark samples (both green and beetle infested) were divided into two groups (four groups altogether). One group (per species) was used for holocellulose determination and another one in lignin determination.

Reagents used were stock solution A (60 ml glacial acetic acid and 20 g NaOH per liter distilled water), stock solution B (200 g Sodium Chlorite; NaClO<sub>2</sub> per liter distilled water), acetone, 1% acetic acid solution and chilled distilled water.

#### **Equipment:**

250 ml Erlenmeyer flasks, 50 ml Erlenmeyer flasks, pipettes, 15 ml coarse fitted crucibles (oven-dried tared), conditioning chamber, water bath (set to 70°C), thermometer were used.

#### **Method:**

The process followed TAPPI standards T264 om-82 and T204 os-76. 0.70 g of air-dried extractive free bark sample was weighed in 250 ml Erlenmeyer flask (3 flasks for each group). 10 ml of stock solution A and immediately after that 1 ml of stock solution B was added to each flask. 50 ml Erlenmeyer flasks were used as stopper for the containers. Chemical were properly mixed by swirling. Flasks were placed into the water bath of temperature of 70±2°C. Three additions of 1-1 ml of stock solution B were added after 45, 90 and 150 minutes respectively of beginning of experiment. After 4 hours flasks were placed into an ice-water bath. Samples were filtered by suction and then oven-dried. Finally oven-dry weight of

holocellulose was calculated after completion of the process, which took place 4-6 days. Timing for the addition of prepared chemical solutions, proper mixing, temperature of bath etc. are the important factors for complete dissolution of holocellulose.

### **3.2.1.3 Alpha-cellulose determination:**

The chlorite reduction followed in the previous part produced a fine white substance which should be mainly composed of the three basic cellulosic polymers. At this point, a further acid reduction was carried out to remove all but the purest cellulose chains. This proportion of the bark is often referred to as simply 'cellulose', but is more properly defined as ' $\alpha$ -cellulose'. It can be described as that portion of the cellulose which contains only D-glucose monomers, unlike hemicellulose, which contains a variety of base sugar components.

#### **Materials:**

Bark samples which were produced after holocellulose determination were used in this experiment.

Reagents were 17.5% NaOH solution, 10% acetic acid solution, acetone (analytical grade).

#### **Equipment:**

Equipments and glassware used in this experiment included Syracuse watch glass, glass rods, filter flask, pipette, oven etc.

#### **Method:**

For this experiment the process also followed TAPPI standards T264 om-82 and T204 os-76. On completion, oven-dry mass of  $\alpha$ -cellulose was calculated as a percentage of extractive free dry bark.

#### **3.2.1.4 Klason lignin determination:**

After determination of extractives, holocellulose and  $\alpha$ -cellulose, lignin analysis was the last step in the chemical characterization of bark. Sulfuric acid is used to hydrolyze the polysaccharides in the bark, leaving behind the various lignin components. A small proportion of the lignin is hydrolyzed as well; this portion can be analyzed as soluble lignin.

#### **Materials:**

As described before that after extraction, extractive free bark samples were divided into two groups one was already used for holocellulose determination and second one was used in this experiment.

72% Sulphuric Acid solution was used for polysaccharide hydrolysis.

#### **Equipment:**

50 ml beakers, medium crucibles, 1 liter flasks, glass rods, oven, dessicator, pH paper, hot plates etc.

#### **Method:**

The procedure for this experiment was based on TAPPI standard T222 om-83 and TAPPI UM250. 1 g of three samples of each group's extractive free bark was placed in 50 ml beaker. 15 ml of 72% Sulphuric Acid solution was then added slowly while stirring gently. Further procedure was performed as described in standards to get the amount of Klason and soluble lignin.

### 3.2.2 Results and Discussion:

Chemical characterization of green and beetle infested lodgepole pine bark gave the results shown in Table 3.1.

Table 3.1: Extractive contents/solubility of green and beetle infested lodgepole pine barks by extraction with different solvents.

<b>Group</b>	<b>Solvents</b>	<b>Extractives/Solubility %</b>
Green lodgepole pine	Ethanol-Toluene	18.19 (0.4)*
	Hot water (after ET)	3.92 (1.2)
	1% NaOH	61.86 (0.3)
	Dichloromethane	14.70 (0.8)
Beetle infested lodgepole pine	Ethanol-Toluene	17.65 (0.5)
	Hot water (after ET)	7.45 (1.2)
	1% NaOH	68.06 (0.5)
	Dichloromethane	14.20 (0.5)

\*Values in brackets showing standard deviation.

### Bark Extraction with Different Solvents

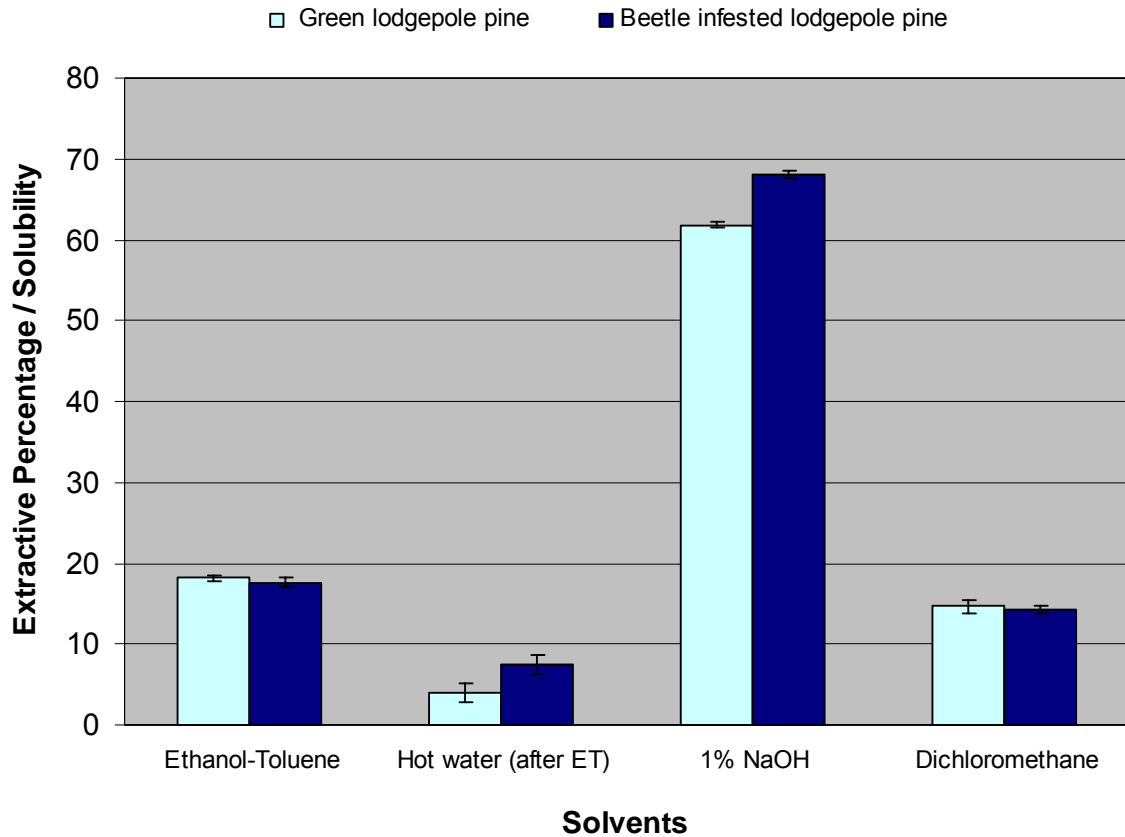


Figure 3.2: Green and beetle infested lodgepole pine bark extraction with different solvents.

Extractive content of green lodgepole pine and beetle infested lodgepole pine barks is shown in table 3.1 and figure 3.2. Results were compared by the statistical t-test. It can state by the t-test value for this comparison that there is no significant difference in organic solvent extractives for these two kinds of barks at the level of  $p = 0.05$ . The beetle infested pine bark has a higher amount of 1% NaOH solubility than the green pine bark. Generally, 1% NaOH soluble of woody material is a sign of the degree of fungal decay, or degradation by other factors. Since the hot alkali removes low molecular weight carbohydrates, mainly composed of hemicellulose and degraded cellulose in the bark, the beetle infested pine bark gave a higher amount of hot alkali extractives as predicted.

Table 3.2: Holocellulose,  $\alpha$ -cellulose and lignin contents of green and beetle infested lodgepole pine barks.

Group	Constituents	Values in Percentage
Green lodgepole pine	Holocellulose	46.50 (0.4)*
	$\alpha$ -cellulose	24.90 (3.2)
	Klason lignin	45.10 (0.6)
	Ash	4.10 (2.8)
Beetle infested lodgepole pine	Holocellulose	46.70 (1.2)
	$\alpha$ -cellulose	20.50 (1.1)
	Klason lignin	42.60 (0.7)
	Ash	4.00 (1.8)

\*Values in brackets showing standard deviation.

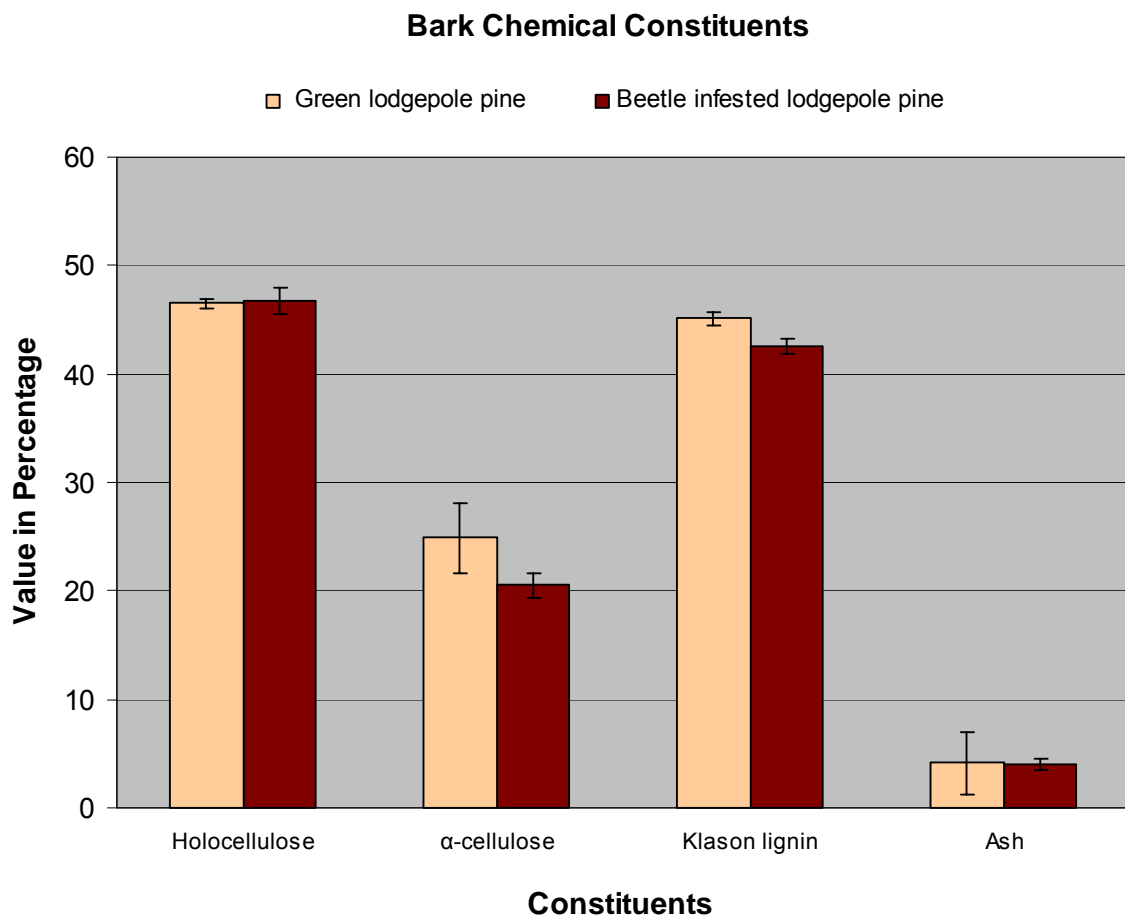


Figure 3.3: Chemical constituents of green and beetle infested lodgepole pine bark.

In case of chemical constituents, green pine bark has a higher  $\alpha$ -cellulose and Klason lignin contents, then the beetle infested one, which point out that some  $\alpha$ -cellulose and lignin had also decayed due to beetle infestation. The beetle infested barks also had a higher amount of hot water extractives, possibly related to the resin production response of the tree to the beetle attack. These barks are also shown no significant difference in their chemical constituents by the t-test value.

### **3.2.3 Conclusion:**

In this study, green lodgepole pine and beetle infested lodgepole pine barks were analyzed for their chemical constituents and compared. Compared with the green lodgepole pine bark, beetle infested lodgepole pine bark had a higher 1% NaOH solubility, more hot water extractives, and lower  $\alpha$ -cellulose and lignin contents. Statistical t-test proved that there was no significant difference in holocellulose amount and organic solvent extractives between these two barks.

Chemical analysis results also support the possibility of utilization of both barks in production of barkboards in later part of the projects because they contained high amount of extractives and lignin which are supposed to play a significant role in self-adhesion of particles without resin.

### **3.3 Bark Thermal Analysis:**

Similar to the chemical constituents, thermal response of bark is also very important in its utilization in self-bonded barkboards. It is meaningful to know at which temperature barks start to lose their weight or at which range of temperature maximum degradation occurs and how barks react to elevated temperatures. Such data can be used to design pressing parameters.

The main objective of this part was to study the thermal behavior of different bark samples with different chemical compositions. For this purpose different bark samples from the previous part of research were utilized. To study the

thermal properties of bark samples, Thermal Gravimetric Analysis (TGA) technique was used. A comparative study of thermal behavior of beetle infested lodgepole pine bark samples was performed.

### 3.3.1 Experimental:

TGA runs were performed for given combinations of beetle infested lodgepole pine barks. These combinations were chosen to investigate the effects of different conditions of bark on its thermal behavior. Results may be applied to modify the bark prior to making of boards.

- (i) Normal beetle infested lodgepole pine bark
- (ii) Beetle infested lodgepole pine bark with 1%  $\text{NH}_4\text{Cl}$
- (iii) Beetle infested lodgepole pine bark with 3%  $\text{NH}_4\text{Cl}$
- (iv) Beetle infested lodgepole pine bark with 5%  $\text{NH}_4\text{Cl}$
- (v) Ethanol-Toluene-Hot water extractive free beetle infested lodgepole pine bark
- (vi) 1%  $\text{NaOH}$  extractive free beetle infested lodgepole pine bark
- (vii) Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) extractive free beetle infested lodgepole pine bark

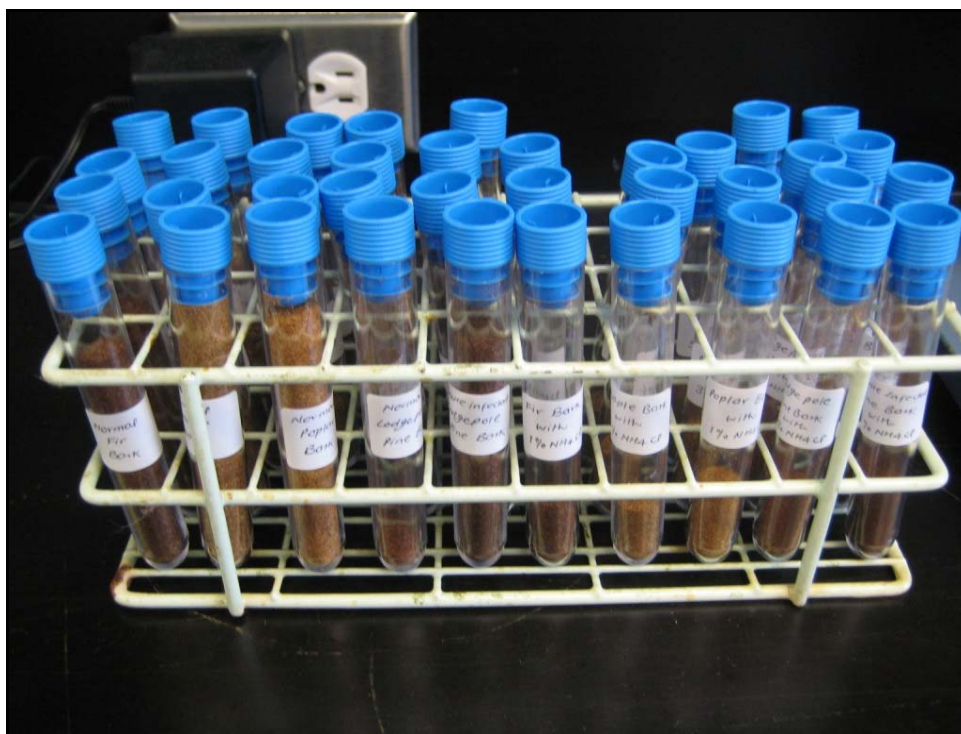


Figure 3.4: Samples showing various combinations of extraction and catalyst for beetle infested lodgepole pine barks.

### **TGA Methodology:**

Each type of bark sample was used to get a TGA curve. The sample was placed in an aluminum pan in a furnace tube. Nitrogen gas was passed through the system and the furnace tube was slowly heated at a constant rate. The temperature was raised up to 700°C at a heating rate of 10°C per minute. The percent of weight loss was measured as a function of temperature and was plotted by TA software.

### **3.3.2 Results and Discussion:**

Different TGA thermograms plotted for different bark samples are shown in the figures below. A curve plotted for normal beetle infested lodgepole pine bark can be described as follows: when the bark is heated from room temperature to 100°C, very few chemical reactions take place. At approximately 100°C, the moisture in the bark evaporated. As the temperature of the bark increases, very little degradation occurs until about 240°C, when chemical bonds start to break via dehydration and, possibly, free radical mechanisms to eliminate water and produce volatile gases.

Whole bark starts to thermally degrade at about 250°C. Between about 250-400°C, the majority of the carbohydrate polymers degrade and only lignin remains. The decomposition of cellulose leads mainly to volatile gases, while lignin decomposition leads mainly to tars and char. In the early stages of cellulose degradation (below 300°C), the molecular weight is reduced by depolymerization caused by dehydration reactions.

It is observed that the basic pattern in curves is quite similar but there is a significant difference in onset temperatures of degradation which can also be clearly seen in combined figure 3.9; these distinctive onset temperatures and weight losses up to 230°C (as it is the highest temperature used in board pressing in next part of project) are also presented in Tables 3.3 and 3.4.

It is shown that extractives and catalyst concentration affects degradation onset temperature of barks. If more extractives were removed from barks (as in case of different solvents), the value of degradation onset temperature goes up. It is opposite in case of catalyst. If the catalyst % increased, barks degradation onset temperature decreased significantly. It was observed that the degradation onset temperature for control bark was calculated 248.4°C which goes higher up to 303.24°C for 1%NaOH extractive free bark where solubility% was 68.06% while in case of CH<sub>2</sub>Cl<sub>2</sub> extractive free bark, which has extraction value of 14.2% degradation onset temperature was found 265.47°C. In case of catalyst addition, it decreased for barks with 1%, 3% and 5% NH<sub>4</sub>Cl with the values of 228.88°C, 196.1°C and 168.08°C respectively.

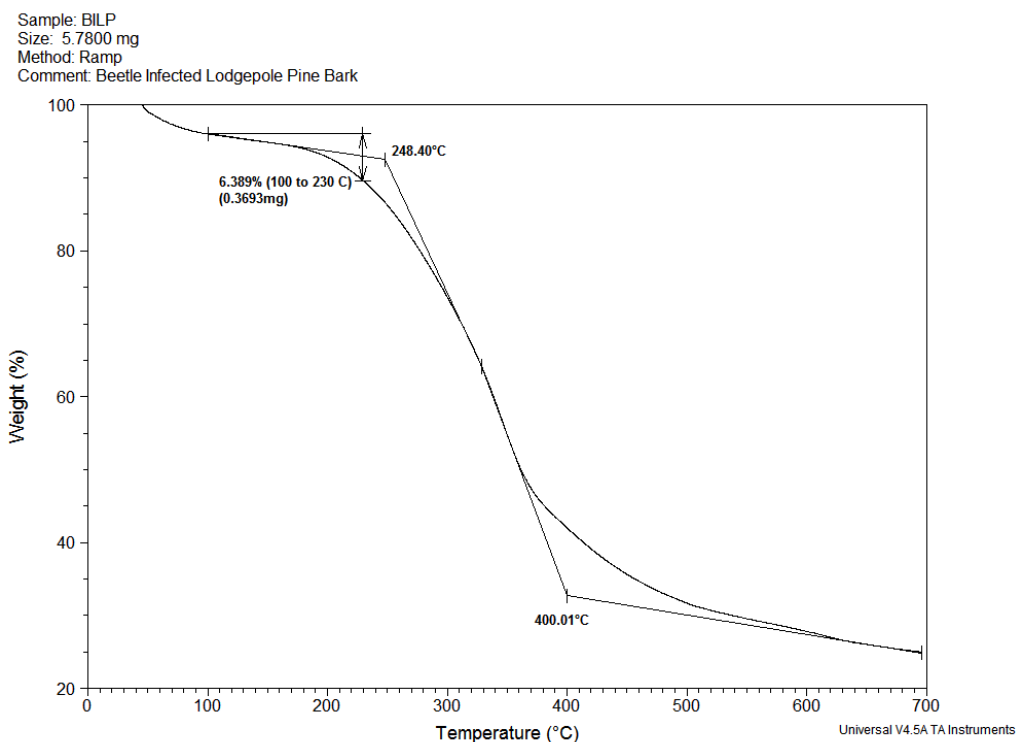


Figure 3.5: TGA Curve of normal beetle infested lodgepole pine bark.

Sample: BILPETH  
Size: 5.4160 mg  
Method: Ramp  
Comment: Ethanol-Toluene-Hot Water extractive free BI Lodgepole Pine Bark

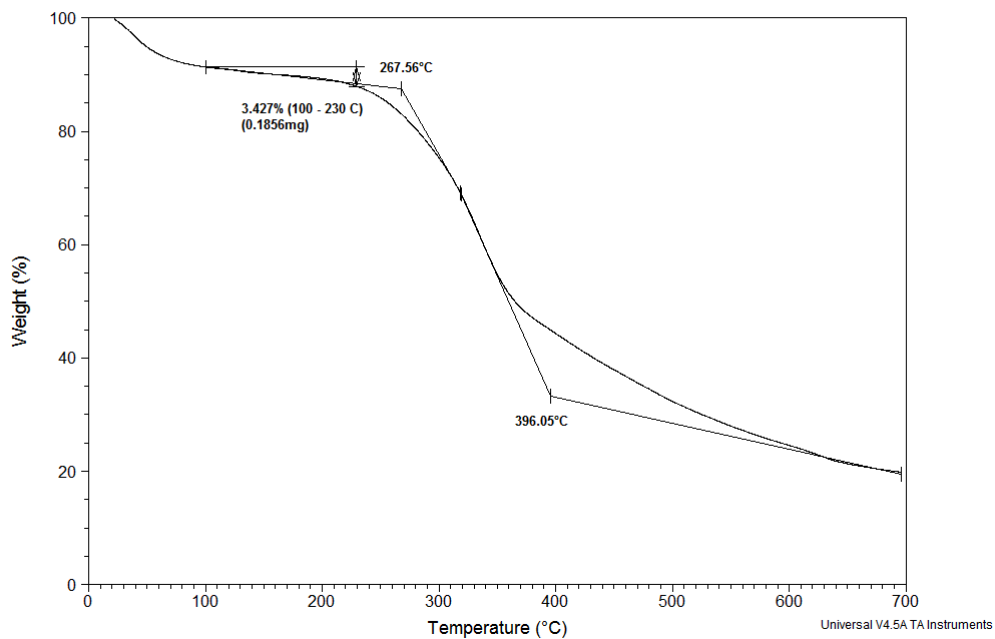


Figure 3.6: TGA Curve of ethanol-toluene-hot water extractive free beetle infested lodgepole pine bark.

Sample: BILPNa  
Size: 5.6560 mg  
Method: Ramp  
Comment: 1% NaOH Extractive free BI Lodgepole Pine Bark

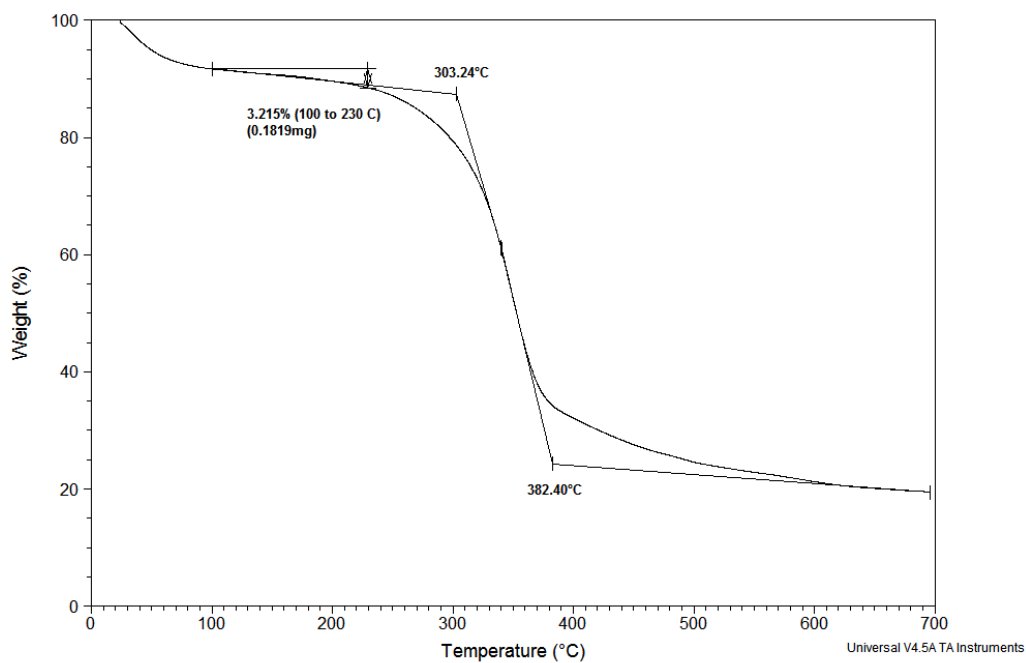


Figure 3.7: TGA Curve of 1% NaOH extractive free beetle infested lodgepole pine bark.

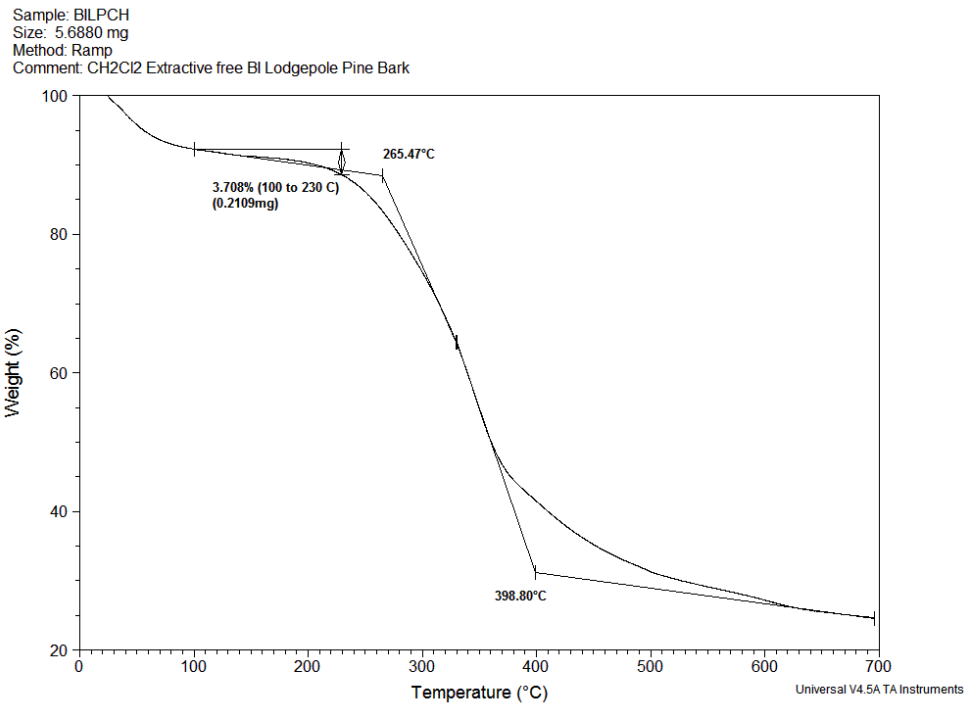


Figure 3.8: TGA Curve of CH<sub>2</sub>Cl<sub>2</sub> extractive free beetle infested lodgepole pine bark.

