

**SYNTHESIS AND CHARACTERIZATION OF FIRE RETARDANT PAPER VIA  
PHOSPHORYLATION**

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**SYNTHESIS AND CHARACTERIZATION OF FIRE RETARDANT PAPER VIA  
PHOSPHORYLATION**

**BY**

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## **LIST OF ABBREVIATIONS**

RSM	Response surface method
CCD	Central composite design
OI	Oxygen index
SEM	Scanning electron microscopy
IR	Infrared
DSC	Differential scanning calorimetry
SFI	Sabah Forest Industry
DMF	Dimethylformamide
FTIR	Fourier transform infrared
RH	Relative humidity

## LIST OF