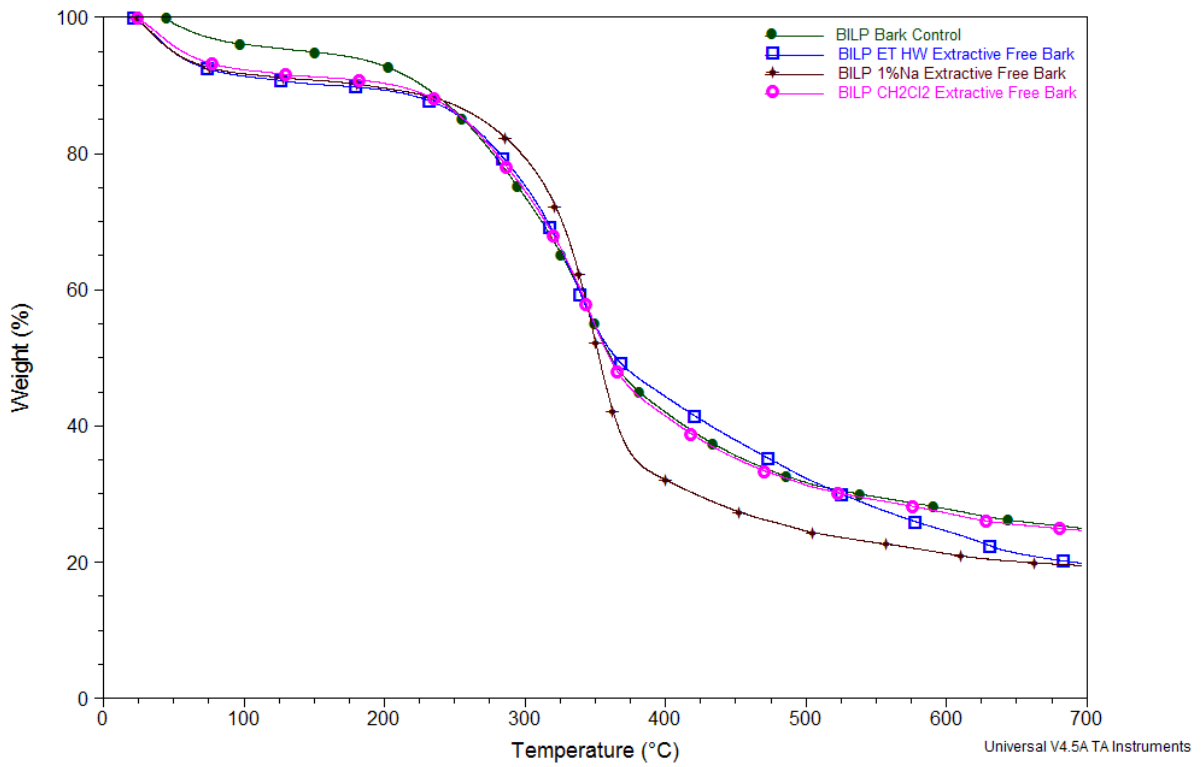


Figure 3.9: Combined TGA curves showing effect of extraction on weight loss and degradation onset temperature of beetle infested lodgepole pine bark.

Sample: BILPC1  
Size: 4.8830 mg  
Method: Ramp  
Comment: Beetle Infested Lodgepole Pine Bark with 1% Catalyst (NH<sub>4</sub>Cl)

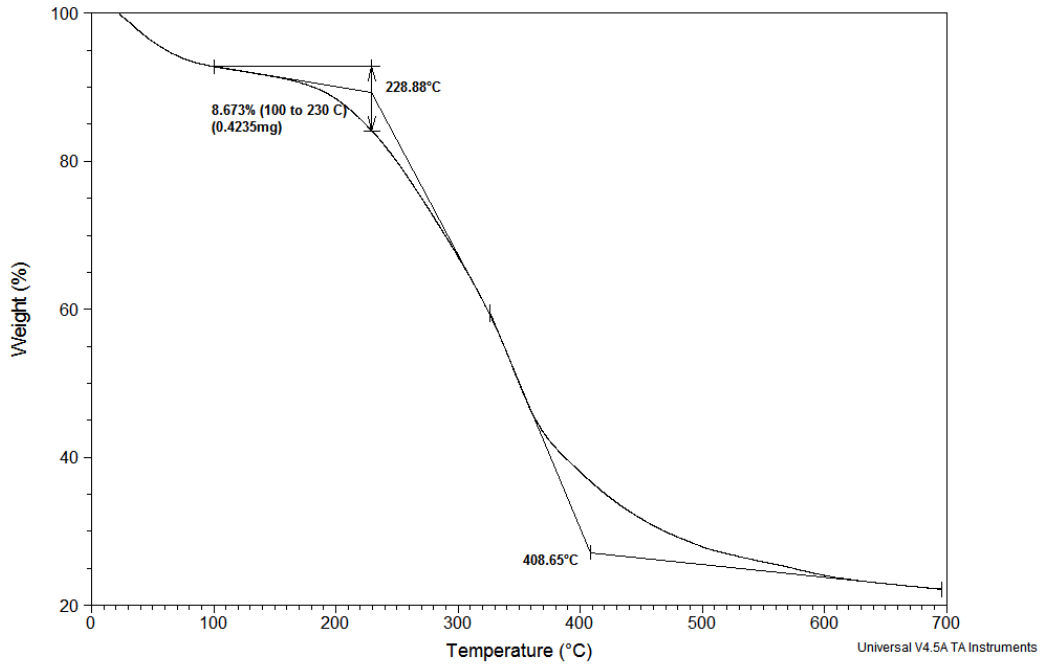


Figure 3.10: TGA Curve of beetle infested lodgepole pine bark with 1% NH<sub>4</sub>Cl catalyst.

Sample: BILPC3  
Size: 5.4500 mg  
Method: Ramp  
Comment: Beetle Infested Lodgepole Pine Bark with 3% Catalyst (NH<sub>4</sub>Cl)

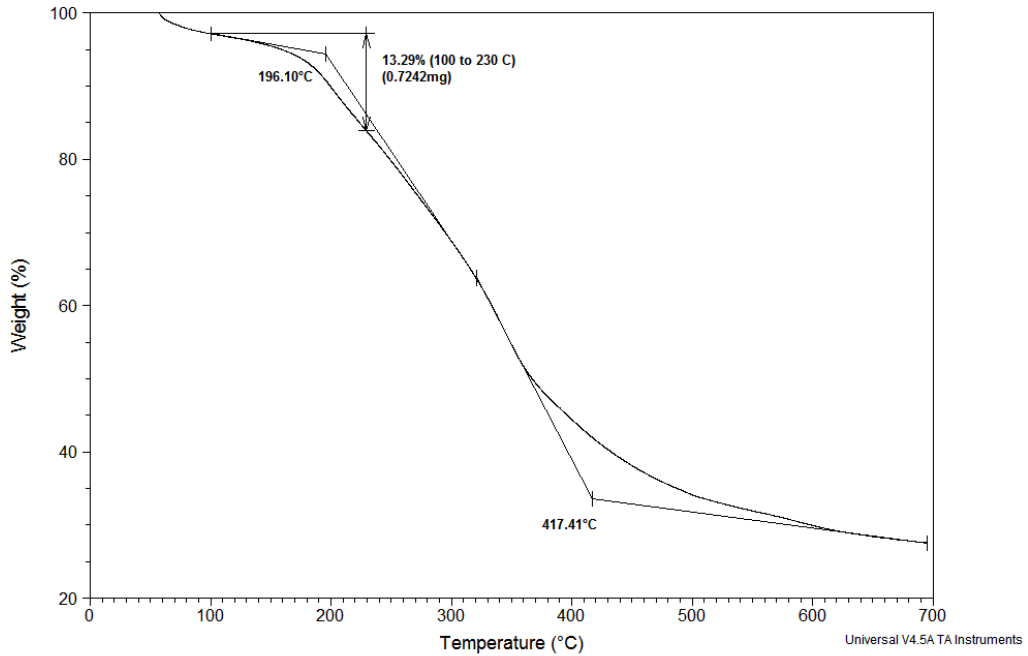


Figure 3.11: TGA Curve of beetle infested lodgepole pine bark with 3% NH<sub>4</sub>Cl catalyst.

Sample: BILPC5  
Size: 5.7070 mg  
Method: Ramp  
Comment: Beetle Infested Lodgepole Pine Bark with 5% Catalyst (NH4Cl)

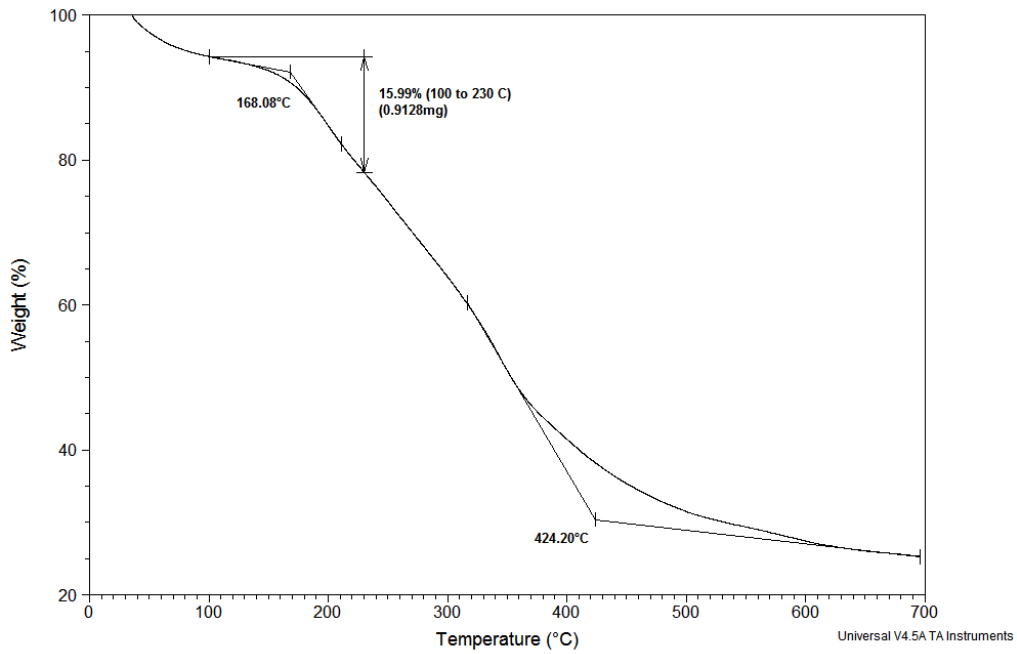


Figure 3.12: TGA Curve of beetle infested lodgepole pine bark with 3% NH<sub>4</sub>Cl catalyst.

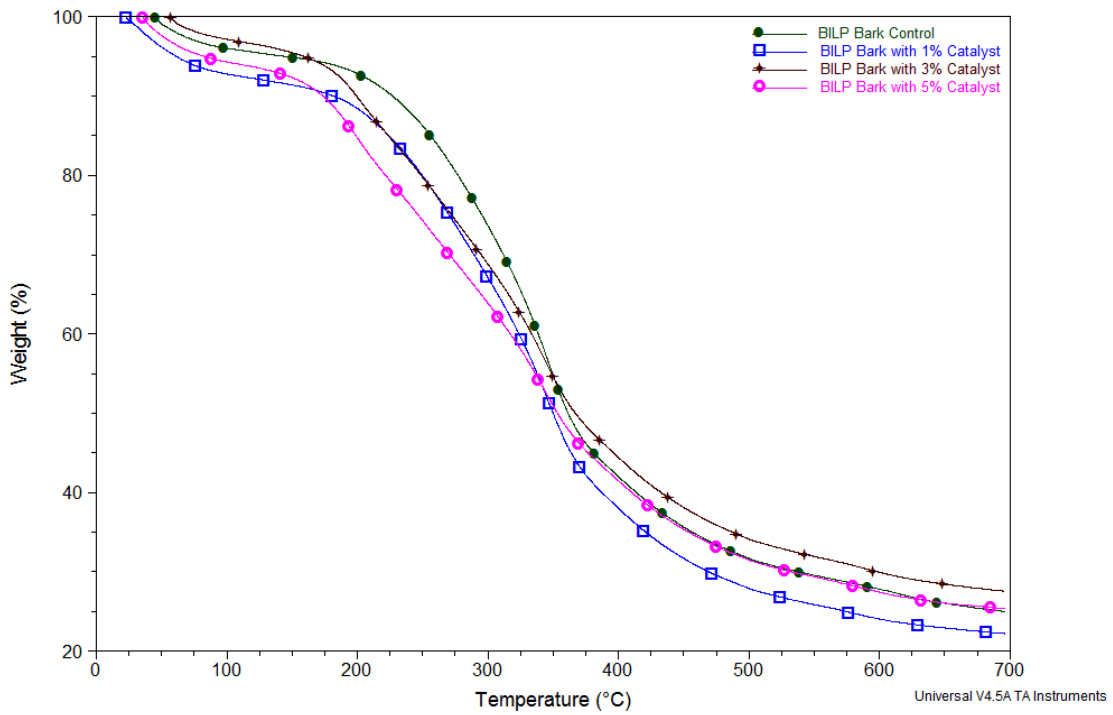


Figure 3.13: Combined TGA curves showing effect of catalyst concentration on weight loss and degradation onset temperature of beetle infested lodgepole pine bark.

Table 3.3: Effects of extraction on degradation onset temperature and weight loss between 100-230°C.

<b>Type of Bark</b>	<b>Extraction/ Solubility %</b>	<b>Degradation Onset Temperature (°C)</b>	<b>Weight Loss % (100 to 230°C)</b>
Control (without extraction)	0	248.4°C	6.39%
ET-Hot water extractive free bark	25.1	267.56°C	3.42%
1%NaOH extractive free bark	68.06	303.24°C	3.21%
CH <sub>2</sub> Cl <sub>2</sub> extractive free bark	14.2	265.47°C	3.70%

Table 3.4: Effects of catalyst concentration on degradation onset temperature and weight loss between 100-230°C.

<b>Type of Bark</b>	<b>Degradation Onset Temperature (°C)</b>	<b>Weight Loss % (100 to 230°C)</b>
Control (without extraction)	248.4°C	6.39%
Bark with 1% NH <sub>4</sub> Cl	228.88°C	8.67%
Bark with 3% NH <sub>4</sub> Cl	196.1°C	13.29%
Bark with 5% NH <sub>4</sub> Cl	168.08°C	15.99%

### **3.3.3 Conclusions:**

Chemical and thermal properties of bark are important in its ultimate use. Thermal analysis of barks performed by TGA studies on control & different conditions of extractives and catalyst provide various interesting results which can be used in characterization of bark as raw material in making of self-bonded boards.

The following conclusions can be drawn on the basis of chemical and thermal analysis of green and beetle infested barks and barks under different conditions of extraction and catalyst:

1. Chemical and thermal analysis results support that bark contained higher amounts of phenolic compounds compared to similar wood.
2. Extractive content and chemical composition of both green and beetle infested lodgepole pine barks have no significant differences in organic solvent extractives; however, the beetle infested lodgepole pine bark has a higher amount of 1% NaOH solubility probably due to fungal decay.
3. Amount of  $\alpha$ -cellulose and Klason lignin are also lower in beetle infested lodgepole pine bark, but overall there is no constraints in use of this bark for production of barkboards.
4. Bark's components undergo degradation at higher temperatures. A sharp degradation or weight loss of bark material occurs in the temperature range of 240-400°C, varying with condition of extractive and catalyst. Higher amount of extraction causes an increase in degradation onset point while increasing amount of catalyst reduced this point significantly.

# **CHAPTER 4: BARKBOARDS DEVELOPMENT AND PRELIMINARY INVESTIGATIONS**

## **4.1 Introduction:**

Introductory chapters described the necessities and advantages of using bark as raw material for composite products due to changing scenario of forestry sector and environmental issues. Various research attempts have been made previously to study bark as a raw material for manufacturing of composite boards including hardboards, fiberboards, particleboards etc. Manufacture of barkboards without addition of synthetic resins has long been pursued, but an effective and commercial process remains to be found.

Previous researchers use a heat and pressure technique to utilize the bark's natural chemicals as a binder rather than adding resin. Polymerization of phenolic compounds and plasticization of lignin probably plays a major role in binding bark particle together. Major work in the area of barkboard has been carried out by *S. Chow* and he has described a method of making satisfactory barkboards using only bark particles without adhesives; however, pressing temperature in the range from 250°C to 300°C was impractical for its commercial production. After *Chow* other researchers also tried to improve the process parameters and quality of barkboards by different approaches, but available knowledge in this area is still insufficient. Many facts related to barkboard processing are still unknown.

This part of the project is an attempt to study, re-explore and develop the barkboard manufacturing techniques at laboratory level. The objective was to utilize beetle infested lodgepole pine bark. In contrast to other similar composites like plywood, particleboard etc., barkboard hasn't any well-defined production process. For that reason, various technical problems are experienced during making of boards entirely from bark particles without any synthetic resin. However, supplementary efforts made it possible to develop satisfactory barkboards.

## **4.2 Experimental:**

### **4.2.1 Methodology:**

Different researchers used different processing parameters and came to an end with different conclusions. Complex nature of bark, both chemically and anatomically also hinder the possibility of a unique method. However, most satisfactory method as per literature review (mainly based on the work of *Chow* and *Troughton*) was applied here, even though during the project results required changing the approach for success in making boards without resin.

#### **4.2.1.1 Raw Material Preparation:**

Beetle infested lodgepole pine bark, received from Rangers Board Ltd. Alberta was used throughout the project. At the time of arrival, bark was very fresh (moisture content was around 40%) and in the form of full pieces. For grinding purpose, bark was initially air-dried under shades for a week. After the initial drying, bark was ground in a Wiley mill. Next to grinding, screening was performed by different mesh screens to separate the particles in desired sizes. These bark particles were again dried in forced air oven at 80°C for 24 hrs. At this time the moisture content of bark was around 2-3% and it was ready for board pressing.

Photos of material preparation, taken during project work, are presented on next page.



Figure 4.1: Preparation of bark for board production.  
(I. Air-drying, II. Grinding, III. Screening, IV. Oven-drying)

#### 4.2.1.2 Board Development and Pressing Studies:

Bark particles were shaped in the form of mats of thickness around 18.75 mm and 30X30 cm size, made with the help of a wooden mould; using 600 g of bark. So the standard size of targeted boards was fixed to 30X30 cm with a targeted board thickness of 6.25 mm and density of 0.8 to 1 g/cm<sup>3</sup>.

According to the experimental design, in the beginning of the experiments, boards were pressed at varying pressures and temperatures, ranging from 170°C, to 230°C. Some boards were also pressed at higher temperatures up to 300°C to see their initial response but it was observed that at higher temperatures they had highly charred surfaces and likely degradation of main chemical constituents which would adversely affect the strength properties. However it is mentioned in some literature that this higher temperature is favorable from the extractive polymerization, which contributes to self-adhesion of bark particles.



Figure 4.2: Hot pressing of barkboard.

Initial efforts of making of boards, were frustrating due to blowing and cracking of boards during hot pressing. After many alterations in pressing techniques, finally it was possible to prepare sound boards with better and improved quality. Various pressing combinations and experiences during hot pressing of boards supported Chow's (1975) prescribed pressing conditions (28.1 kg/cm<sup>2</sup> or 400 psi for 1 minute followed by 12.3 kg/cm<sup>2</sup> or 175 psi for 19 minute worked satisfactorily). High pressure in the beginning and gradual reduction in pressure helped in release of moisture and gases built up in the board's core layers at the time of hot pressing. A sudden reduction in pressure from 28.1 to 12.3 kg/cm<sup>2</sup> caused blowing and cracks development in boards. Moisture and gases are generated due to condensation process of phenolic compounds in bark (Chow 1975). Further, use of special caul screens also helped in release of moisture and gases.

Because the analysis of temperature effect was the part of research study, different temperatures were tried as per the experimental design. Varying particle size was also a factor considered in this research.

In the initial findings, it was found that boards have density around 0.8-0.9 g/cm<sup>3</sup> and 6-7 mm average thickness. Boards pressed at different conditions of temperature, particle size etc. as per experimental design, showed high variation in their mechanical and physical properties. Physically, boards looked good but satisfactory bond strength was an issue especially at moderate and low temperatures (below 200°C). All results in detail are presented in the next chapters.

#### **4.2.2 Self-adhesion Technique:**

It was hypothesized earlier that due to high content of bark extractive and lignin there is a possibility of self-adhesion by higher temperature and pressure. It can also be explained on the basis of the sharp contrast between the results at lower temperatures (170°C and below) and higher temperatures (230°C and above). The formation of board at 170°C consists mainly of a plasticization effect with little or no lignin/extractive polymerization. At the higher temperature ranges (up to 300°C), thermal polymerization becomes the prominent factor and all mechanical properties increased significantly.

This hypothesis was also supported by *Chow's* work on thermal reactions of bark. He performed a kinetic study which indicated that the phenolic substances in Douglas-fir and red alder bark can be polymerized by high-temperature heating. On the basis of thermal softening studies it was postulated that the thermal softening of moistened wood and bark at temperatures below 200°C was more physical than chemical in nature and was attributed to plasticization by water. This plasticization effect is believed to be important for setting pressing schedules in the manufacture of hardboard and particleboard. The thermal reaction of bark at a temperature greater than 180°C was attributed to the polymerization and partial degradation of bark components. TGA studies of bark described in previous section also reveal quite similar results for beetle infested lodgepole pine bark.

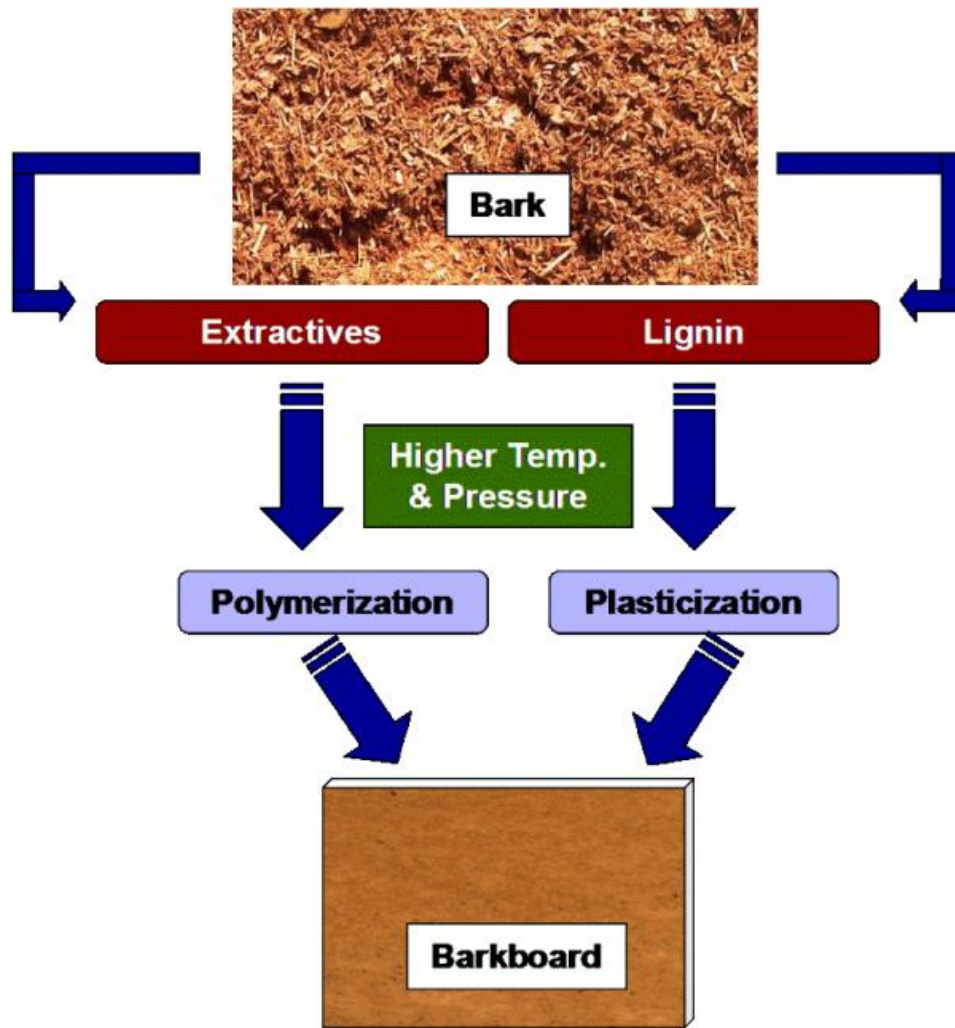


Figure 4.3: A simplified diagram showing principles behind self-adhesion in barkboard.

### **4.3 Results and Discussion:**

Knowledge derived from preliminary studies of barkboards production at laboratory level provided considerable information regarding the board making technique and challenges associated with it. However, there were many problems faced during the development of barkboards. After various attempts, satisfactory boards were produced by adaptations of some innovative measures but it was realized that there is still needs for further improvements and an optimized process.



Figure 4.4: Barkboards made from fine (I) and mixed (II) size particles.

#### **4.3.1 Challenges in barkboard production:**

The following are some challenges experienced during barkboard production at laboratory scale:

- I. The most challenging issue was the development of high vapor pressure, generated by the resulting steam in the boards at the time of pressing. This pressure was responsible for blowing of bark particles during pressing or blisters or cracks generation in pressed boards. Boards were usually blown, if core gas pressure exceeded  $1.4 \text{ kg/cm}^2$  or 20 psi. In the beginning it was understood that it may be because of moisture in bark but the problem remained even after oven-drying of bark particles. After the literature study and working experience it was clear that this moisture release was attributed to the chemical condensation and dehydration of bark chemicals. Previous researchers (*Chow et al date*) found up to 9% water release during hot pressing of dry bark. They also found that percentage of moisture release was linearly related to the board's strength properties.

Barkboard without Synthetic Resin  
(Mixed Particles, Temp. 230 C, Pressure 400 psi 1 min. followed by 175 psi 19 min., No Catalyst)

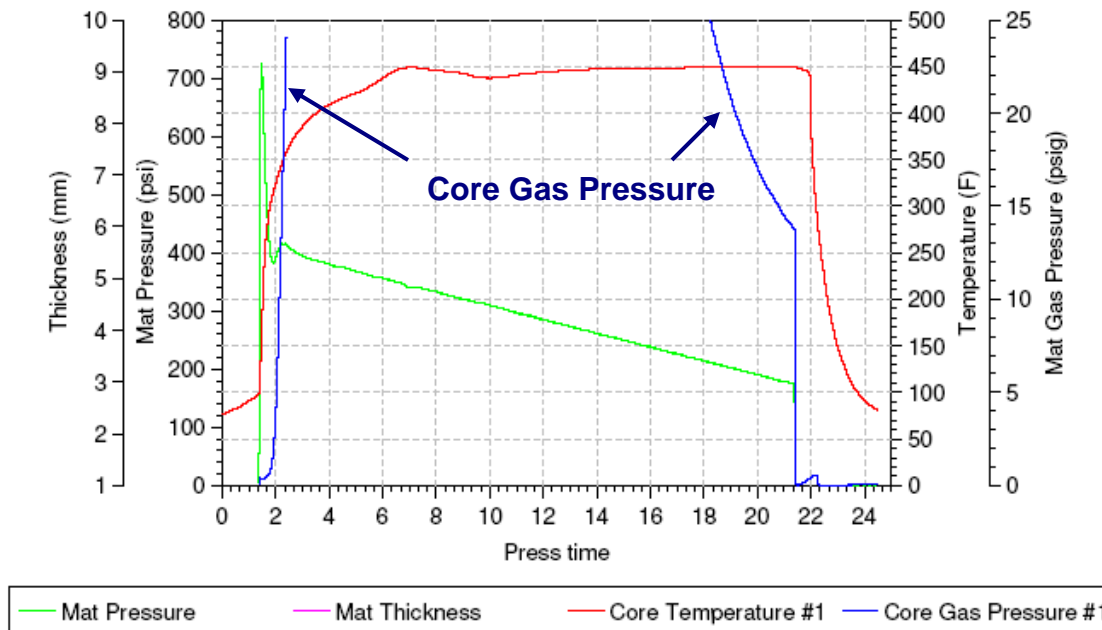


Figure 4.5: Hot press graph of barkboard showing very high mat gas pressure (presented by blue line which goes very high, resulted in blowing of board).

- II. During the pressing, heat transfer and core temperature was measured by a thermocouple. When the gas pressure problem was controlled by the use of caul screens, another difficulty occurred related to difference in temperature of plate and core due to obstruction by caul screens, as hot press platens were not in close contact with the bark mat. Further, low thermal conductivity of bark (according to literature it is 20% less than wood of similar density) also contributed to this issue. A big difference was measured in the core and platen temperatures. For example when platen temperature was kept around 230°C (446°F) the core temperature was recorded around 190°C (374°F). This huge difference was causing difficulties in achieving desired curing, especially in middle layers of boards.
- III. High temperature requirement for barkboard curing is big issue especially for its production on commercial level.

- IV. Some suggestions regarding the improvement of bark's thermal conductivity with addition of moisture do not work for barkboards as all the boards with higher moisture content are blown due to high gas pressure in internal layers.
- V. The plan to study the effects of extractives on board properties by making of boards with extractive free bark was dropped as it was realized during the project that it is not practically possible to produce extractive free bark in the large quantity required for pressing of boards.
- VI. It is concluded by some pioneer researchers that higher temperature (up to 300°C or 572°F) is perfect from the extractive polymerization and self-adhesion point of view, but it was experienced here that at this temperature boards have charred surfaces and possible degradation of bark constituents which can also adversely affect the strength properties.
- VII. The highly complex and variable nature of bark even for the same species also is an obstacle in process optimization for barkboards.

#### **4.4 Conclusion and Feasible Solutions:**

There are several constraints in barkboard production, which might be the reason that even though this product has several advantages, it still is not produced at commercial level. It is most important to overcome the difficulties experienced in barkboard manufacturing and to investigate the feasible solutions.

Application of special caul screens (Figure 4.6) during the hot pressing of boards, efficiently controlled the problems of blowing by evacuation of vapors and gases produced due to chemical reactions of bark components in response to high temperature.



Figure 4.6: Special caul screens used during the hot pressing of boards to control the core gas pressure.

It can be seen in pressing graph below that the core gas pressure (blue line) is negligible when the caul screens were used. Previously it reached more than 100 psi or  $7.03 \text{ kg/cm}^2$  (figure 4.5) but application of caul screens controlled it to below 1 psi or  $0.07 \text{ kg/cm}^2$  (figure 4.7) which causes no blowing or blistering at the time of hot pressing.

Figure 4.7 reveals that core temperature is also well controlled and is equal to platen temperatures. Previous low core temperature was also a problem which occurred due to low thermal conductivity of bark and use of caul screens on both faces but it was possible to manage it by repeated experiments for improvement, maintaining balanced moisture content of bark and use of caul screens on one side only.

All boards which were made using these screens appeared normal, without any blister or surface or internal cracks. *Troughton* et al (2000) also described use of interwoven stainless steel wire mesh screen in U.S. patent nos. 6,120,914 and 5,725,818 to avoid using a vacuum press (as suggested by *Chow*) to control blister and blowing problems.

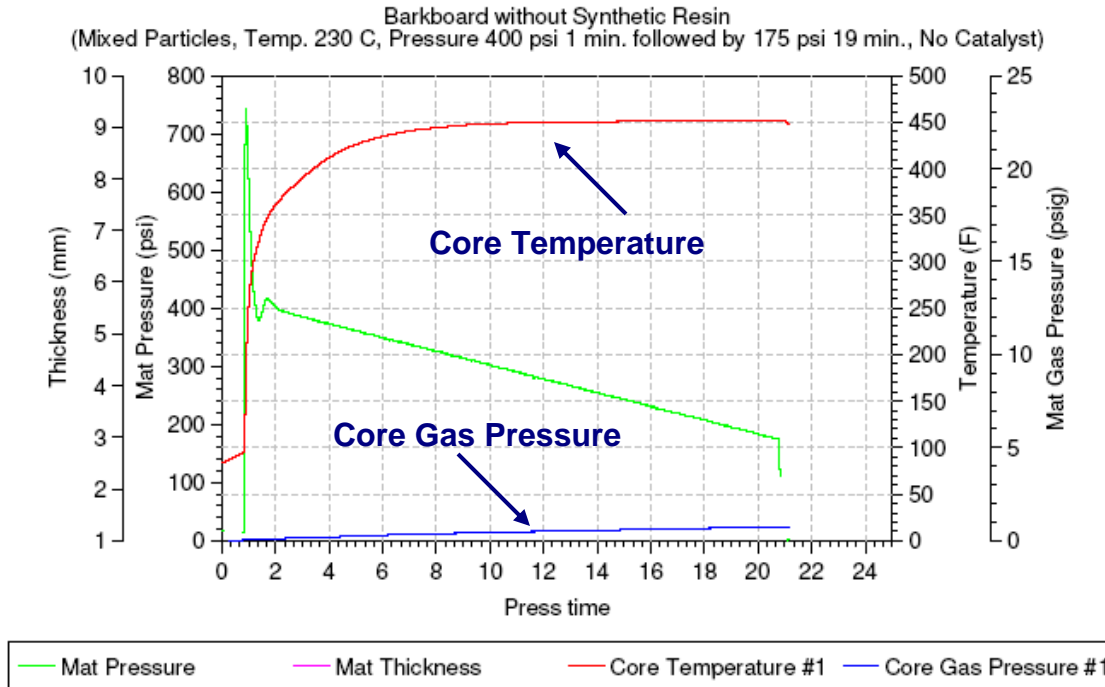


Figure 4.7: Core gas pressure was controlled by the use of special caul screens (Blue line representing core gas pressure showing very less value).

There was a small problem associated with the use of caul screens. It was found that when caul screens were used, core temperature was much lower than platen temperature. It was certainly due to the obstacle between mat and hot platen in the form of caul screens. To improve the temperature in core layer, one caul screen from bottom was removed (used one on top only) and it resulted in a better heat transfer to the core layer.

It is also realized that bone-drying (absolutely dry) barks performed better to prepare boards without any blowing or cracking as compared to barks with low moisture contents. Lower temperatures with longer pressing times were better than higher temperatures with shorter pressing times, from the blowing and board's quality point of view.

Regarding the issues of higher temperature requirement in barkboards, some efforts have been done by previous workers but still a perfect solution is awaited. *Troughton*, in his patent (US 6,544,649B1) has suggested use of a catalyst

ammonium chloride ( $\text{NH}_4\text{Cl}$ ), as a partial solution of higher pressing temperature problems. He explained that the presence of a catalyst, uniformly distributed over the hog fuel mat, significantly lowers the temperature required at the heating press platens to form a board. He found that boards with 3% ammonium chloride pressed at  $260^\circ\text{C}$  ( $500^\circ\text{F}$ ) were better than those of the non-catalyzed control boards pressed at  $300^\circ\text{C}$  ( $572^\circ\text{F}$ ).

Various other issues still need more research work. Further application of liquefied bark or similar environmental-friendly additives is also an option to improve the boards' qualities, which is tried in this project and gave some encouraging results.

## **CHAPTER 5: STUDIES ON PRESSING TEMPERATURE & PARTICLE SIZE EFFECTS**

### **5.1 Introduction:**

Barkboard development and other technical issues related to production processes are discussed in detail in chapter 4. It was experienced that various factors significantly affect the board's properties. It is also hypothesized that different pressing parameters and type of raw materials including species and condition at the time of pressing have a direct influence on the board's properties.

Pressing temperature is one of the most important issues in production of barkboards. The whole concept of binding bark particles without any resin is based on the temperature effects on physical and chemical constituents of bark. Therefore quality, strength and success in making boards highly depend on the pressing temperature. Previous researchers did various temperature manipulations while pressing the boards. *Burrows* (1960), *Wellons and Krahmer* (1973), *Chow and Pickles* (1971), *Chow* (1975), *Troughton* (2000) etc. have performed many experiments on the role of temperature in polymerization and plasticization techniques. Various phenomena related to board pressing and their explanations were based on reactions of extractives and lignin.

Other than temperature it may be assumed that bark particle size and the packing of particles in boards should also affect the board's properties. There was no significant work reported in the literature in this area. It may be hypothesized that for boards without any resin, most of the inter-particle spaces remain as voids if particles are coarse and the board is made with uniform particles. For fine or mixed particles there are greater chances of tight packing and close contact among particles, which may positively contribute to barkboard's properties.

In this chapter, studies were made to investigate the role of varying temperature conditions and different particle sizes on barkboard properties, specifically for beetle infested lodgepole pine. With the help of testing results for mechanical properties and chemical analysis of boards made under the different conditions, it is possible to establish optimized conditions.

## **5.2 Experimental:**

Barkboards were produced according to the general methodology described in section 4.2.1.2. Standard size for targeted boards was fixed at 30X30 cm with a target board thickness of 6.25 mm and density of 0.8 - 1 g/cm<sup>3</sup>. This board size was large enough to allow the samples to be cut for different mechanical tests. For each board 600 g of oven-dry bark was used. Experiments were performed as per the experimental design which is presented in figure 5.2. There were 3 replicates for each group.

### **5.2.1 Experimental Design:**

Experiments were designed on the basis of the following two objectives for this part of research:

- I. Determination of the effects of pressing temperature on board properties.
- II. Determination of the effects of particle size on board properties.

To get these objectives, the following two factors were considered in the experimental design (Figure 5.2):

- I. 3 pressing temperatures, 170°C (338°F), 200°C (392°F) and 230°C (446°F) (with mixed particles, passing 4.75 mm sieve) pressed at 28.1 kg/cm<sup>2</sup> (400 psi) for 1 min. followed by 12.3 kg/cm<sup>2</sup> (175 psi) for 19 min.
- II. 3\* particle sizes; coarse, medium and fine (with temperature 230°C selected from I, on the basis of superior performance):

Particle Size Categories	Pass Mesh ( Sieve Opening mm)	Retain Mesh ( Sieve Opening mm)
Coarse	4 (4.75 mm)	7 (2.81 mm)
Medium	7 (2.81 mm)	18 (1.40 mm)
Fine	18 (1 mm)	-
Mixed	4 (4.75 mm)	-

\* Mixed particles were used throughout in part I, so experiments were not repeated again with it.

For the determination of effects of temperature, 3 replications were made for each temperature so a total of 9 boards were pressed. On the basis of testing results, the best temperature was determined and used in all boards for determination of particle size effect. In addition, 3 replications were made for each group of particles so a total of 9 boards were pressed (mixed group was not included here, as mixed particles were already tested in part I for temperature study). All boards were tested and analyzed for their properties.



Figure 5.1: Three different particle sizes were considered in the experimental design of barkboards (I. Fine, II. Medium, III. Coarse).

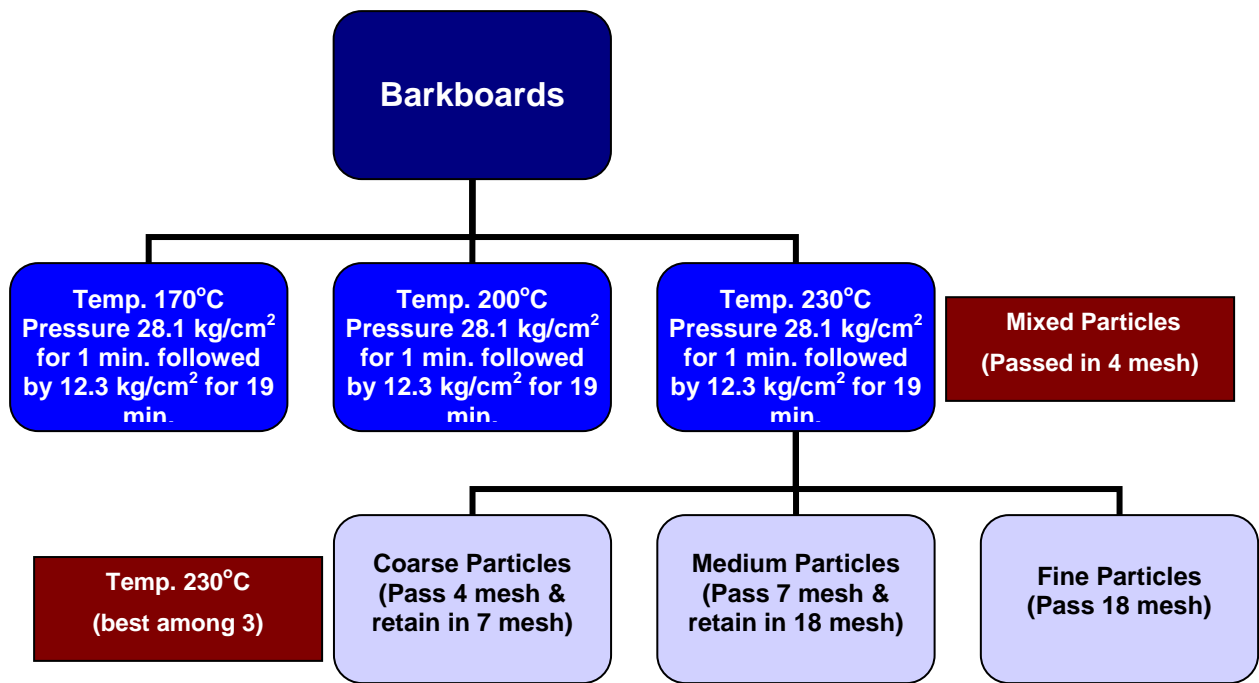


Figure 5.2: Experimental design chart to determine the temperature & particle size effects on the barkboards.

### 5.2.2 Board Pressing Methodology:

A total of 18 barkboards (9 for temperature study and 9 for particle size study) with targeted dimensions and density were prepared in the hot press at the wood composite lab in the Faculty of Forestry. Mixed type particles (which contained all particles passing through no. 4 mesh screen) were used in the temperature study. A thermocouple sensor was inserted in the middle of the mat before pressing to get the core temperature and core gas pressure. The core temperature, core gas pressure, platen pressure and position were recorded. Pressman® software was used to control and measure the pressing parameters.

Mentioned temperature and pressure were used with a constant pressure control press cycle. In this case a force was applied to the platen by the hydraulic cylinder, which causes the platen to move to a position, where the force developed by the resistance of the material was equal to that developed by the hydraulic system at the current operating pressure. The table below summarizes the mat and pressing parameters.

Table 5.1: Mat and pressing parameters.

<b>Mat / Press Parameter</b>	<b>Value</b>
Target panel density	0.8 - 1 g/cm <sup>3</sup>
Weight of bark particles in one sample	600 g
Moisture content	2-3 %
Particle Type	Mixed, Fine, Medium, Coarse
Resin content	Nil
Platen temperature	170°C, 200°C, 230°C
Pressing time	1200 s
Press closing time	50 s
Average board thickness	6.25 mm
Initial mat thickness	18.75 mm
Number of layers in mat/board	1

### **5.2.3 Testing and Evaluation of Barkboard Properties:**

All boards were tested for their mechanical properties for comparison. All tests were conducted according to the procedure specified in ANSI A208.1-1999 and ASTM D-1037-06a. First, the most suitable temperature was evaluated on the basis of part I of the experiments (temperature effects) and then it was applied in part II of the experiment (particle size effects).

Each of the 30X30 cm panels was cut into samples for static bending (MOE & MOR), Internal Bond (IB), Tensile Strength, Thickness Swelling and Water Absorption tests, as per standard size described in testing standards (Figure 5.3 & Table 5.2). The samples were then tested according to the standard procedure.

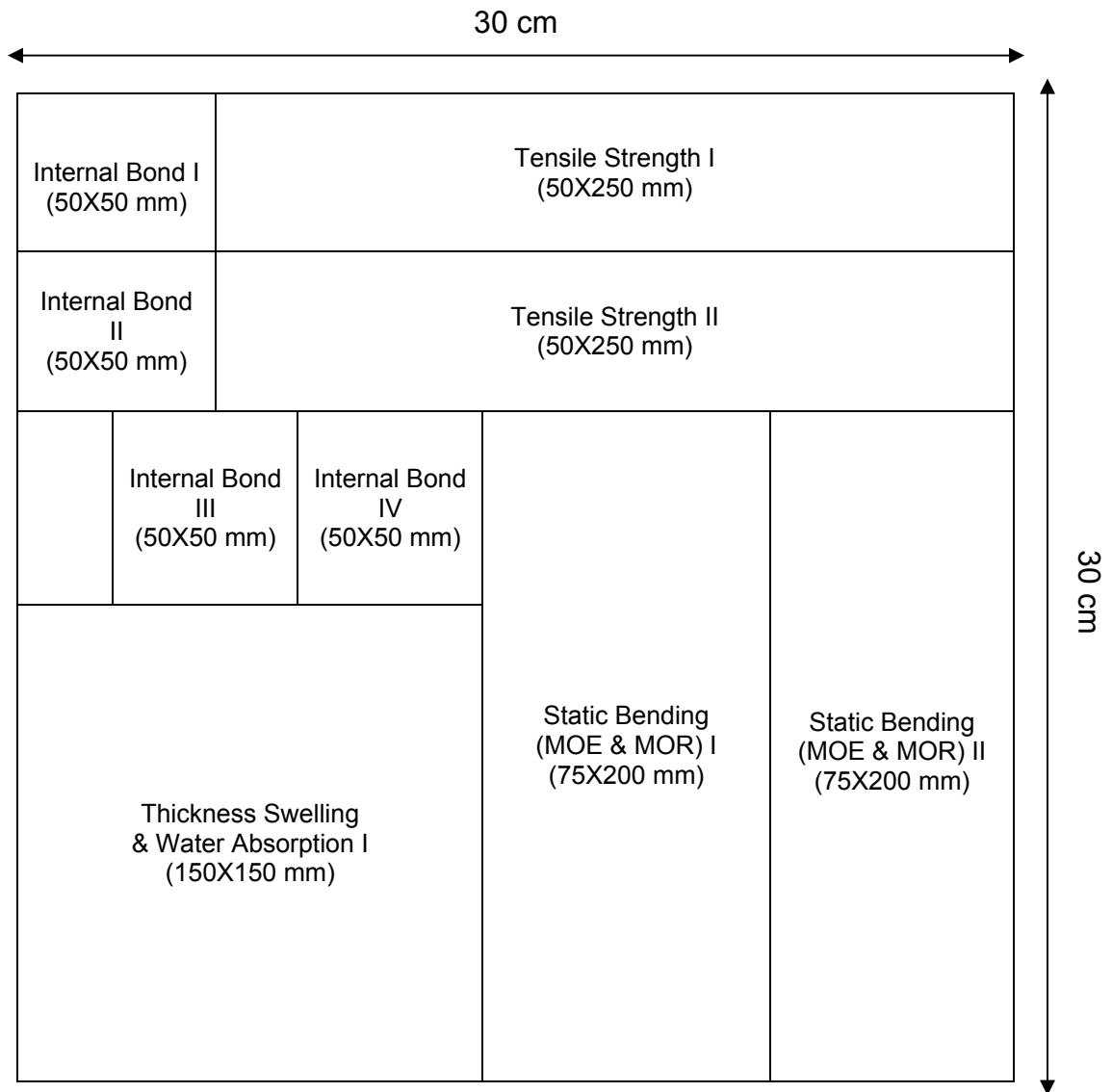


Figure 5.3: Sample cutting pattern for a 30X30 cm barkboard  
(Boards thickness above 6 mm)



Figure 5.4: Mechanical testing of barkboard  
(I. Static Bending, II. Internal Bond, III. Tensile Strength).

Table 5.2: Testing Details, according to ASTM D-1037-06a (Standard Test Methods for Evaluating Properties of Wood-Base Fiber and Particle Panel Materials).

S. No.	Type of Test	Sample Size*	Loading Speed	Remarks
1.	Static Bending	76 X 51 mm + 24 t (t > 6 mm) 51 X 51 mm + 24 t (t < 6 mm)	3 mm/min. (t = 6mm)	Span = 24t
2.	Internal Bond	50 X 50 mm	0.08 cm/cm of t/min.	-
3.	Tensile Strength	50 X 250 mm	4 mm/min.	Special design
4.	Water Absorption & Thickness Swelling	150 X 150 mm	-	2 & 24 hrs

\* t = thickness

All boards were also evaluated for their physical properties (density, moisture content etc.) and surface characteristics. On the basis of mechanical test results and statistical comparisons, it was possible to evaluate the temperature and particle size effects on barkboards.

After the mechanical testing, in the final part of dissertation, all boards were also undergone characterized using the following methods (these results are described in chapter 7 of the thesis):

- I. Chemical Analysis: Constituents determination & extraction (TAPPI standards)
- II. Image Analysis: Scanning Electron Microscopy (SEM) of fractured surfaces
- III. Compound's Investigation: Fourier Transform Infrared Spectroscopy (FTIR)

## 5.3 Results and Discussion:

### 5.3.1 Mechanical Testing:

Test results of all boards under different conditions of temperatures and particle sizes are given in tables 5.3 & 5.4 and figures 5.5 to 5.20.

Table 5.3: Effects of Temperature on Barkboard's Properties (Tested as per ASTM-1037D-06a).

Properties	Average Value @Temperature*			Min. Requirement (ANSI A208.1-1999)
	170°C	200°C	230°C	
Density (g/cm <sup>3</sup> )	0.80	0.86	0.92	-
Moisture Content (%)	2.52	2.44	1.46	-
MOE (N/mm <sup>2</sup> )	420 (104) **	724 (108)	1684 (218)	2400
MOR (N/mm <sup>2</sup> )	2.01 (0.22)	3.22 (0.4)	7.18 (0.64)	16.5
Internal Bond (psi)	15 (5.65)	22 (1.45)	140 (32.37)	130
Tensile Strength (N/mm <sup>2</sup> )	1.55 (0.2)	2.08 (0.23)	3.82 (0.29)	-
Thickness Swelling (%) (2 hrs/24 hrs)	24.90/64.93 (0.34/3.1)	13.17/41.77 (1.75/2.45)	2.96/10.46 (0.08/0.61)	-
Water Absorption (%) (2 hrs/24 hrs)	29.78/72.82 (3.46/0.92)	13.64/57.27 (1.56/0.21)	3.64/15.36 (0.34/1.95)	-

\* (Pressure 28.1 kg/cm<sup>2</sup> for 1 minute followed by 12.3 kg/cm<sup>2</sup> for 19 minutes).

\*\*Values in brackets showing standard deviation.

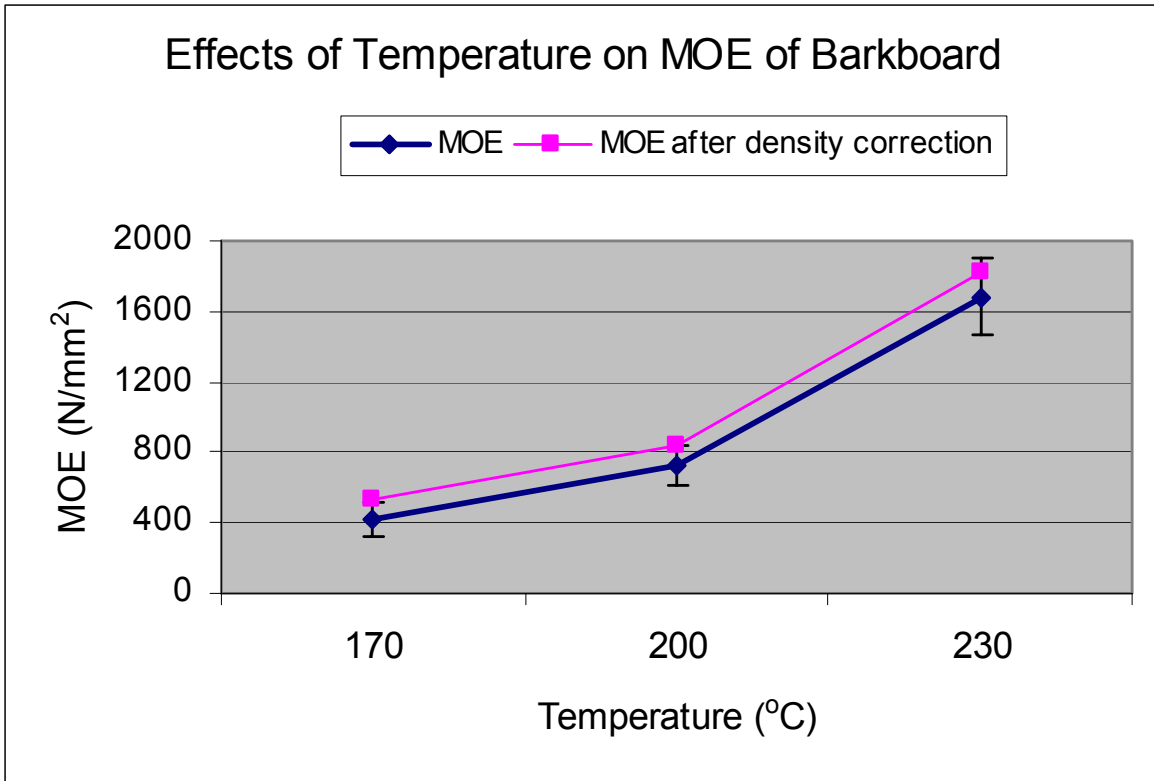


Figure 5.5: Effects of temperature on MOE of barkboards.

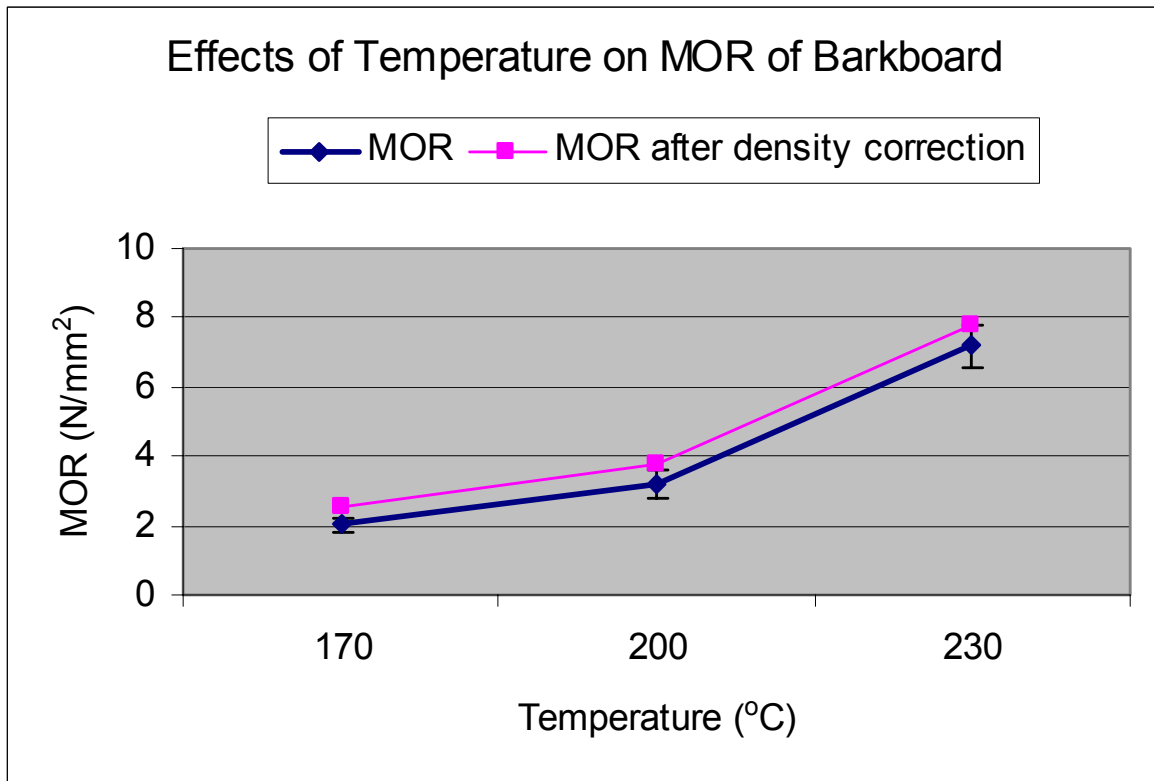


Figure 5.6: Effects of temperature on MOR of barkboards.

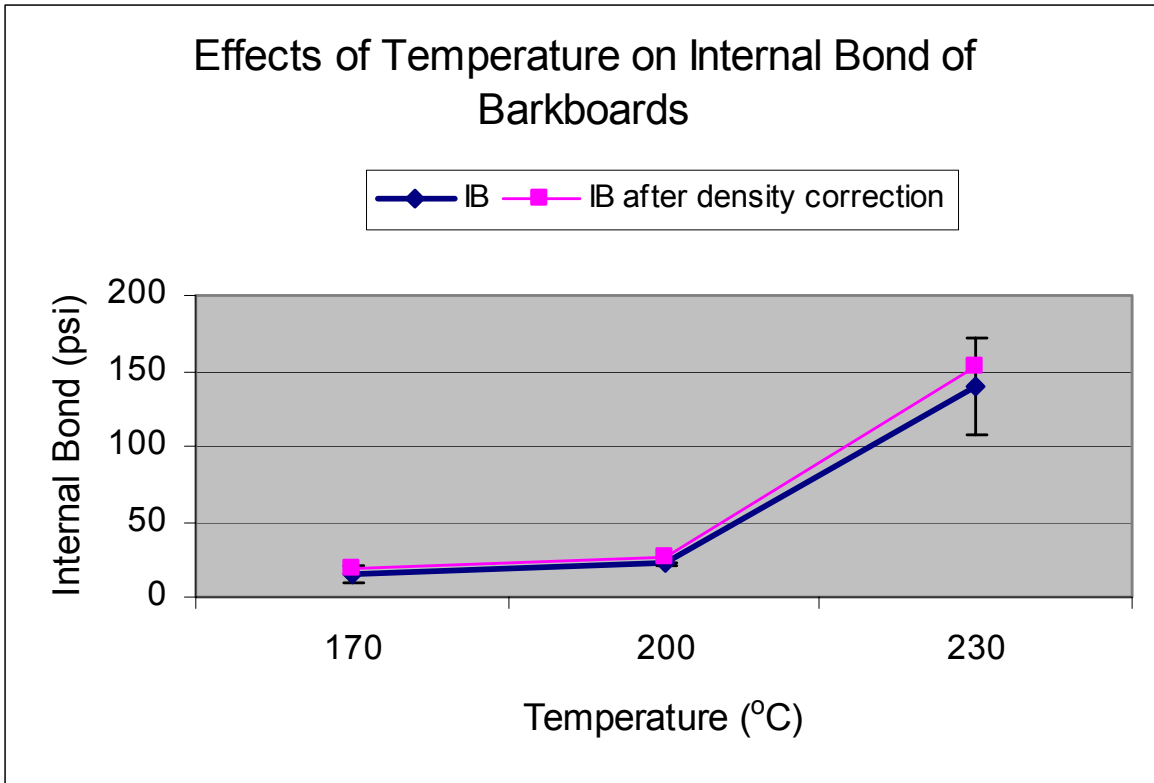


Figure 5.7: Effects of temperature on internal bond of barkboards.

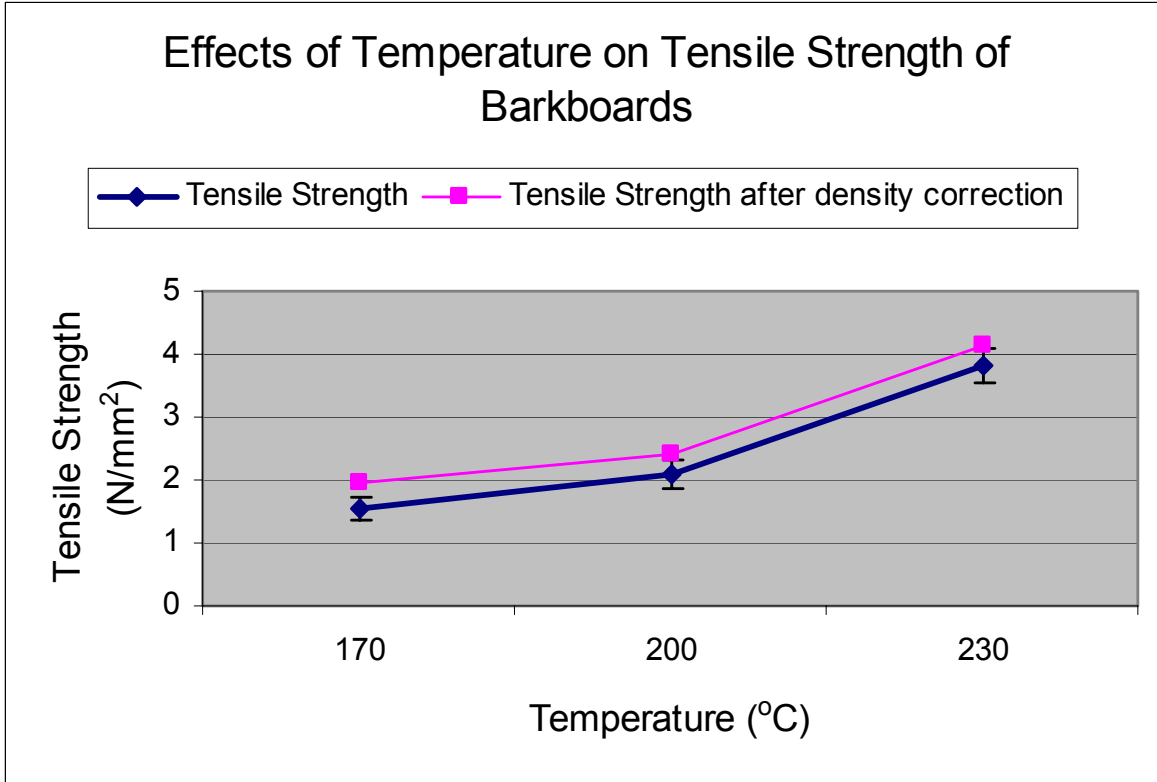


Figure 5.8: Effects of temperature on tensile strength of barkboards.

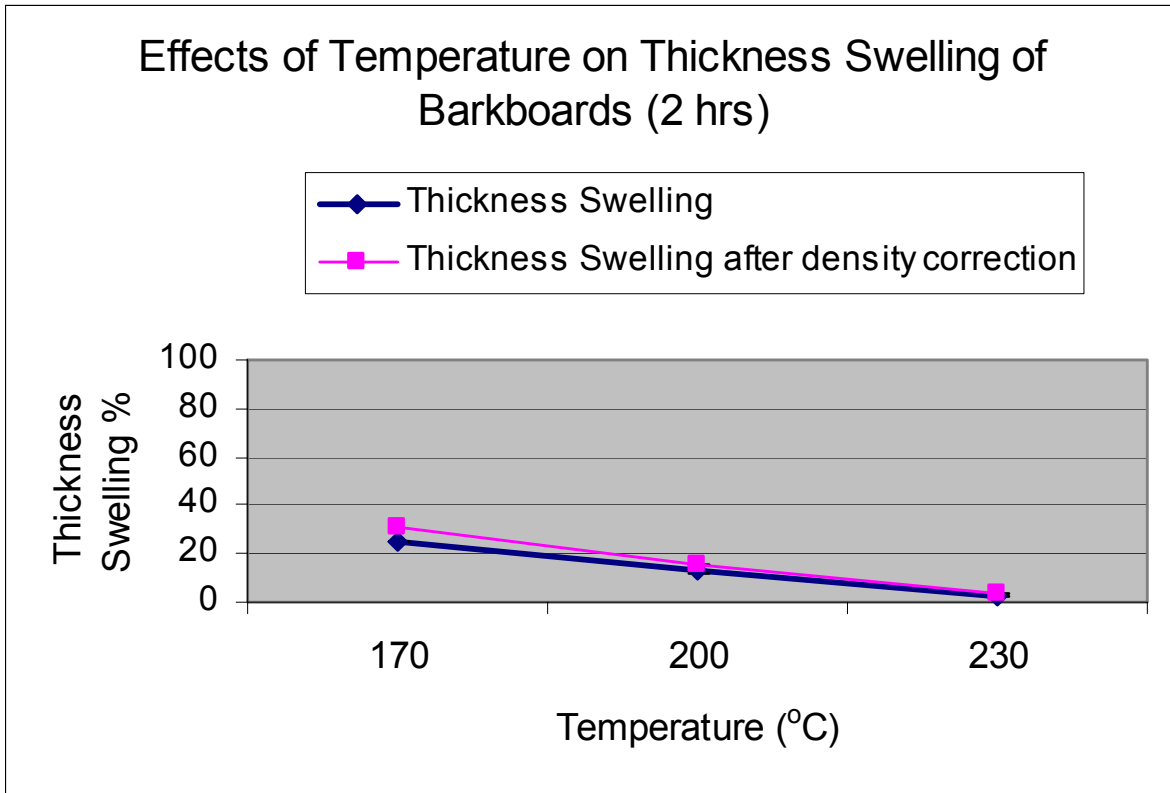


Figure 5.9: Effects of temperature on thickness swelling (2 hrs) of barkboards.

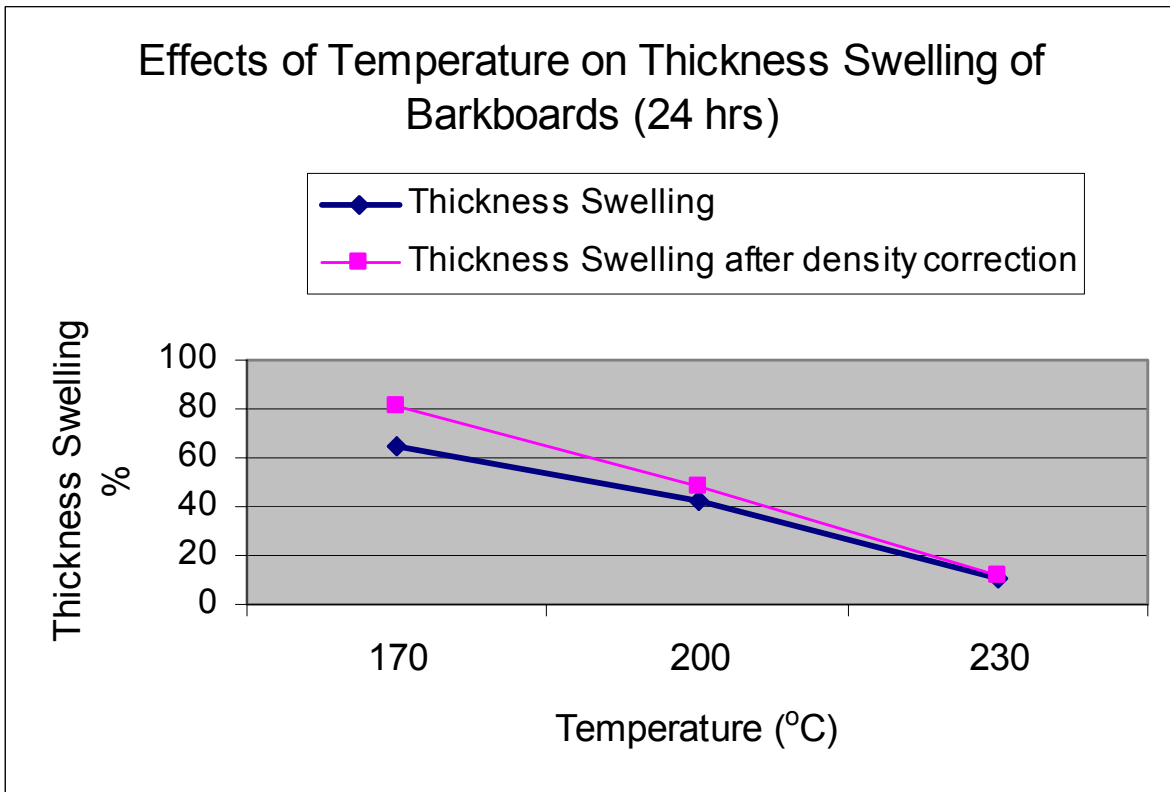


Figure 5.10: Effects of temperature on thickness swelling (24 hrs) of barkboards.

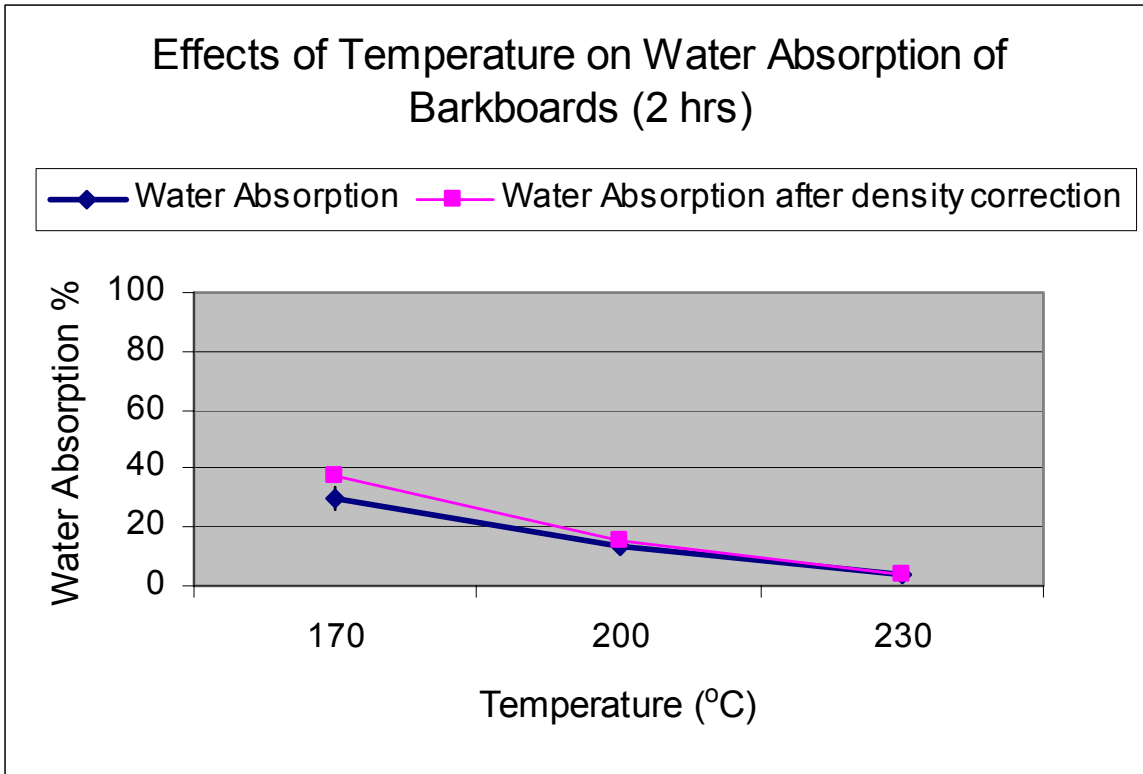


Figure 5.11: Effects of temperature on water absorption (2 hrs) of barkboards.

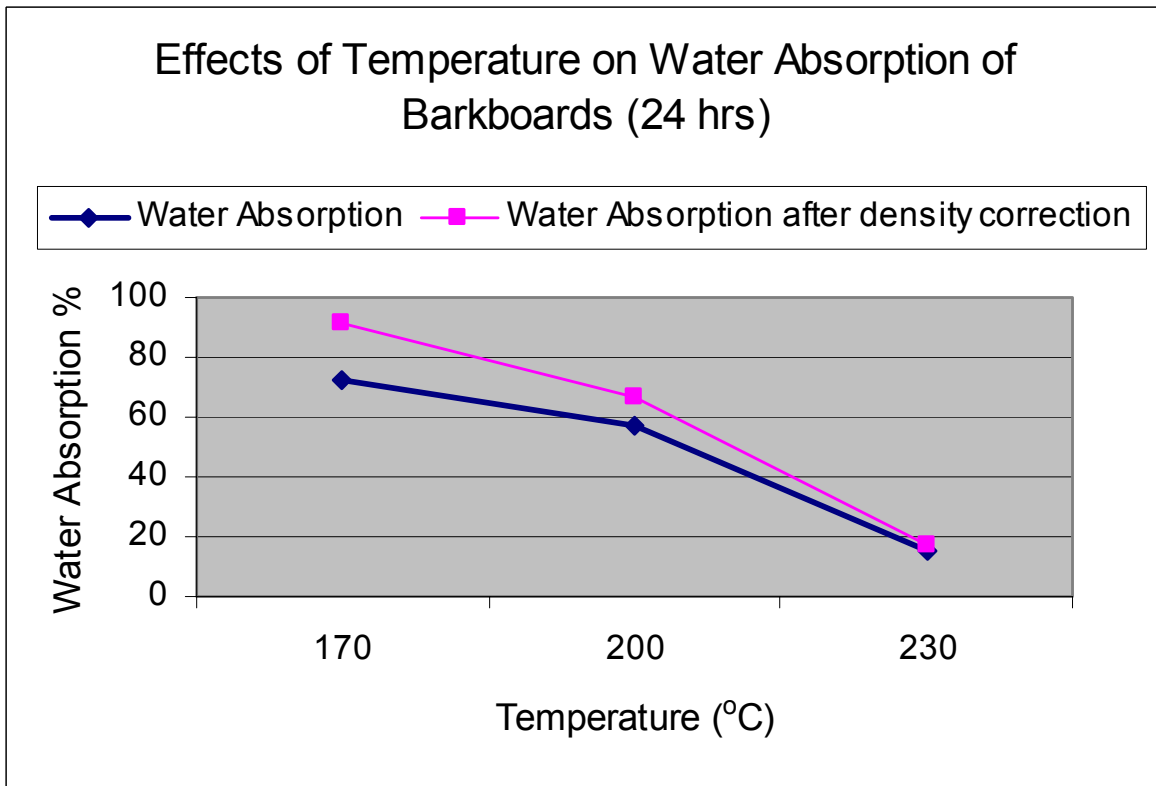


Figure 5.12: Effects of temperature on water absorption (24 hrs) of barkboards.

After the analysis of above mentioned tables and graphs, it was very clear that there is an increase in all mechanical properties when temperature increases from 170°C to 230°C. It was also found that this increase is more significant after 200°C, which supports the hypothesis of extractives and lignin polymerization at higher temperatures and softening may also contributed here. It is also essential to mention here that there was moisture release during hot pressing, which entered into the small pores of the platen and was collected through a tube connected to the hot platen. Similar to *Chow's* results, this release was more at higher temperatures, which shows high degree of condensation and polymerization at higher temperatures. Boards made with higher temperatures also have higher densities.

At a pressing temperature of 170°C, MOE and MOR were 420 and 2.01 N/mm<sup>2</sup> respectively, which increased almost 4 times when temperature was changed to 230°C. The internal bond results were increased up to 10 times when the temperature reached 230°C. Similar results were observed for thickness swelling and water absorption (2 and 24 hrs), while in case of tensile strength, the increase was not as sharp. It was also observed for boards pressed at 170°C, that their particles started to separate after 24 hrs water absorption test. It means there was no chemical bonding at this temperature and particles were just attached due to physical bonds or by the thermoplastic effects of wax, resin etc. in bark. This phenomenon also supports the opinion that chemical bonding only occurs at higher temperatures.

Statistical t-test comparisons among 170-200°C, 200-230°C and 170-230°C shows that difference found maximum in case of 170-230°C comparison.

It was also found that the density of boards increased when temperature goes up. To compensate the effect of density, a density correction line is plotted on all graphs, which shown that the increasing densities is not responsible for increase in mechanical properties and temperature is the only factor.

Physically all boards looked good, but some charred spots and blackish surfaces were observed on boards which were pressed at higher temperatures. It is also one of the reasons that temperature higher than 230°C is not good for board manufacturing, even though it gives higher mechanical properties.

For all boards pressed at 230°C, all properties except internal bond were below the minimum requirement as per ANSI A208.1-1999 for use for construction purposes, so it is obvious that these boards need further improvements in their properties by means of bark modification, use of additives or alteration in bark's physical state.

After finding the most suitable temperature i.e. 230°C in section 5.3.1, the next phase of the research was designed to see the effects of particle size (fine, medium, coarse and mixed) on the board's properties. In this case temperature of 230°C was applied to all boards prepared from different particles. Results of this investigation are presented below in table 5.4 and figures 5.13 to 5.20.

Table 5.4: Effects of Particle Size on Barkboard's Properties at 230°C Temperature (Tested as per ASTM-1037D-06a).

Properties	Average Value @ Particle Size*				Min. Req. (ANSI A208.1-1999)
	Coarse	Medium	Fine	Mixed	
Density (g/cm <sup>3</sup> )	0.89	0.91	1.0	0.92	-
Moisture Content (%)	1.21	1.29	2.2	1.46	-
MOE (N/mm <sup>2</sup> )	1350 (145)**	990 (47)	1871 (142)	1684 (218)	2400
MOR (N/mm <sup>2</sup> )	5.99 (1.33)	4.65 (0.04)	9.81 (1.25)	7.18 (0.64)	16.5
Internal Bond (psi)	44 (5.11)	38 (3.24)	90 (14.96)	140 (32.37)	130
Tensile Strength (N/mm <sup>2</sup> )	2.47 (0.16)	3.29 (0.22)	5.27 (0.41)	3.82 (0.29)	-
Thickness Swelling (%) (2 hrs/24 hrs)	2.42/ 11.99 (0.86/2.33)	8.47/18.44 (1.16/2.94)	1.02/ 5.1 (0.17/0.3)	2.96/ 10.46 (0.08/0.61)	-
Water Absorption (%) (2 hrs/24 hrs)	5.36/ 18.33 (0.45/0.95)	13.97/31.8 (3.56/4.16)	0.67/6.31 (0.07/0.4)	3.64/ 15.36 (0.34/1.95)	-

\* (Pressure 28.1 kg/cm<sup>2</sup> for 1 minute followed by 12.3 kg/cm<sup>2</sup> for 19 minutes).

\*\*Values in brackets showing standard deviation.

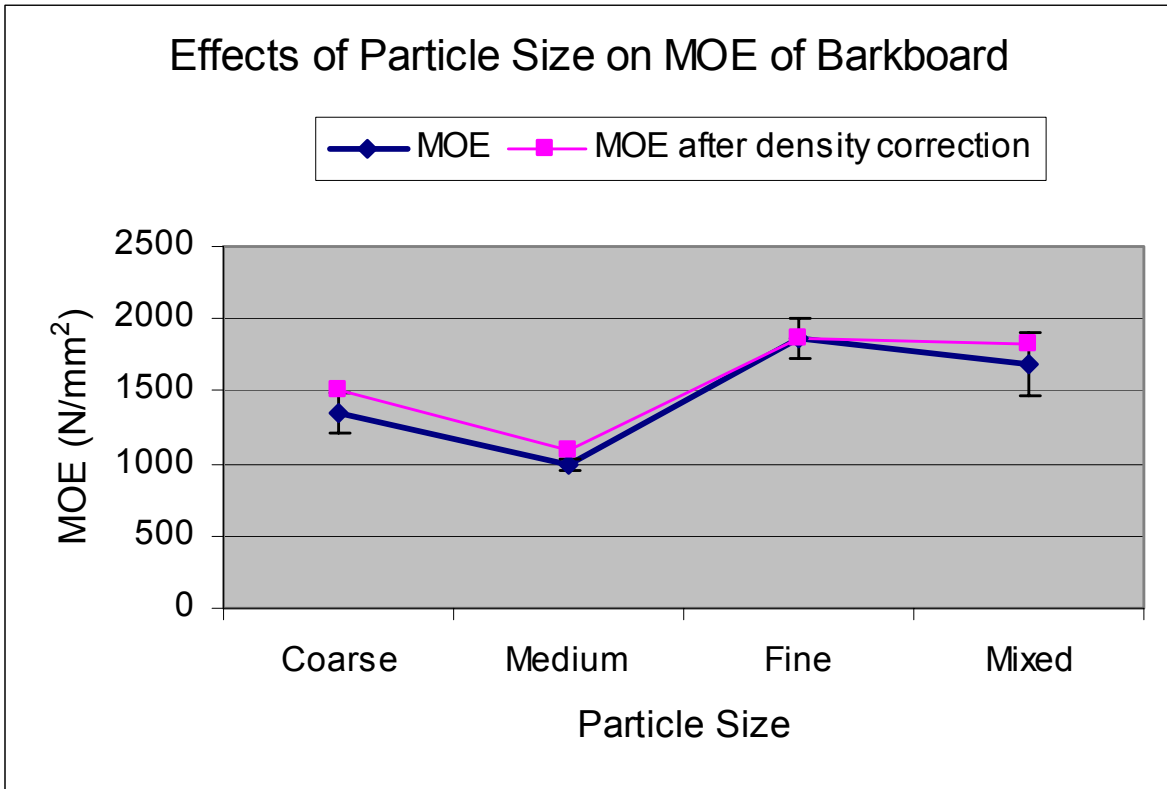


Figure 5.13: Effects of bark particle size on MOE of barkboards.

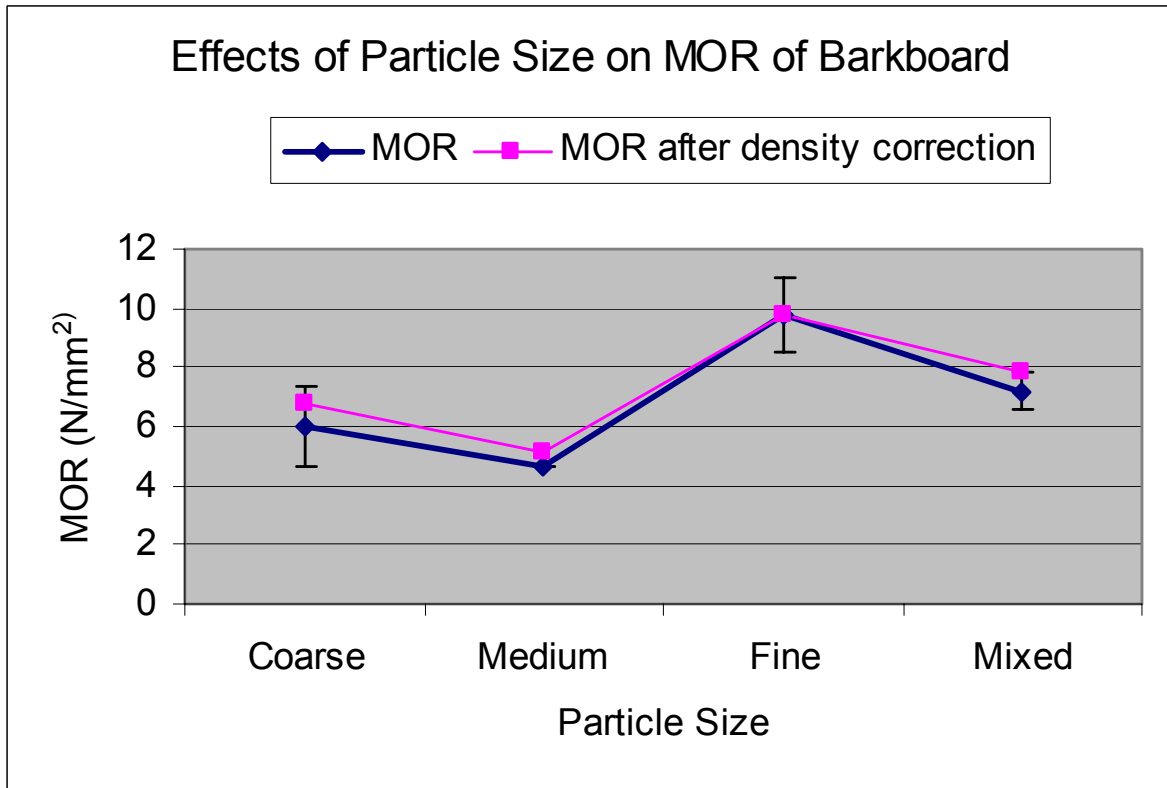


Figure 5.14: Effects of bark particle size on MOR of barkboards.

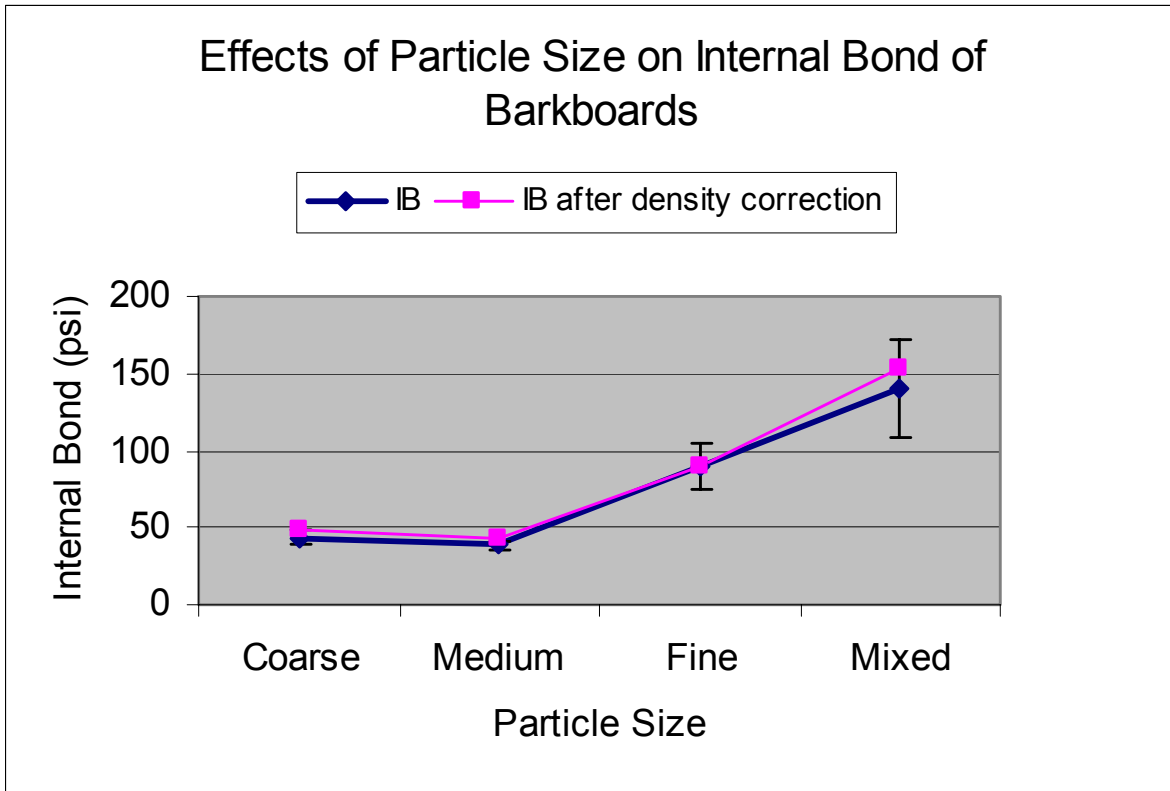


Figure 5.15: Effects of bark particle size on internal bond of barkboards.

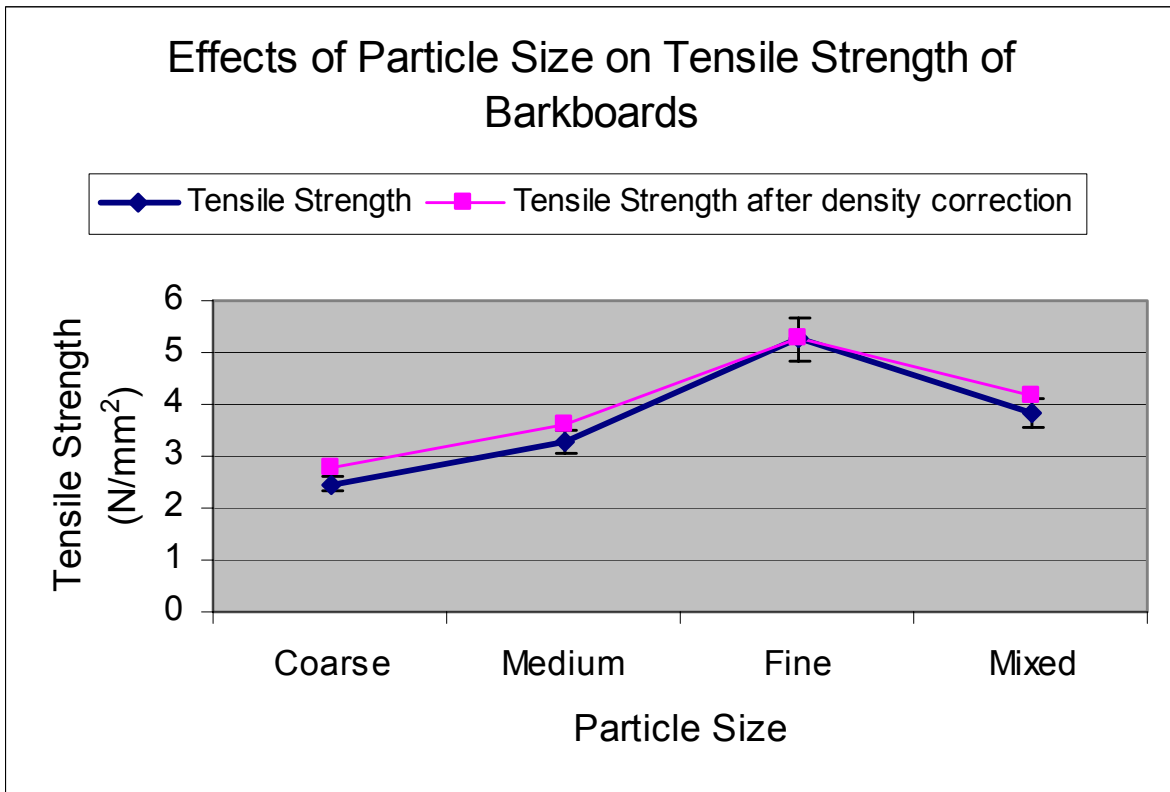


Figure 5.16: Effects of bark particle size on tensile strength of barkboards.

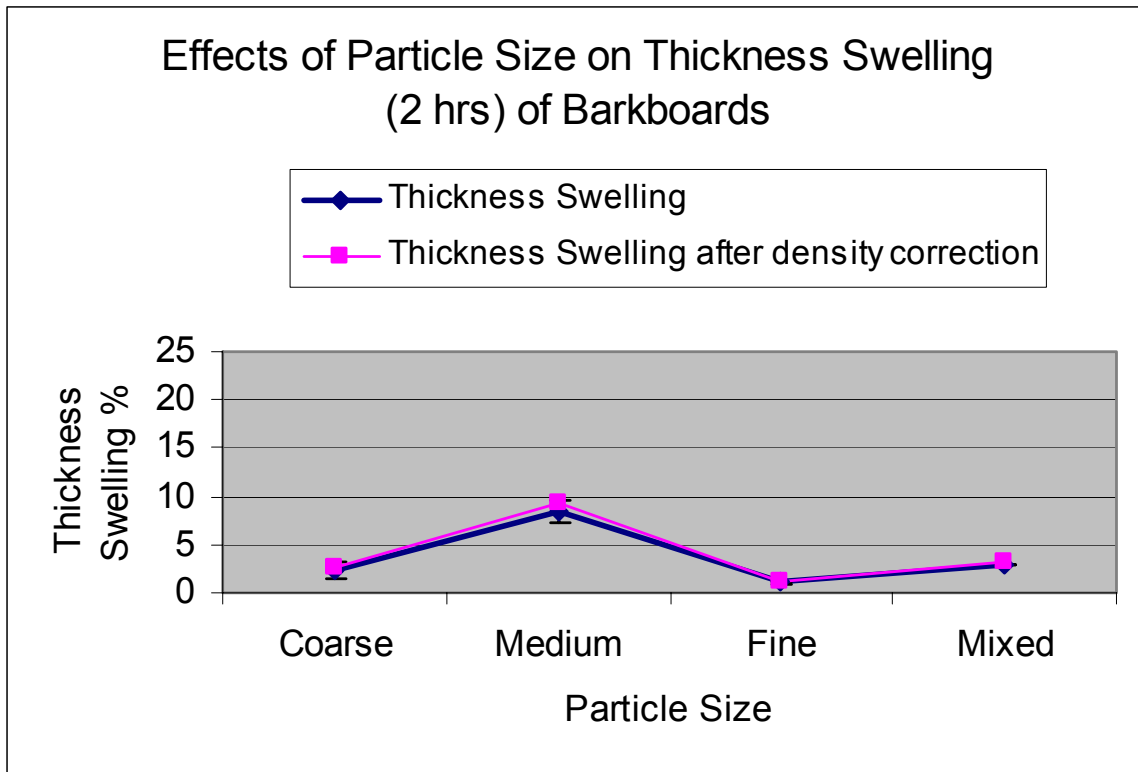


Figure 5.17: Effects of bark particle size on thickness swelling (2 hrs) of barkboards.

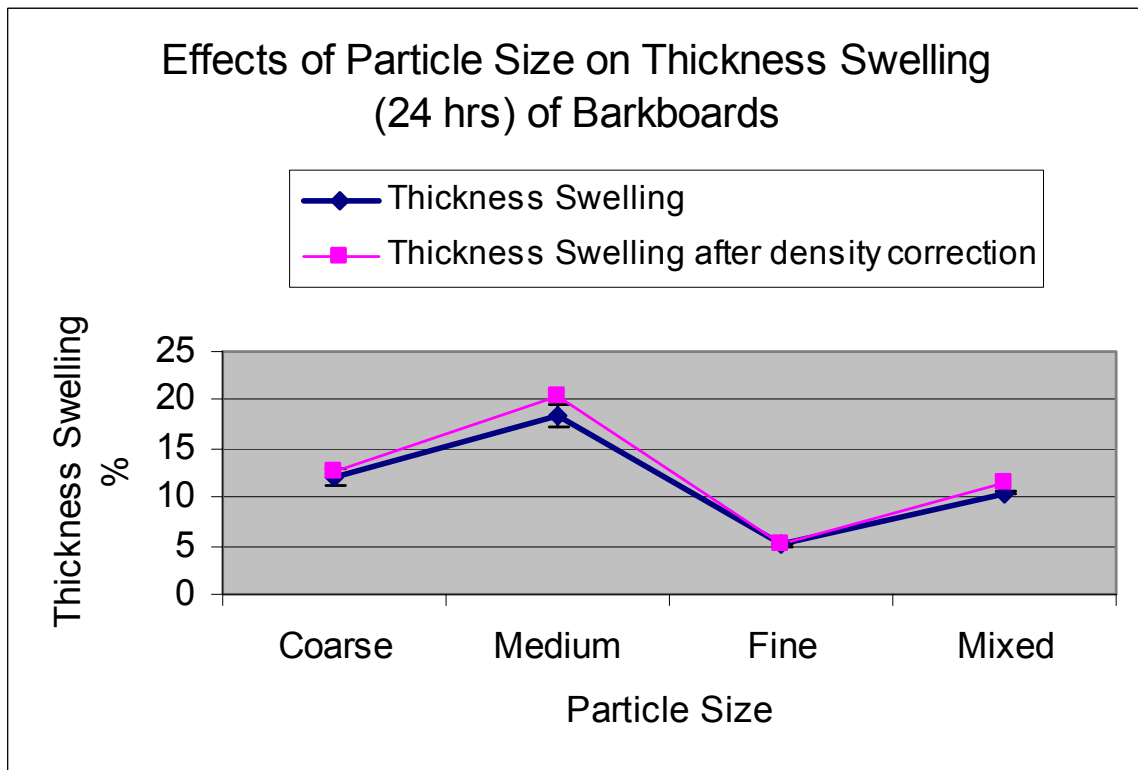


Figure 5.18: Effects of bark particle size on thickness swelling (24 hrs) of barkboards.

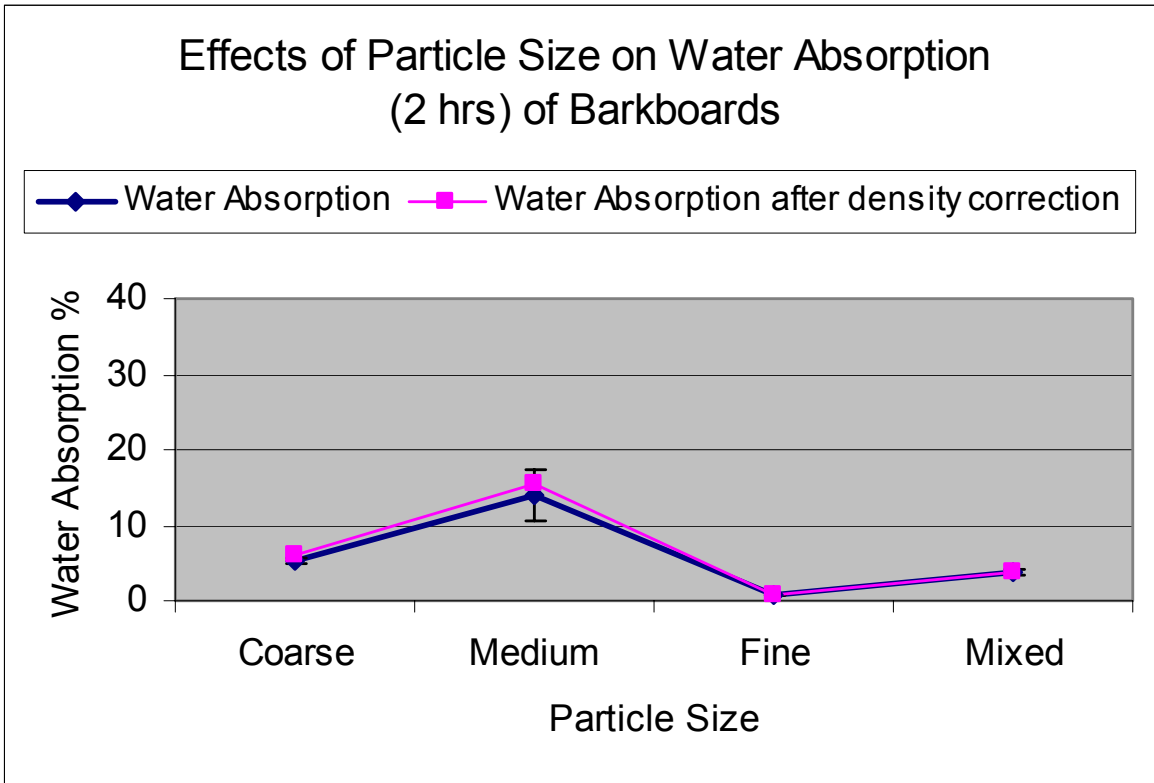


Figure 5.19: Effects of bark particle size on water absorption (2 hrs) of barkboards.

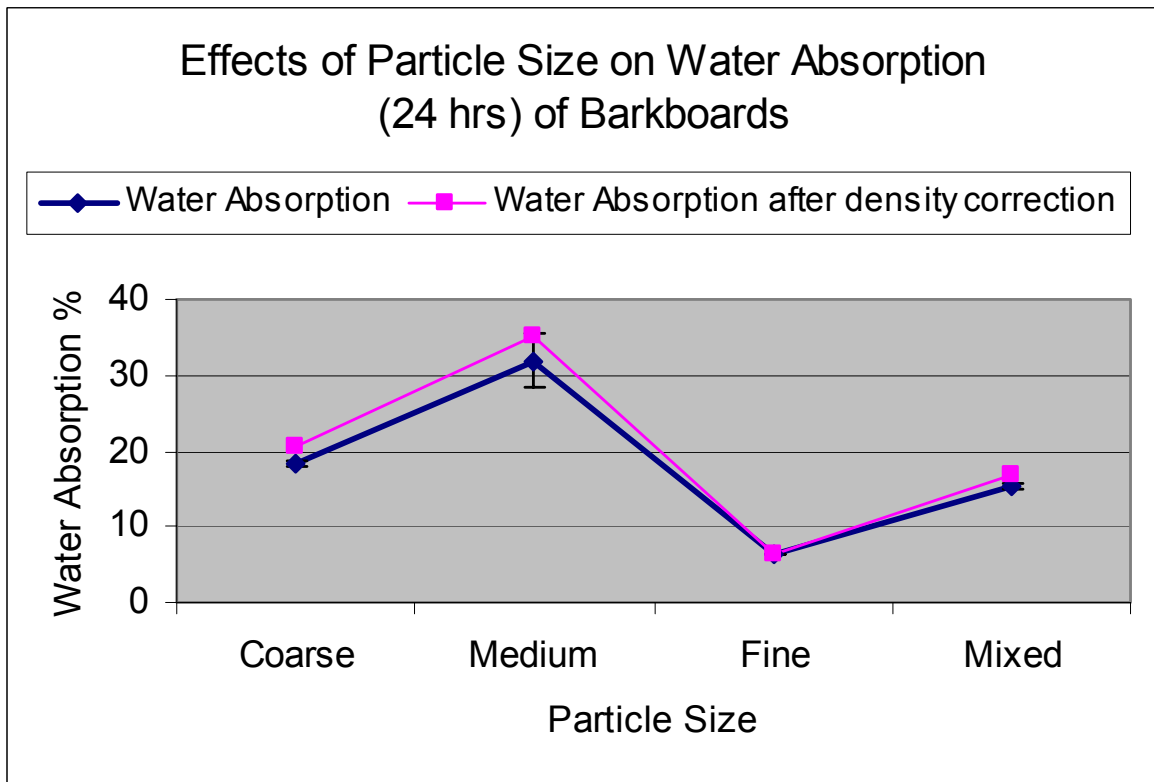


Figure 5.20: Effects of bark particle size on water absorption (24 hrs) of barkboards.

Investigations of effect of bark particle size on barkboard properties gave attractive results in terms of mechanical properties for fine particles. Boards made from fine size particles (particles passing 18 mesh) showed superiority for almost all properties (except internal bond) over boards made from coarse (particles passing 4 mesh & retained in 7 mesh), medium (particles passing 7 mesh & retained in 18 mesh) and mixed (particles passing 4 mesh) size particles. Fine particle's boards were physically better looking with smooth and even surfaces. They also possess highest density which was around  $1 \text{ g/cm}^3$ . Most properties were much closer to the minimum requirement as per ANSI A208.1-1999 for use in building purposes.

For values of MOE and MOR their performance was superior, followed by boards prepared from mixed and then coarse particle's. In this case, medium size particles showed very poor values. In case of internal bond, fine particles were better than coarse and medium but their values were lower than for mixed particles. The probable reason behind this may be in case of fine particles, the better interlinking of particles was missing due to their small shape while mixed particles having many long fibers which may have inter-weaved between each other. For tensile strength, thickness swelling and water absorption, boards made from fine particles gave excellent values. Even after the 24 hrs in water, their swelling and water absorption was much less and particle binding was intact. The superiority of fine particles in most of the mechanical properties should be because of the close contact of particle's surfaces and compact packing in void volumes. When resin is used as for commercial particle boards, it fills the void volumes or inter-particle spaces. Since there was no resin in barkboards, there should be more void spaces or less surface interaction, especially in coarse and medium sized particles as compared to fine and mixed particles, so their properties are reflected accordingly.

Similar to the temperature effects, particles sizes also affect density of boards. It was found that the density of boards made with fine particles was highest. Density correction lines on all graphs show that the density factor doesn't contribute in increase of mechanical properties.

## **5.4 Conclusion:**

Based on the study of temperature and particle size effects on beetle infested lodgepole pine barkboard's properties, two conclusions can be drawn:

- I. It is very clear that temperature has a great influence on all mechanical properties of boards. As expected all mechanical properties increased with increased temperature. These results are similar to work done by previous researchers on other species.
  
- II. Boards made with fine particles, performed very well in all properties (except internal bond which had lower IB than for mixed particles but higher than for coarse and medium particles). They also have better physical appearance and smooth surfaces with the highest density.

The hypothesis of extractive and lignin polymerization and high temperature plasticization and their role in self-adhesion of bark particles is also supported by these results. It can be explained that higher temperature led to chemical reactions resulting in chemical bonds rather than physical. Furthermore, fine particles have closer contact and resulted in denser board in the absence of resin (Also refer to SEM Analysis conclusion in chapter 7). They have closer interactions due to the probable binding by bark's phenolic compounds in response to high temperature polymerization.

# **CHAPTER 6: BARKBOARDS WITH ADDITION OF LIQUEFIED BARK**

## **6.1 Introduction:**

Chapter 4 and 5 described the barkboard production techniques and effects of temperature and particle size on board's properties. It was found that barkboard's properties can be improved by alteration in temperature and particle size. However, it was clear after various trial and error experiments that barkboards cannot meet the requirements of by specifications for construction boards. To explore the possibility of making all-bark based panels, efforts were made to use liquefied bark as the adhesive for the barkboard.

Therefore, trials were made to evaluate the role of liquefied bark in improvement of board properties and its comparison with PF resin and control boards. Since liquefied bark has adhesive properties and is environmental-friendly as compare to synthetic resins, it is logical to expect improvement in barkboard properties. The experiments were completed at 170°C temperature so that the effect of the addition is highlighted and the contribution though whole barks' phenolic compounds is minimized.

## **6.2 Experimental:**

### **6.2.1 Board Production with Liquefied Bark & PF Resin:**

In this experiment, barkboards were produced with a variable amount of liquefied bark and PF resin separately. The general methodology was the same as described in sections 4.2.1 & 5.2.2, except that liquefied bark and PF resin were thoroughly mixed in bark before hot pressing. Boards were made with 600 g of bark in 30X30 cm size with a desired board thickness of 6.25 mm and density of 0.8 - 1 g/cm<sup>3</sup>. Bark particles were of mixed sizes, passing through 4 mesh screen after grinding. There were 3 repetitions for each group of liquefied bark and PF resin.

Three different amounts of liquefied bark or PF resin i.e. 2%, 4% and 8% on solid content basis were used to see the variations in properties. Control boards (without liquefied bark or resin) were also produced for comparison purpose. 170°C pressing temperature was used in hot pressing which is quite similar to what is used in commercial production of composite particleboards with synthetic resins. Pressure was same (28.1 kg/cm<sup>2</sup> for 1 minute followed by 12.3 kg/cm<sup>2</sup> for 19 minutes) for all barkboard pressing.

The liquefied bark used in this experiment was synthesized by a fellow student working on bark liquefaction. The same bark species used for board's raw material (beetle infested lodgepole pine) was used for liquefaction. The commercial PF resin in the liquid form was received from FP Innovations-Forintek, Vancouver. The solid contents of liquefied bark and PF resin were recorded as 38.09 and 64.37% respectively.

Because of the high viscosity of the liquefied bark, it was difficult to mix it uniformly with bark particles so it was thinned with acetone to achieve a uniform spread over all bark particles. After mixing, bark particles were kept in a fume hood for 24 hrs for complete evaporation of solvent which was used as thinner for liquefied bark. After the mixing of 2%, 4% and 8% liquefied bark and PF resin on the solid content basis and drying, the bark samples were hot pressed.

Table 6.1: Experimental design to study liquefied bark and PF resin effects on barkboard's properties.

S. No.	Code No.	Description	Objective
1.	MXT	Mixed Particles, Pressing Temp. 170°C, Without Liquefied Bark or PF Resin	Comparison
2.	MXLB1	Mixed Particles, Pressing Temp. 170°C, Liquefied Bark 2% (solid content basis)	To investigate liquefied bark effects on barkboard's properties
3.	MXLB2	Mixed Particles, Pressing Temp. 170°C, Liquefied Bark 4% (solid content basis)	
4.	MXLB3	Mixed Particles, Pressing Temp. 170°C, Liquefied Bark 8% (solid content basis)	
5.	MXPF1	Mixed Particles, Pressing Temp. 170°C, PF Resin 2% (solid content basis)	To investigate PF resin effects on barkboard's properties and to compare with liquefied bark effects
6.	MXPF2	Mixed Particles, Pressing Temp. 170°C, PF Resin 4% (solid content basis)	
7.	MXPF3	Mixed Particles, Pressing Temp. 170°C, PF Resin 8% (solid content basis)	

### 6.2.2 Bark Liquefaction:

For liquefaction purpose, beetle infested lodgepole pine bark was first converted into powder (passing through 35 mesh screen) and then dried in the oven at 105°C for 12 hrs before the liquefaction experiments. 1 part of bark powder with 3 part of phenol in crystal form and 96% sulfuric acid (3% based on the weight of phenol) were charged into a three neck flask. The reaction was carried out in a heating oil bath at 150°C under atmospheric pressure. The liquefaction reaction time was 120 minutes. After the liquefaction reaction, the system was cooled down to room temperature using cold water. After cooling, liquefied bark was stored in refrigerator and used in boards within a week.

### 6.3 Results and Discussion:

Results based on the testing of barkboards with liquefied bark and PF resin at 170°C and their comparison are presented in table 6.2 and figures 6.1 to 6.6:

Table 6.2: Effects of Liquefied Bark on Barkboard's Properties (Tested as per ASTM-1037D-06a).

Properties	Values @ Liquefied Bark Percentage (Solid Content Basis)				Min. Req. (ANSI A208.1-1999)
	0%	2%	4%	8%	
Density (g/cm <sup>3</sup> )	0.80	0.82	0.87	0.90	-
Moisture Content (%)	2.52	0.60	0.90	0.98	-
MOE (N/mm <sup>2</sup> )	420 (104) **	1207 (41)	1676 (19.28)	2028 (13)	2400
MOR (N/mm <sup>2</sup> )	2.01 (0.22)	4.97 (0.68)	5.75 (0.06)	7.19 (0.71)	16.5
Internal Bond (psi)	14.53 (5.65)	16.04 (4.15)	29.29 (6.19)	77.26 (15.71)	130
Tensile Strength (N/mm <sup>2</sup> )	1.55 (0.2)	2.06 (0.19)	4.34 (0.28)	7.67 (0.84)	-
Thickness Swelling (%) (2 hrs/24 hrs)	24.90/64.9 (0.34/3.1)	13.29/39.7 (6.55/8.78)	23.39/63.5 (4.32/2.19)	14.1/50.6 (3.15/4.1)	-
Water Absorption (%) (2 hrs/24 hrs)	29.78/72.8 (3.46/0.92)	17.65/71.9 (4.56/11.2)	22.58/90.7 (0.51/9.91)	12.5/60.3 (1.24/5.4)	-

\* (Temperature 170°C, Pressure 28.1 kg/cm<sup>2</sup> for 1 min. followed by 12.3 kg/cm<sup>2</sup> for 19 min.).

\*\*Values in brackets showing standard deviation.

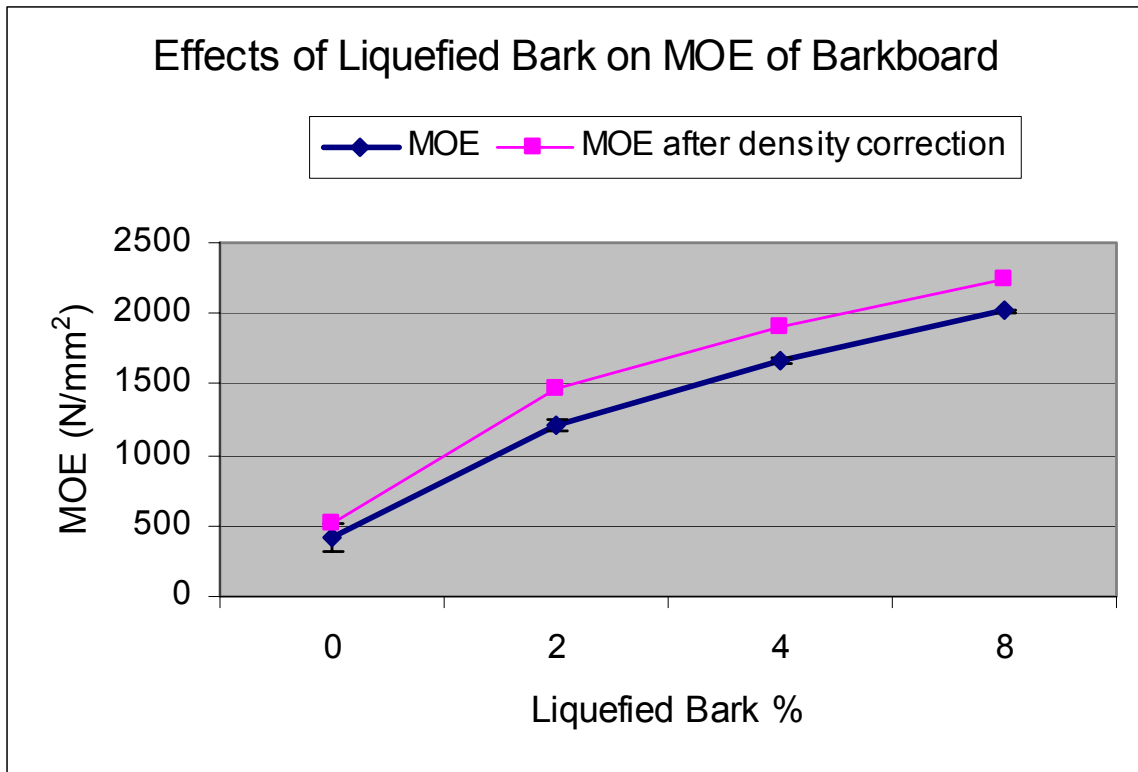


Figure 6.1: Effects of liquefied bark on MOE of barkboards.

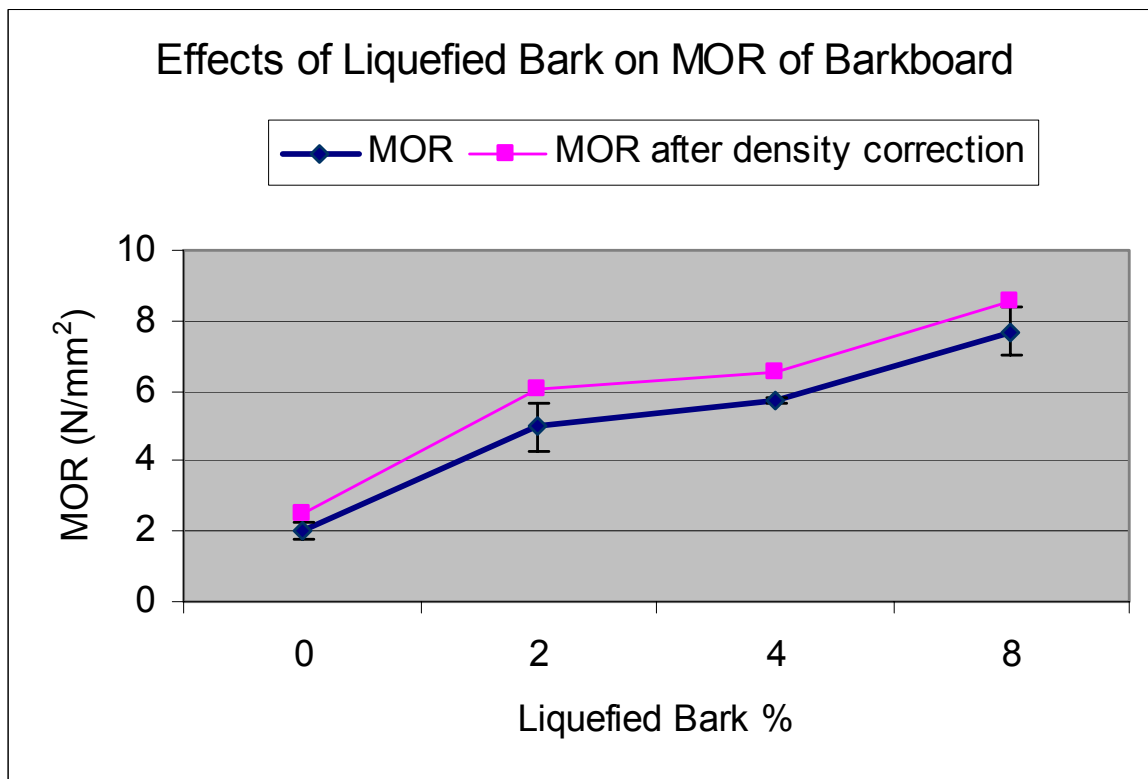


Figure 6.2: Effects of liquefied bark on MOR of barkboards.

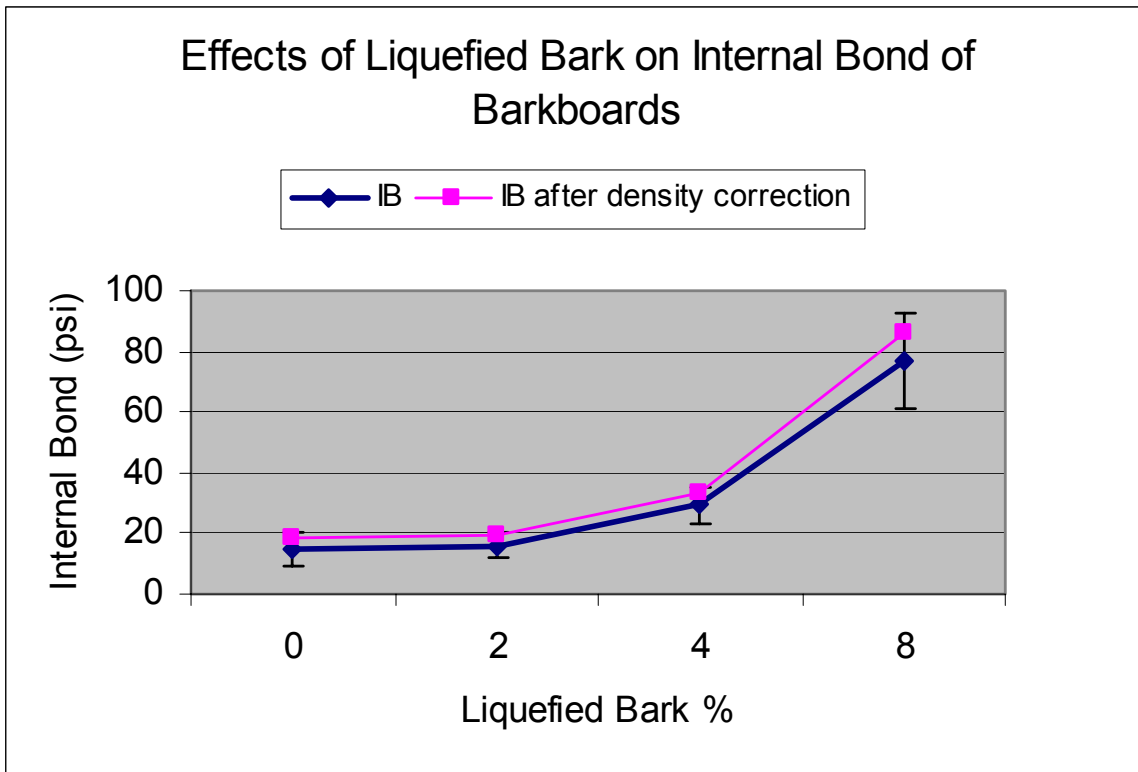


Figure 6.3: Effects of liquefied bark on internal bond of barkboards.

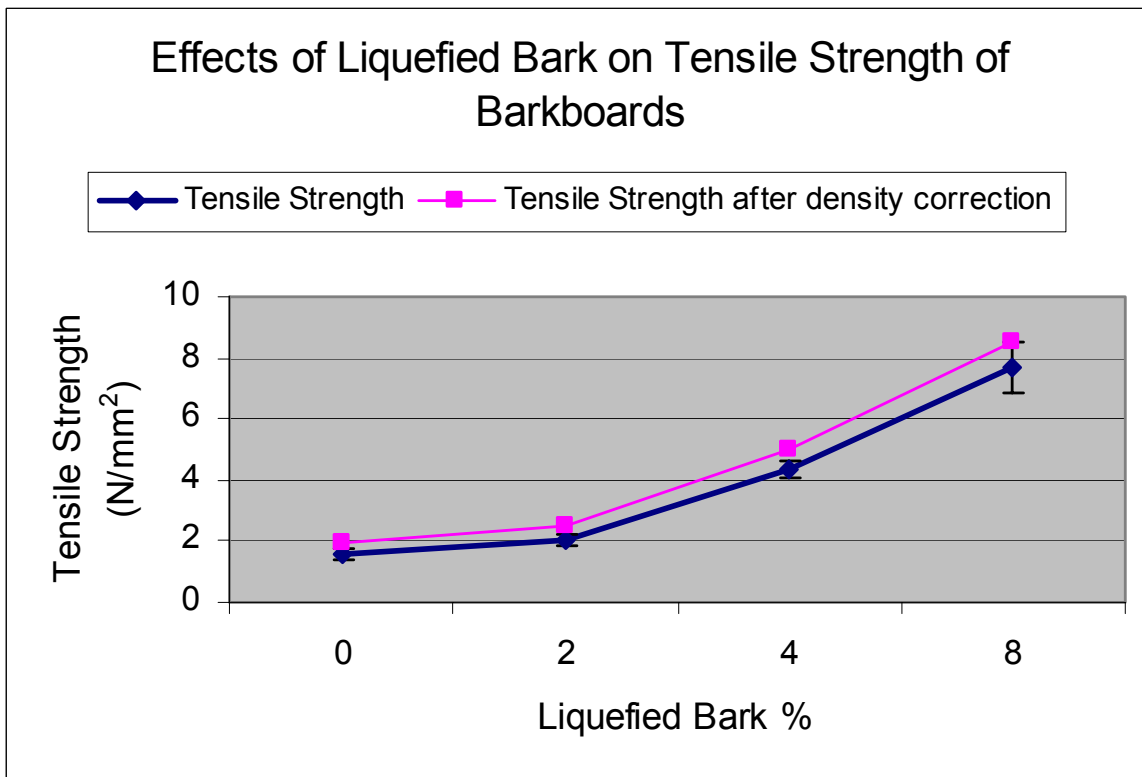


Figure 6.4: Effects of liquefied bark on tensile strength of barkboards.

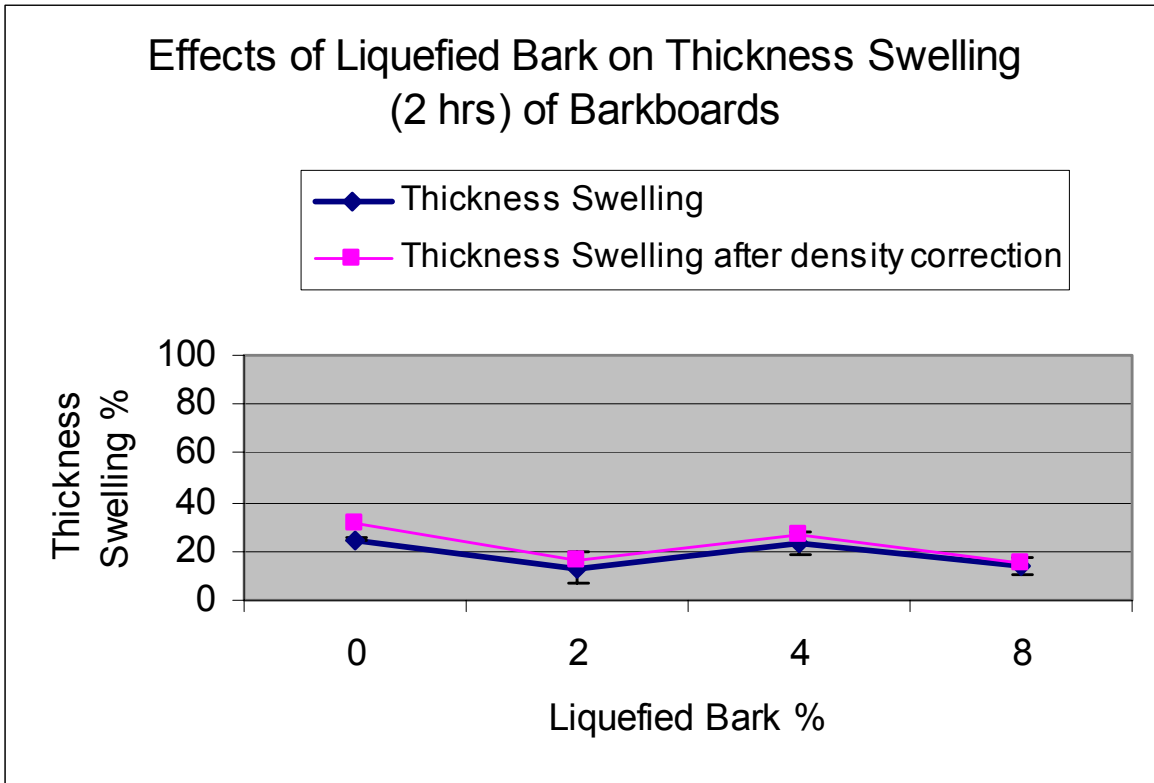


Figure 6.5: Effects of liquefied bark on thickness swelling (2 hrs) of barkboards.

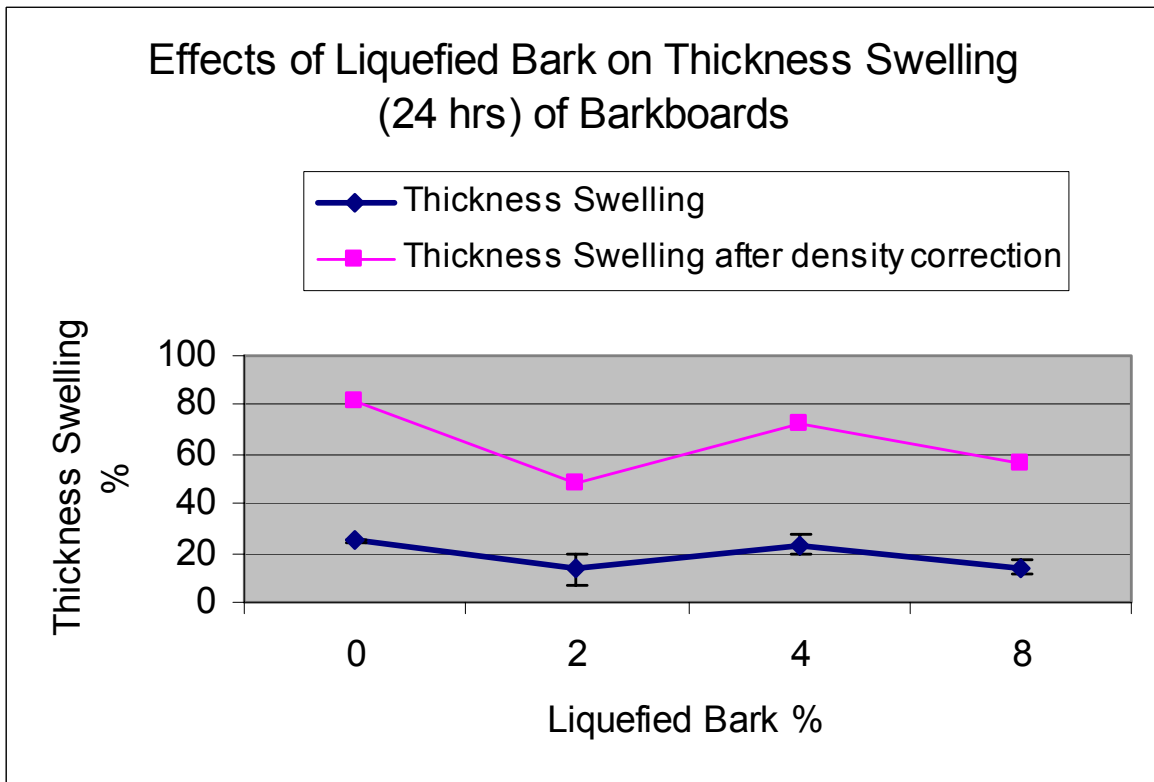


Figure 6.6: Effects of liquefied bark on thickness swelling (24 hrs) of barkboards.

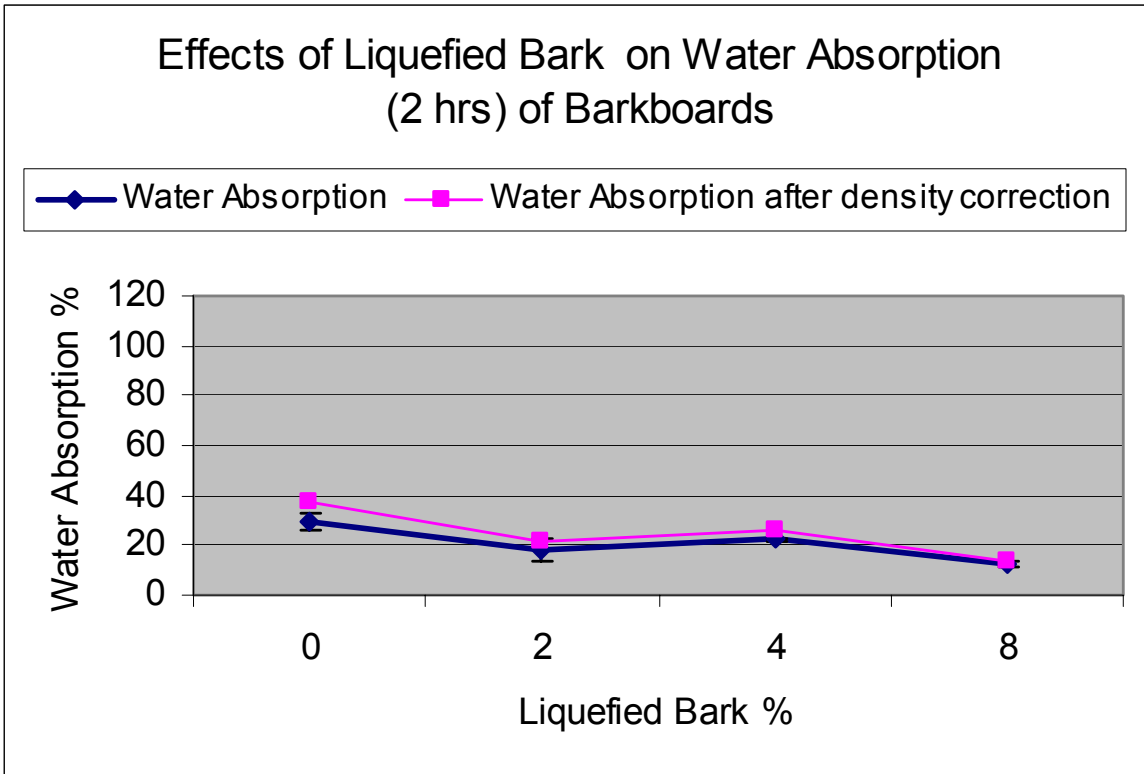


Figure 6.7: Effects of liquefied bark on water absorption (2 hrs) of barkboards.

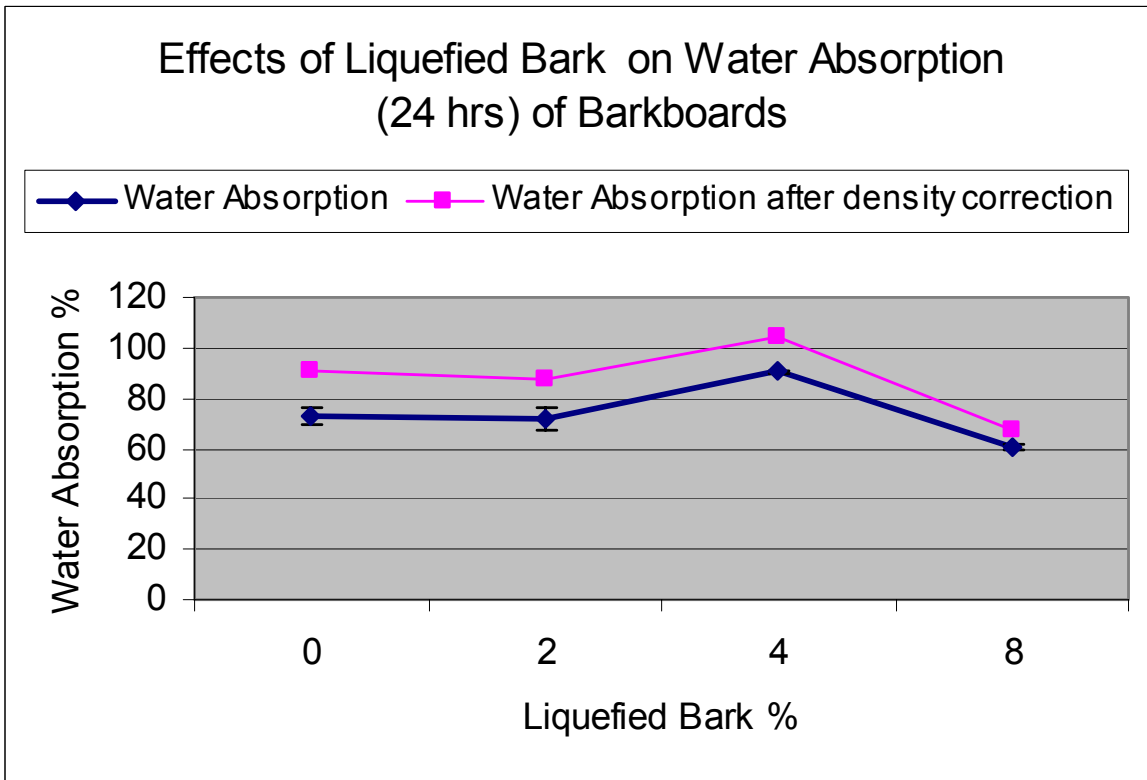


Figure 6.8: Effects of liquefied bark on water absorption (24 hrs) of barkboards.

From tables 6.2 and figures 6.1 to 6.4, it is clear that MOE, MOR, internal bond and tensile strength properties increased as the amount of liquefied bark increased from 2% to 8%. If values for these properties at 8% liquefied bark are compared with the control boards (without any liquefied bark) it is 4-5 times higher. However, no significant effect was observed for thickness swelling and water absorption properties under different conditions.

Table 6.2 has also shown that the density increases with the increasing amount of liquefied bark but its correction lines on relevant graphs indicated that density is not responsible for increase in mechanical properties.

Table 6.3: Effects of PF Resin on Barkboard's Properties (Tested as per ASTM-1037D-06a).

Properties	Value @ PF Resin % (Solid Content Basis)				Min. Req. (ANSI A208.1-1999)
	0%	2%	4%	8%	
Density (g/cm <sup>3</sup> )	0.80	0.83	0.86	0.92	-
Moisture Content (%)	2.52	1.28	2.02	1.77	-
MOE (N/mm <sup>2</sup> )	420 (104)**	1447 (52)	1824 (22)	2396 (19.27)	2400
MOR (N/mm <sup>2</sup> )	2.01 (0.22)	6.89 (0.72)	8.29 (0.12)	12.83 (0.86)	16.5
Internal Bond (psi)	14.53 (5.65)	37.25 (4.56)	49.36 (7.1)	101 (7.79)	130
Tensile Strength (N/mm <sup>2</sup> )	1.55 (0.2)	3.19 (0.23)	7.18 (0.86)	10.68 (1.49)	-
Thickness Swelling (%) (2 hrs/24 hrs)	24.9/64.9 (0.36/3.1)	11.2/32.4 (4.25/3.75)	10.9/29.7 (2.3/2.99)	8.7/28 (2.01/2.33)	-
Water Absorption (%) (2 hrs/24 hrs)	29.8/72.8 (3.46/0.92)	13.4/62.6 (4.06/4.9)	12.1/36.7 (2.21/2.95)	10.45/35 (1.87/2.73)	-

\* (Temperature 170°C, Pressure 28.1 kg/cm<sup>2</sup> for 1 min. followed by 12.3 kg/cm<sup>2</sup> for 19 min.)

\*\*Values in brackets showing standard deviation.

Table 6.4: Comparison of barkboards without any resin, with liquefied bark and with PF resin (Tested as per ASTM-1037D-06a).

Board's Properties	Type of Boards						
	Control	With Liquefied Bark			With PF Resin		
	0%	2%	4%	8%	2%	4%	8%
MOE (N/mm <sup>2</sup> )	420	1207	1676	2028	1447	1824	2396
MOR (N/mm <sup>2</sup> )	2.01	4.97	5.75	7.19	6.89	8.29	12.83
Internal Bond (psi)	14.53	16.04	29.29	77.26	37.25	49.36	101
Tensile Strength (N/mm <sup>2</sup> )	1.55	2.06	4.34	7.67	3.19	7.18	10.68
Thickness Swelling % (2 hrs)	24.9	13.29	23.39	14.1	11.2	10.89	8.7
Thickness Swelling % (24 hrs)	64.9	39.7	63.5	50.6	32.4	29.7	28
Water Absorption % (2 hrs)	29.8	17.65	22.58	12.5	13.4	12.1	10.45
Water Absorption % (24 hrs)	72.8	71.9	90.7	60.3	62.6	36.7	35

\* (Temperature 170°C, Pressure 28.1 kg/cm<sup>2</sup> for 1 min. followed by 12.3 kg/cm<sup>2</sup> for 19 min.)

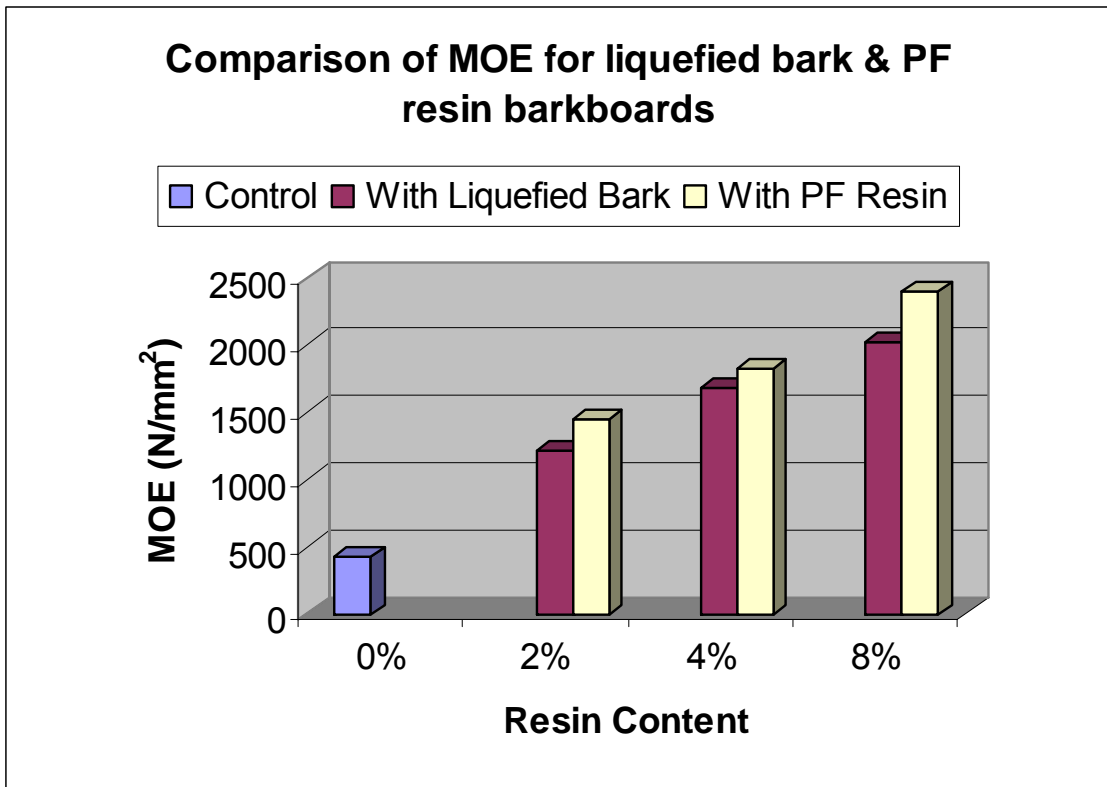


Figure 6.9: Comparison of MOE for liquefied bark & PF resin barkboards.

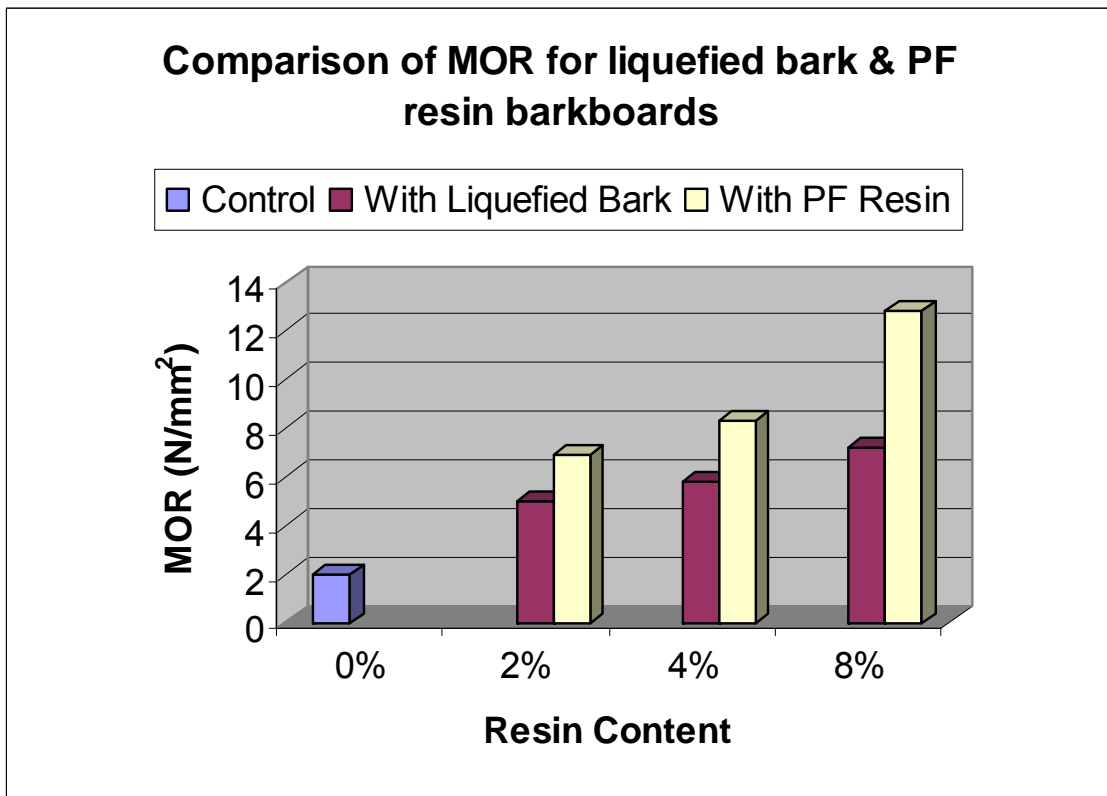


Figure 6.10: Comparison of MOR for liquefied bark & PF resin barkboards.

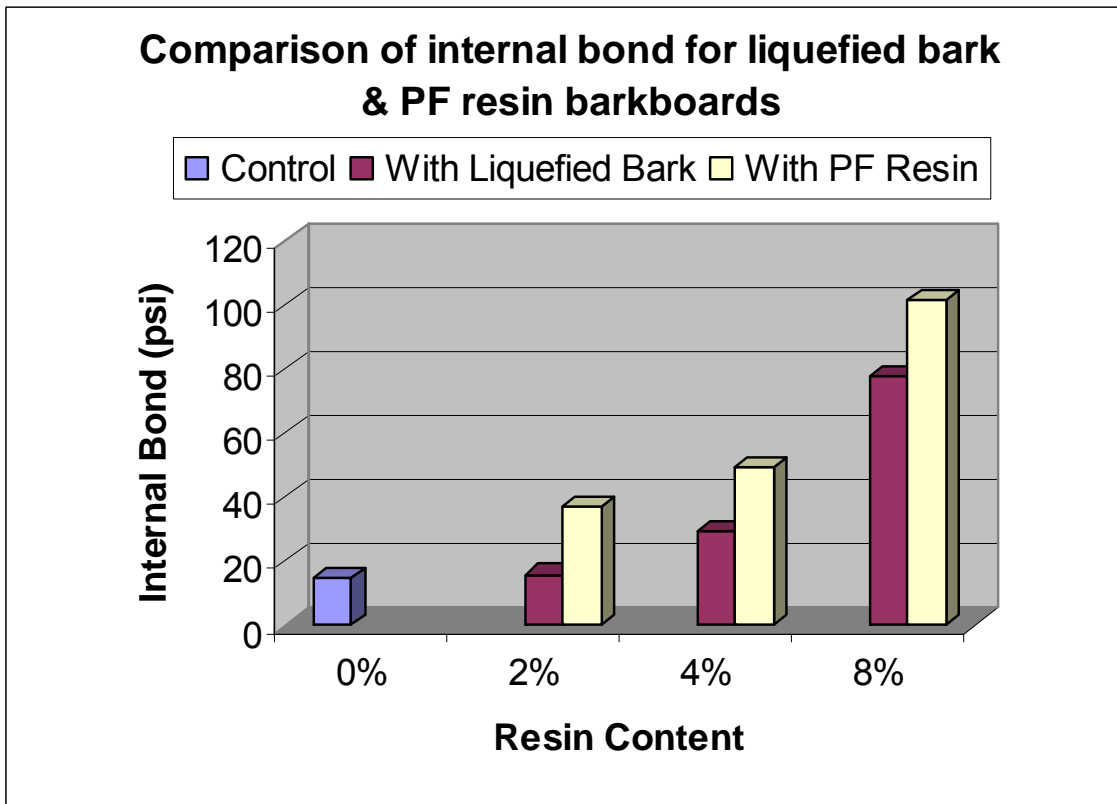


Figure 6.11: Comparison of internal bond for liquefied bark & PF resin barkboards.

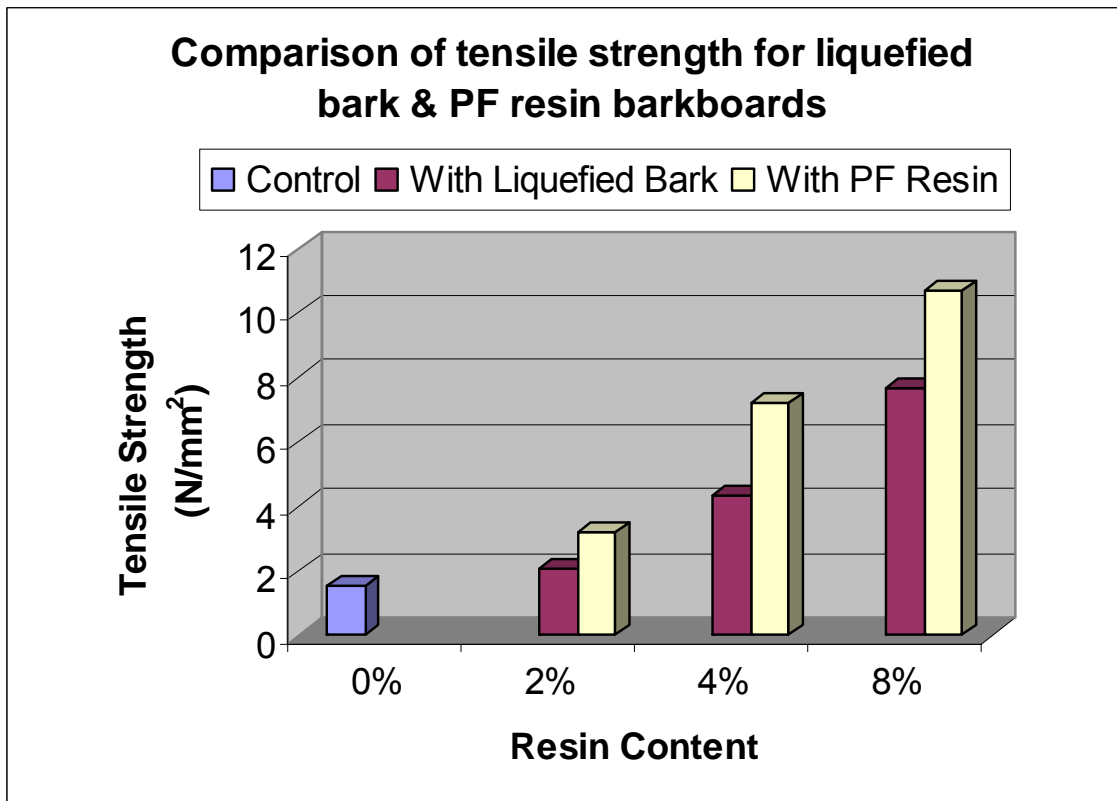


Figure 6.12: Comparison of tensile strength for liquefied bark & PF resin barkboards.

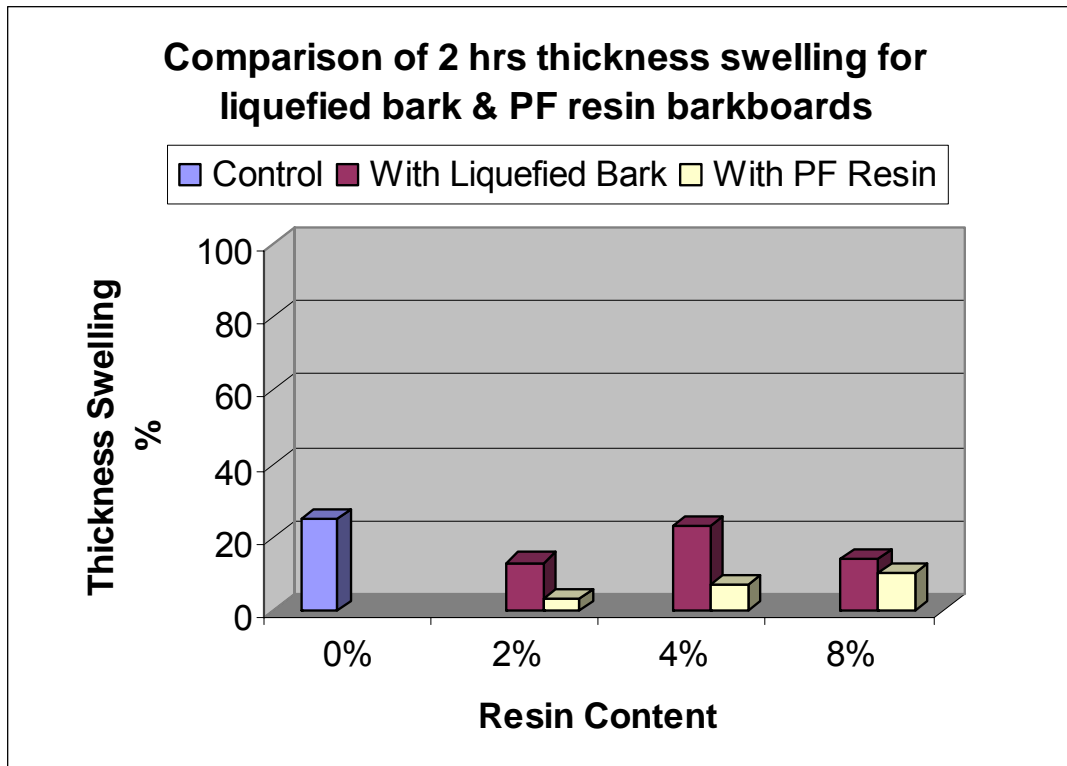


Figure 6.13: Comparison of 2 hrs thickness swelling for liquefied bark & PF resin barkboards.

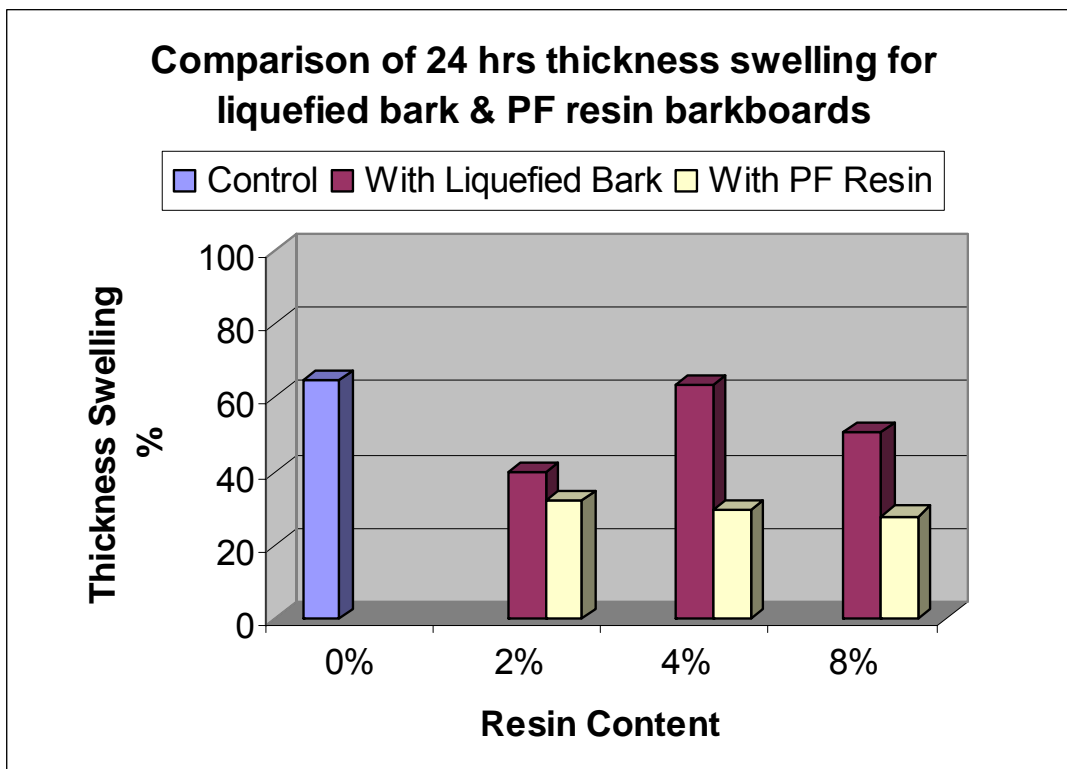


Figure 6.14: Comparison of 24 hrs thickness swelling for liquefied bark & PF resin barkboards.

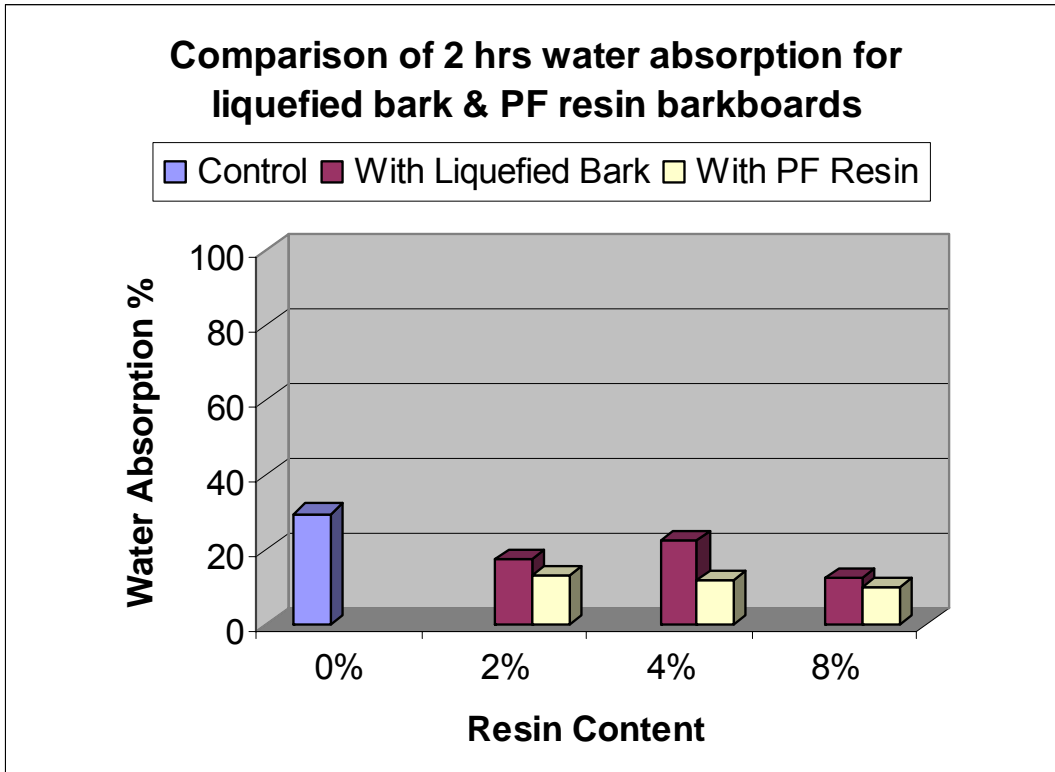


Figure 6.15: Comparison of 2 hrs water absorption for liquefied bark & PF resin barkboards.

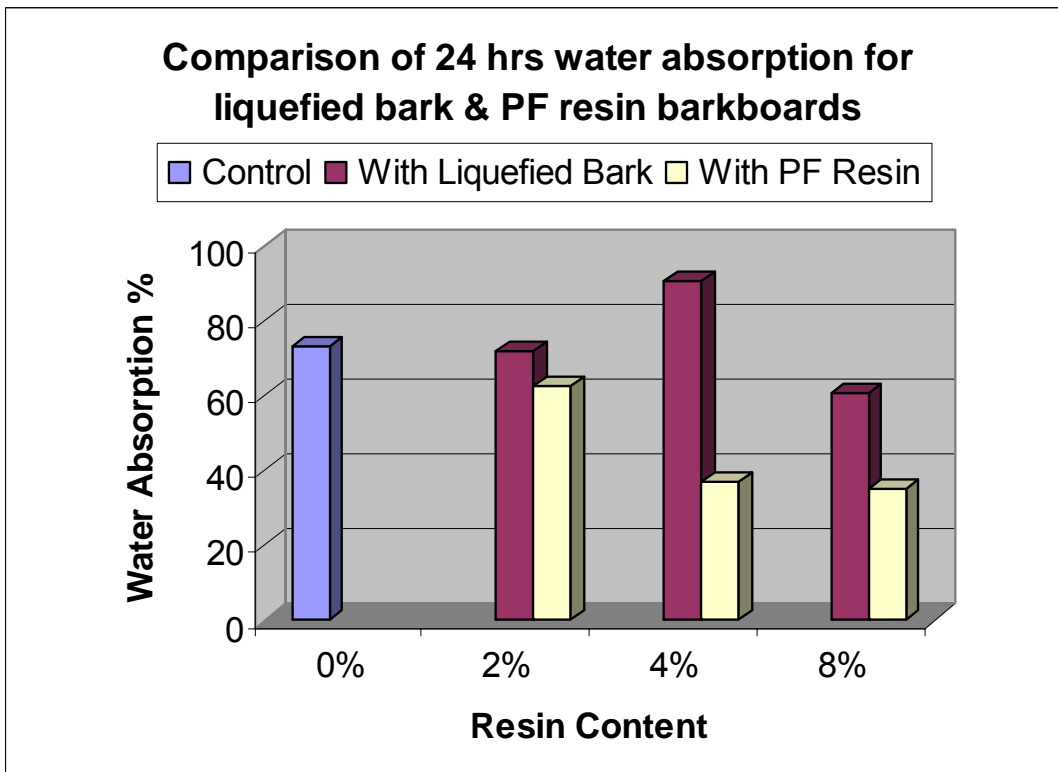


Figure 6.16: Comparison of 24 hrs water absorption for liquefied bark & PF resin barkboards.

Boards made with PF resin performed better in all properties compared to their counterparts (2%, 4% and 8%) of liquefied bark's boards. Statistical t-test also reveals that comparison of control boards to 8% LB or 8% PF resin boards shown higher difference in their properties as compare to comparison of 8% LB boards with 8% PF resin boards.

There were no appreciable improvements in board's properties with liquefied bark or PF resin, pressed at 170°C, compared to boards without any resin at 230°C. The probable reason should be at 170°C temperature, improvements are due to cross-linking of liquefied bark or PF resin only and there is no contribution from barks phenolic compound's polymerization effects (which has been concluded in temperature effects experiments). These compounds contribute appreciably in case of 230°C temperature.

#### **6.4 Conclusion:**

This study compared the effects of liquefied bark and PF resin on barkboard's properties at 170°C with boards pressed without any additives (control) under the same conditions. Liquefied bark has considerable adhesive characteristics which improved all mechanical properties; however boards made with PF resin demonstrated better properties compared to boards using liquefied barks or control boards.

The liquefied bark used here was just a product of bark liquefaction; more research required to seek a possibility to convert it into a novel resin by modification or reaction with a cross-linking agent.

Moreover, it is a question whether use of any kind of resin in barkboard production is technically and commercially feasible. Since the concept of barkboard is based on utilization of bark's phenolic compounds at higher temperatures (230°C and above), and lower temperatures are not suitable for their polymerization reactions. In contrast, commercial resin curing is mostly required around 160°C temperature which is not suitable for bark's phenolic compound's polymerization

reactions. Use of such resins at higher temperatures is technically and commercially not recommended. So these two situations are contradictory and one has to be compromised at the time of choosing pressing parameters.

Further research scope is available in this area to combine the positive effects of use of liquefied bark & fine particle size or at other temperatures to get an improved board.

## **CHAPTER 7: BARKBOARD CHARACTERIZATION**

### **7.1 Introduction:**

Previous experiments examined the mechanical properties of barkboards under different conditions of pressing parameters, raw materials and additives. Although these mechanical properties gave an overview of board performance, further studies are required to explore chemical analysis, characterization and micro level image analysis of particle arrangement. For barkboards, it is believed that self-binding of particles or curing occurred due to the chemical changes in their chemical constituents including various extractives and lignin, so it is informative to confirm if such changes occurred.

The main objective of this part of study was chemical analysis and characterization of all boards made under different conditions of pressing temperatures viz. 170, 200 and 230°C. This characterization can determine the changes of bark constituents by comparison of results before and after pressing at different temperatures. Image analysis of fractured surfaces of the boards pressed under different conditions provides an indication of the particle arrangements or packing in the boards. It can be assumed that size of the particles and temperature influences their structural patterns due to contact area. Fine particle at high temperature should have comparatively close contacts and dense packing.

FTIR spectroscopy of cured board was also performed to characterize the chemical changes. A comparison of FTIR spectra of different boards with original bark is used to examine the possible changes in composition before and after pressing under different conditions.

## **7.2 Experimental:**

Similar to original bark analysis in section 3.2; holocellulose, lignin and extractives were analyzed for their composition in pressed boards. The procedure for determination of chemical composition was the same as described in detail in chapter 3.

For this study, samples were taken in the form of small pieces from different positions of the boards pressed at 170, 200 and 230°C. These samples were separately ground into a fine powder and then screened through a 35 mesh screen. These screened and dried bark specimens were used for bark analysis.

Other than the chemical analysis, small amounts of fine powder from each group were again hand-ground into minute particles for FTIR study. FTIR was used in the tensor mode (KBr pellet) with standard procedure to get spectra of corresponding board's material. Original bark was used for comparison.

Fractured surface analyses of board samples (broken cross-sections of samples after mechanical tests) were examined by Scanning Electron Microscopy. These were performed for the boards made from mixed, fine, medium and coarse size particles with different press temperatures. Images were compared, to see the difference in packing of particles as a result of auto-adhesion.

## 7.3 Results and Discussion:

### 7.3.1 Chemical Analysis & Characterization:

The results for chemical analysis of original bark and barkboards produced at three different temperatures are given below in table 7.1 and figure 7.1:

Table 7.1: Holocellulose,  $\alpha$ -cellulose, Klason lignin and ET-HW extractives contents of raw barks and barkboards produced at three different temperatures.

Constituents	Percentage			
	Bark (Before Pressing)	Barkboard (After pressing at 170°C)	Barkboard (After pressing at 200°C)	Barkboard (After pressing at 230°C)
Holocellulose	46.7	47.5	46.86	46.33
$\alpha$ -cellulose	20.5	29	30.04	28.97
Klason lignin	42.6	42.01	41.86	41.57
ET-HW* Extractives	25.1	32.09	29.22	28.64

\*Ethanol-toluene extraction followed by hot water.

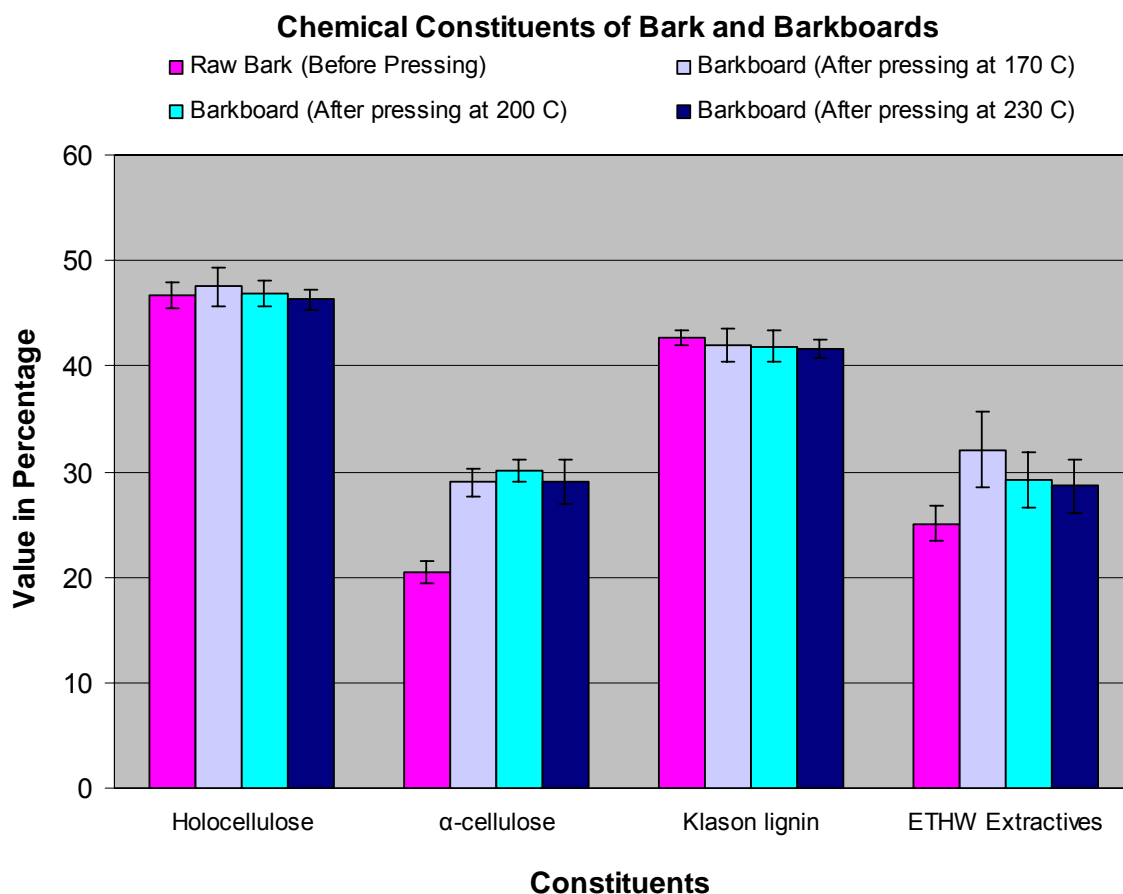


Figure 7.1: Comparison of chemical constituents of raw bark and barkboards at different pressing temperatures.

As shown in Tables and figures above, the most significant difference in chemical constituents among the samples can be observed in the values of  $\alpha$ -cellulose of barkboards of all groups when compared to original bark. It roughly increased from 20% in bark to 30% in pressed boards. The reason of this increase in  $\alpha$ -cellulose is difficult to explain but it can be assumed that short chain hemicellulose molecules are restructured into long chain polymers which are then dissolved in the form of  $\alpha$ -cellulose. This conversion is possible from hemicellulose since it is thermally least stable. This also supports the hypothesis of chemical components polymerization by high temperature during hot pressing.

Another noticeable difference was observed in the value of Ethanol-Toluene Hot Water extractive contents. Their values increased in all boards as

compared to original bark but this increase was highest for boards pressed at 170°C and was lowest for 230°C boards. How this change occurred, is unclear without an in-depth study of chemical structures of all extractives. A possibility is structural changes of other phenolic compounds. The values of holocellulose and lignin showed only slight changes under all conditions.

All results were also compared by statistical t-test on  $p = 0.05$  and there was no significant difference was found in chemical constituents of boards with varying conditions of temperature.

### 7.3.2 Fourier Transform Infrared (FTIR) Spectroscopy:

The FTIR spectra of the original bark, barkboards pressed at different temperatures and barkboard with liquefied bark are shown below:

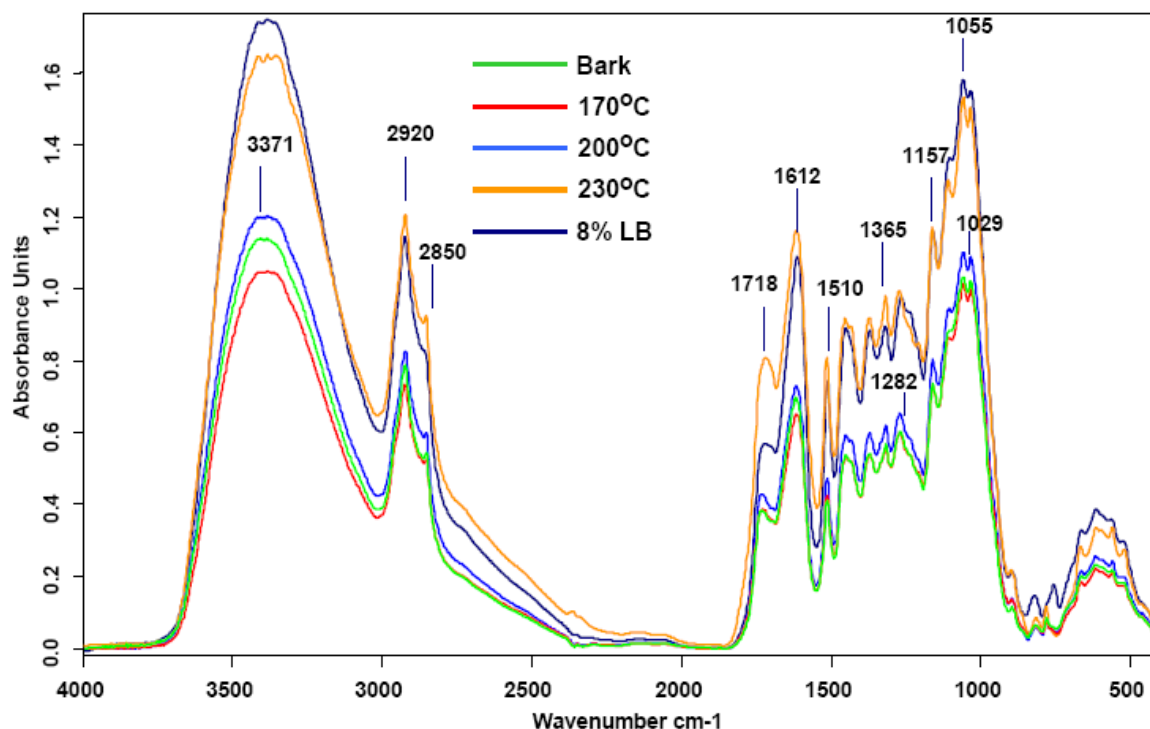


Figure 7.2: Comparison of FTIR spectra of original bark and barkboards at different pressing temperatures.

Figure 7.2 shows the FTIR spectra of these different conditions of barkboards. The extensive peak at around 3371  $\text{cm}^{-1}$  is attributed to the -OH groups from carbohydrates or lignin. The peaks at 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  correspond to the C-H stretch in methyl and methylene groups. The peaks at 1718  $\text{cm}^{-1}$  is attributed to C=O stretching in un-conjugated ketone, carbonyl and ester groups while 1612  $\text{cm}^{-1}$  corresponding to aromatic skeletal vibrations plus C=O stretch. The peak at 1510  $\text{cm}^{-1}$  shows the aromatic skeletal vibrations. Peaks at 1365  $\text{cm}^{-1}$  are attributed to phenolic hydroxyl groups and aliphatic C-H stretch in  $\text{CH}_3$ . The intensity of the peak at 1282  $\text{cm}^{-1}$  attributed to phenolic hydroxyl groups and G-rings of lignin. The peak at 1157  $\text{cm}^{-1}$  is attributed to aromatic C-H in plane deformation. Further the peak at 1029  $\text{cm}^{-1}$  is attributed to C-O deformation in primary alcohols with C=O

stretch (un-conjugate) and aromatic C-H in plane deformation. Table 7.2 provides a brief description of assignments of different peaks in the spectra.

Table 7.2: Various peaks and their corresponding assignments from FTIR spectra of original bark and barkboards at different pressing temperatures.

Peak (cm <sup>-1</sup> )	Assignments
3371	-OH groups from carbohydrates or lignin
2920	C-H stretch in methyl and methylene groups
2850	C-H stretch in methyl and methylene groups
1718	C=O stretching in un-conjugated ketone, carbonyl and ester groups
1612	aromatic skeletal vibrations plus C=O stretch
1510	aromatic skeletal vibrations
1365	phenolic hydroxyl groups, aliphatic C-H stretch in CH <sub>3</sub>
1282	G ring plus C=O Stretch
1157	aromatic C-H in-plane deformation
1055	C-O deformation in secondary alcohols and aliphatic ethers
1029	C-O deformation in primary alcohols and C=O stretch (un-conjugate) and aromatic C-H in-plane deformation

There were no significant changes observed in the spectra of original bark and boards pressed at different temperatures indicating that there are only slight chemical changes especially at higher temperatures. Boards with 8% liquefied bark were also showed minor differences even with the inclusion of the liquefaction products.

There are some limitations with FTIR work. FTIR can only provide an indication of probable chemical changes. It cannot offer the quantitative analysis of chemical changes.

### **7.3.3 Scanning Electron Microscopy (SEM):**

Scanning Electron Microscopic (SEM) images of fractured surfaces of barkboards pressed at different conditions of temperature, particle size and with additives were taken to observe the particles packing and their structural changes with these variations. Fine (image II) and mixed (image I) particles are more closely packed than medium (image III) and coarse (image IV) particles. Similarly, tight packing was observed for boards pressed at higher temperatures (images VI, VII). Image VIII shows boards with liquefied bark but resin layers on the particles are not visible.

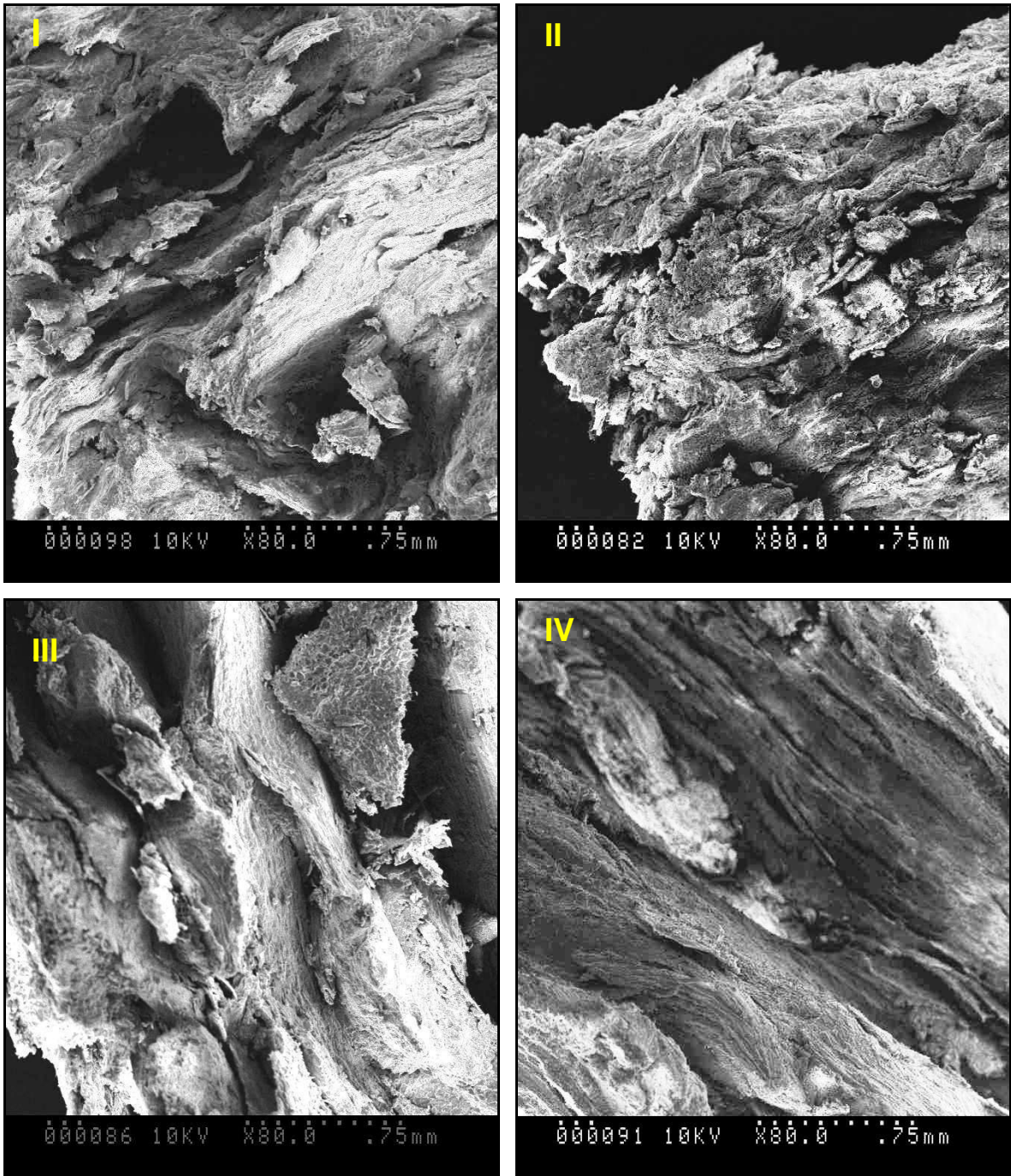


Figure 7.3: Scanning Electron Microscopic (SEM) images of fractured surfaces of barkboards pressed at 230°C (I. Mixed Particles, II. Fine Particles, III. Medium Particles, IV. Coarse Particles).

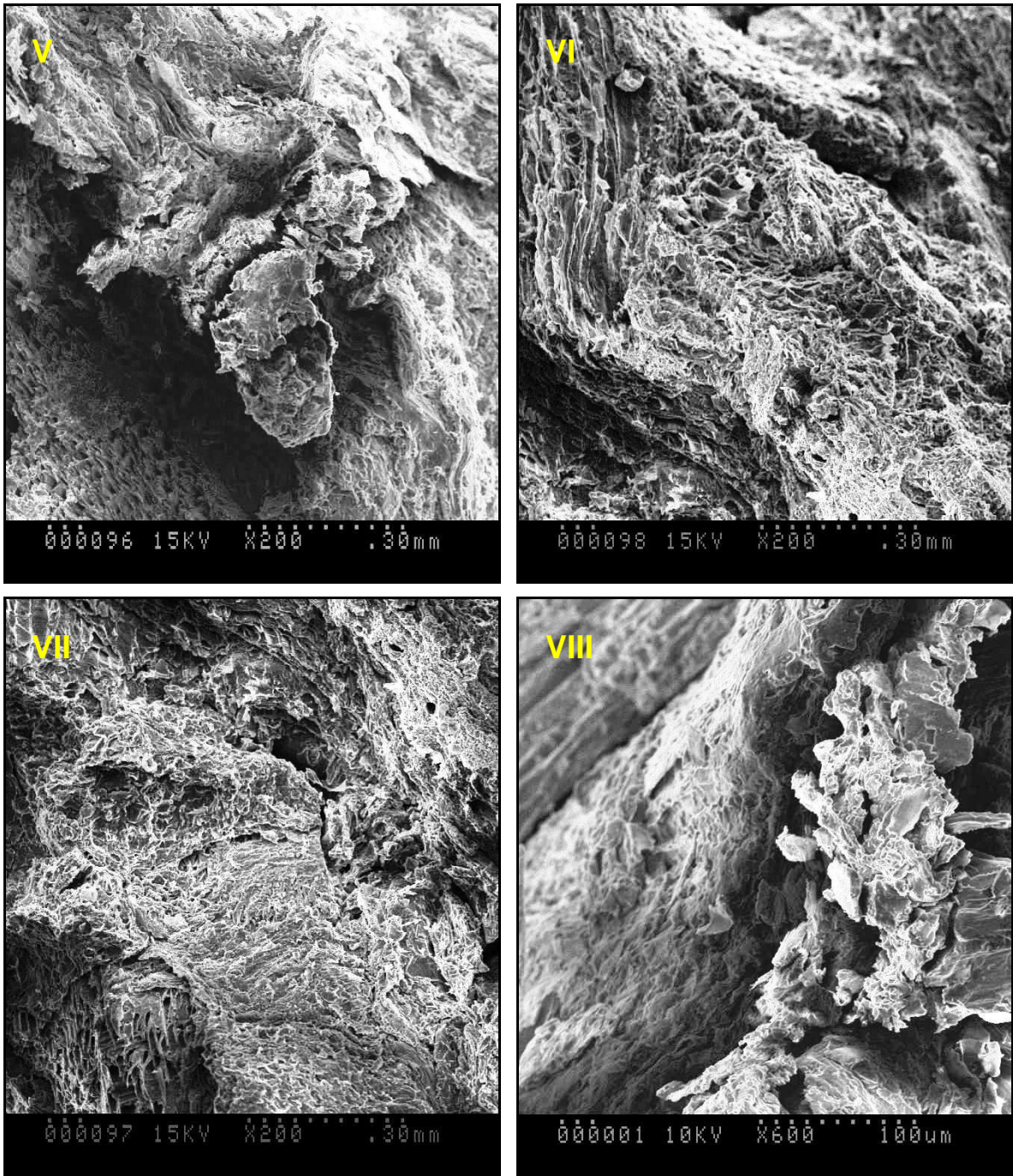


Figure 7.4: Scanning Electron Microscopic (SEM) images of fractured surfaces of barkboards made with mixed particles (V. Pressed at 170°C, VI. Pressed at 200°C, VII. Pressed at 230°C, VIII. Pressed at 230°C with liquefied bark).

## **7.4 Conclusion:**

Chemical analysis results of the original barks and barkboards produced at three different temperatures for holocellulose,  $\alpha$ -cellulose, Klason lignin and ET-HW extractives contents offered complicated results. With the available data it is quite difficult to explain any set trend or hypothesis of self-adhesion of particles. As their overall amount is not significantly changing, it may be possible that instead of their soluble percentage, their chemical structure may have changed due to effects of high temperature and this structural change may have contributed in self-adhesion of bark particles in bark boards.

Scanning Electron Microscopic (SEM) images of fractured surfaces of different types of barkboards pressed at different conditions of temperature, particle size and with additives showed effects on particles packing. Particles are in close interaction and tightly packed at higher pressing temperature and when fine particles were used. These conditions were also found best for mechanical properties results.

FTIR spectra of bark and boards pressed with different conditions indicated that no significant chemical changes occurred in barkboards pressed at different conditions but absorbance peaks are found slightly higher at 230°C pressing temperature.

Even though these characterization techniques provided some basic idea about changes in chemistry of bark when it is converted into barkboard at higher temperature and pressure, a more detailed and in-depth study is required to explain unknown facts of self-adhesion of bark particles in barkboards. Chemical analysis techniques may provide more elaborate results since exact quantification and separation of components is possible by them.

## **CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS**

This thesis is aimed at developing environmental-friendly barkboards from mountain pine beetle infested lodgepole pine bark without any synthetic resin. Boards' development by auto-adhesion techniques or by manipulation of thermal conditions or particle size is one of the critical operations during the manufacturing of barkboards. In hot pressing, moisture, mass transfer, heat transfer, chemical changes and bark particles densification interact, resulting in continuing changes in the board's physical, chemical and mechanical properties.

Few approaches can be found in the literature to consolidate the bark particles into composites. Although some researchers did remarkable work in this area, their focus was mostly on the commercial feasibility of the product & production process and barkboards still lack of scientific understanding. The experiences and conclusions of previous researchers were mixed. It is always challenging to use bark as raw material for composite products due to its complex and highly variable nature.

This research intended to better understand various facts related to self-adhesion of bark particles, the role of temperature and particle size and probable changes in chemical composition during hot pressing. The major scientific contribution of this research is the exploration of practical feasibility and application of beetle infested lodgepole pine bark for making of barkboards. The studies provide the relevant scientific data which are specific for mountain pine beetle infested lodgepole pine bark and can provide additional scientific knowledge for barkboards, in general. Significant investigations of this thesis include chemical and thermal analysis of mountain pine beetle infested lodgepole bark on different conditions, effects of particle size on barkboard's properties, effects of addition of liquefied bark on barkboard's properties, characterization of barkboards including analysis of chemical constituents after pressing, FTIR, SEM studies etc. These experiments were not performed before and investigations are expected to add major scientific contributions to the existing body of knowledge of barkboards.

## 8.1 Conclusions:

Based on this thesis study, the following are the final conclusions:

- I. Mountain pine beetle infested lodgepole pine bark has potential for use in composite products, more specifically in barkboards without any synthetic resin due to their chemical components and thermal properties. Even though their properties are lower than building code requirements; there is scope to improve them by better understanding the raw material, process parameters and use of environmental-friendly additives.
- II. Knowledge of chemical and thermal properties of mountain pine beetle infested lodgepole pine bark is vital in its ultimate use or suitability for making of self-bonded barkboards. Extractive content and chemical composition of both green and beetle infested barks have no significant difference in organic solvent extractives; however, the beetle infested lodgepole pine bark has a higher 1% NaOH solubility due to fungal decay. Amount of  $\alpha$ -cellulose and Klason lignin was also lower in beetle infested lodgepole pine bark, but overall there is no constraint in use of this bark for production of barkboards.
- III. Thermal analysis of barks performed by TGA on control & different conditions of extractives and catalyst also provide results which can be used in characterization of bark as raw material in making of self-bonded boards. Bark studies on these conditions were not investigated before. A sharp degradation or weight loss of bark material occurred in the temperature range of 240-400°C, which is different in various conditions of extractive and catalyst. Higher amount of extractives causes an increase in degradation onset point while increasing amount of catalyst reduced this point significantly. Extractives and catalyst concentration also affect melting point or softening temperature of barks. If more extractives are removed from barks (as in case of different solvents), the melting point goes up. If the catalyst amount was increased, bark's softening point decreased significantly.

- IV. There are several complications in barkboard production, including high temperature pressing requirements, blowing of boards during hot pressing because of moisture release, inadequate mechanical properties, complexity of bark etc. These were faced in this project and attempts were made to investigate the feasible solutions; however most of the answers are quite similar to experience of previous researchers.
- V. It was observed that temperature has a great influence on properties of beetle infested lodgepole pine barkboards. All mechanical properties increased when temperature goes up.
- VI. Boards with fine particles, as compared to other particles, also were superior for mechanical properties and obtained better physical appearance and smooth surfaces with highest density. It was not reported before except particle geometry studies by *Blanchet, Cloutier and Riedl (2008)*.
- VII. Barkboard's properties significantly improved with the liquefied bark addition and the effect was comparable to that with the addition of PF resin. It is a quite new idea to improve most desired board's properties with an environmental-friendly additive. These basic results can open a scope for further research with bio-based resins in barkboards. Previous research only explored the efforts with PF, UF or MF resins.
- VIII. Barkboard's characterization using chemical constituent's analysis after pressing, FTIR and SEM studies etc. divulge various changes due to high temperature response of bark material. These were some unknown facts in available knowledge of barkboard research. However, various phenomena including details of self-adhesion were hard to explain exactly without further studies, which can be a part of future research objectives.

The above mentioned conclusions and key findings of this research work, reveal the significant scientific contribution in advancement of existing

barkboard techniques and the better understanding of the various facts related to conversion of beetle infested bark residue in a value-added panel product.

## **8.2 Recommendations:**

Based on the research conclusions, the following recommendations can be suggested:

- I. Proper knowledge of raw material and process parameters helps in successful production of barkboards.
- II. There is a need to develop specially designed hot press and caul screens for better ventilation during pressing to avoid blowing or blister formation.
- III. It is required to explore modification in liquefied bark by reaction with appropriate reagent to improve curing behavior or to use environmental-friendly additives to improve the board's qualities.
- IV. Optimization and modeling of barkboard process parameters is also highly recommended.
- V. Further adaptation of lamination technologies like MF laminations or veneer overlays can give some positive results especially for its end use in various applications.

### **8.3 Limitations:**

Because of the inherent nature associated with the bark raw material, there are following limitations with this product:

- I. It is very difficult to control the end product quality because of complex and highly variable nature of bark, even for the same species.
- II. Performance of self-adhesive barkboards in exterior and wet conditions is poor so the product should not be intended for such uses.
- III. Its commercial feasibility is still unproven due to its impractical production process and requirement of high temperature and long pressing time.
- IV. Most of the physical and mechanical properties are insufficient so it should not be recommended for use for structural purposes.

### **8.4 Significance for Industries:**

The knowledge derived through this research and available information on the basis of literature review in this thesis is beneficial for industries in various ways. It contributes to available body of knowledge on utilization of bark for production of quality composite boards. Productions of improved quality barkboards can help to overcome the problem of bark disposal for the industry and can contribute to reduce environmental issues. Its commercialization for forest products industries is possible by further research and it can also help mitigate the problems of wood shortage which can be seen in many part of the world currently. Furthermore, the possibility of utilization of mountain pine beetle infested bark for barkboard manufacturing, especially in the disease outbreak parts of North America, is also beneficial for industries.

## **8.5 Future Work:**

It is clear from this study that barkboard research is in the very initial stage. To better utilize this material, a large scope is available for further research in the following areas:

- I. More research work is needed to explore the possibility of use of microwave preheating techniques before hot pressing for better curing and lowering the press temperature which is the main problem associated with commercial production of barkboards.
- II. Further board improvements by lamination technologies, use of resin in core layers, coarse particles in core layers (3-layered board), with additional extractives etc. need to be studied.
- III. Bark chemical modifications by paraformaldehyde or other similar reagents.
- IV. Applications of catalyst.
- V. Development of bark softening and plasticization techniques.
- VI. Process optimization and modeling for better pressing techniques.
- VII. Possibility of use of bark in plastic composites.
- VIII. Evaluation of natural durability and long-term performance of barkboards.
- IX. Life Cycle Analysis (LCA) of barkboards.

## **REFERENCES**

**Anderson A.B., K.T. Wu, A. Wong et. (1974).** Utilization of ponderosa pine bark and its extracts in particleboard. *Forest Products Journal* 24(8): 48-53.

**Anonymous (1999).** Forintek, CanFibre seek to make bark-based panels. *Wood Technology* 126 (9): 16.

**Anonymous (2000).** CanFibre plans to make OSB from bark residue. *Wood Technology* 127 (3): 8.

**ANSI (1999).** Particleboard, ANSI A208.1-1999. American National Standard, National Particleboard Association. Gaithersburg, MD, 9 p.

**ASTM (1999).** Standard test methods for evaluating properties of wood-base fiber and particle panel materials, ASTM D-1037-06a. ASTM International West Conshohocken, PA, USA.

**Bhagwat S.G. (1973).** Utilization of bark. State-of-the-art report, based on proceedings (P-73/74-11) of FPRS Annual Meeting.

**Blanchet P., A. Cloutier and B. Riedl (2000).** Particleboard made from hammer milled black spruce bark residues. *Wood Science and Technology* 34: 11-19.

**Blanchet P., A. Cloutier and B. Riedl (2008).** Bark particleboard: pressing time, particle geometry and melamine overlay. *The Forestry Chronicle* 84 (2): 244-250.

**Blankenhorn P.R., W.K. Murphey, L.E. Rishel and D.E. Kline (1977).** Some mechanical properties of impregnated barkboard. *Forest Products Journal* 27(6): 31-38.

**Bowyer J., R. Shmulsky and J. Haygreen (2003).** “Forest Products and Wood Science: An Introduction”. Chapter 7, Iowa State Press, Blackwell Publishing Company, Iowa.

**Chang Y. (1954).** “Bark structure of North-American conifers”. Technical Bulletin no. 1095, Forest Product Laboratory, USDA, Washington.

**Chow S. (1972).** Thermal reactions and industrial uses of bark. Wood and Fiber 4(3): 130-138.

**Chow S. (1975).** Bark boards without synthetic resins, Forest Products Journal 25(11): 32-37.

**Chow S. and K.J. Pickles (1971).** Thermal softening and degradation of wood and bark. Wood Fiber 3(3): 166-178.

**Currier R. A. and M. L. Laver (1972).** “Utilization of bark waste”. National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22151.

**Demirbas A. (2005).** Thermo-chemical conversion of biomass to liquid products in the aqueous medium. Energy Sources 27:1235-1243.

**Deppe H.J. and A. Hoffmann (1972).** Particle board experiments: Utilize softwood bark waste. World Wood 3(7): 8-10.

**Dost W.A. (1971).** Redwood bark fiber in particleboard. Forest Products Journal 21(10): 38-43.

**Eberhardt T.L. (2007).** A reassessment of the compressive strength properties of southern yellow pine bark. Forest Products Journal 57(4): 95-97.

**Ebewele R.O., O.A. Peters and J.Y. Olayemi (1984).** Development of wood products adhesives from mangrove bark, *Journal of Applied Polymer Science*, Vol. 29, 1415-1426.

**Fengel D. and G. Wegener (1984).** "Wood: chemistry, ultra-structure, reactions", Walter de Gruyter, Berlin.

**Geng X., S.Y. Zhang and J. Deng (2006).** Alkaline treatment of black spruce bark for the manufacture of binderless fiberboard. *Journal of Wood Chemistry and Technology* 26: 313-324.

**Harkin J.M. and J.W. Rowe (1971).** "Bark and its possible uses". Forest Research Note-091, 4-056-9-71, Forest Products Laboratory, Forest Service, U.S. Department of Agriculture.

**Hartley I.D. and S. Pasca (2006).** "Evaluation and review of potential impacts of mountain pine beetle infestation to composite board production and related manufacturing activities in British Columbia". Mountain Pine Beetle Initiative Working Paper 2006-12. Canadian Forest Service, Natural Resource Canada.

**Hengst G.E. and J.O. Dawson.** Bark thermal properties of selected central hardwood species. 9<sup>th</sup> Central Hardwood Forest Conference, Department of Forestry, University of Illinois.

**Koch P. (1972).** "Utilization of the southern pines". USDA Forest Service, Washington.

**Koch P. (1985).** "Utilization of hardwood growing on southern pine sites" Vol. I. USDA Forest Service, Washington.

**Lam F. and F.C. Chang (2007).** "Development of MPB wood plastic and wood cement products". Report of Project No. MDP-07-020C, Forestry Innovation Investment Ltd. and Wood Science Department, University of British Columbia.

**Lehmann W.F. and R.L. Geimer (1974).** Properties of structural particleboards from Douglas-fir forest residues. *Forest Products Journal* 24(10): 17-25.

**Maloney T.M. (1973).** Barkboards from four west coast softwood species. *Forest Products Journal* 23(8): 30-38.

**Mun S.P., I.A. Gilmour and P.J. Jordan (2006).** Effect of organic sulfonic acid as catalyst during phenol liquefaction of *Pinus radiata* bark. *Journal Ind. Eng. Chem.* 12(5): 720-726.

**Murphy J.A., P.M. Smith and J. Wiedenbeck (2007).** Wood residue utilization in Pennsylvania: 1988 vs. 2003. *Forest Products Journal* 57(4): 101.

**Muszynski Z. and J.D. McNatt (1984).** Investigation on the use of spruce bark in the manufacture of particleboard in Poland. *Forest Products Journal* 34(1): 28-35.

**Patel R.N. (1974).** Bark anatomy of Radiata pine, Corsican pine and Douglas fir grown in New Zealand. *New Zealand Journal of Botany* 13: 149-167.

**Place T.A. and T.M. Maloney (1975).** Thermal properties of dry wood-bark multilayer boards. *Forest Products Journal* 25(1): 33-39.

**Place T.A. and T.M. Maloney (1977).** Internal bond and moisture response properties of three-layer wood-bark boards. *Forest Products Journal* 27(3): 50-54.

**Prance A.E. and G.T. Prance (1993).** "Bark: The formation, characteristics and uses of bark around the world". Timber Press, p. 176 pages.

**Rowell R.M. (2007).** "Handbook of wood chemistry and wood composites". CRC Press; 1 edition (April 17, 2007).

**Safranyik L. and B. Wilson (2006).** “The mountain pine beetle: A synthesis of biology, management, and impacts on lodgepole pine”. Canadian Forest Service, Natural Resource Canada.

**Sewda K. and S.N. Maiti (2007).** Mechanical properties of HDPE/bark flour composites. Journal of Applied Polymer Science Vol. 105: 2598-2604.

**Singh S.P., J.P. Singh and S.S. Rawat (1996).** Utilization of bark from *Populus deltoides* for particleboard. Forest Products Division, Forest Research Institute, Dehradun. Journal of the Indian Academy of Wood Science. 26-27: 1-2, 15-19.

**Sjostrom E. (1993).** Wood chemistry: fundamentals and applications, Academic Press Limited, UK.

**Troughton G.E. and C. Gaston (1997).** “The utilization of bark in panel production: technical, economical and market feasibility”. 1v. Alberta Economic Development and Tourism, Forest Industry Branch. 22p.

United States Patents on barkboards; Patent numbers 5725818 (March, 1998), 6120914 (Sep., 2000) and 6544649 (Apr. 2003).

Various information from www and news resources.

**Vaucher H. (2003).** “Tree bark”. Translated and edited by James E. Eckenwalder, Timber Press Inc., Oregon, USA.

**Vliet V. and C. Antone (1971).** Converting bark into opportunities: proceedings of a conference held on March 8-9 1971. Oregon state university, school of forestry, Forest Products Dept. p. 86-87.

**Weissmann G. (1983).** Studies on pine bark extracts. Int. J. Adhesion and Adhesives, Jan. 1983, p. 31-33.

**Wellons J.D. and R.L. Krahmer (1973).** Self bonding in bark composites. Wood Science 6(2): 112-122.

**Wisherd K.D. and J.B. Wilson (1979).** Bark as a supplement to wood furnish for particleboard. Forest Products Journal 29(2): 35-39.

**Xing C., J. Deng, S.Y. Zhang, B. Riedl and A. Cloutier (2006).** Impact of bark content on the properties of medium density fiberboard (MDF) in four species grown in eastern Canada. Forest Products Journal 56(3): 64.

**Yamauchi H., O.R. Pulido, L.F. Ma, I. Miura and H. Sasaki (1999).** Processing and utilization of sugi (*Cryptomeria japonica* D. DON) barks - preparation and grading of fibers, Holz als Roh- und Werkstoff 57 (1999).

**Yemele M.C.N., A. Cloutier, P.N. Diouf, A. Koubaa, P. Blanchet and T. Stevanovic (2008).** Physical and mechanical properties of particleboard made from extracted black Spruce and trembling aspen bark. Forest Products Journal 58(10): 38.

**Yemele M.C.N., A. Koubaa, P.N. Diouf, P. Blanchet, A. Cloutier, and T. Stevanovic (2008).** Effects of hot-water treatment of black spruce and trembling aspen bark raw material on physical and mechanical properties of bark particleboard. Wood and Fiber Science 40(3): 339-351.

**Yazaki Y. and P.J. Collins (1994).** Wood adhesives based on tannin extracts from barks of some pine and spruce species. Holz als Roh- und Werkstoff 52 (1994): 307-310.

**Yazaki Y. and P.J. Collins (1994).** Wood adhesives from *Pinus radiata* bark. Holz als Roh- und Werkstoff, 52 (1994): 185-190.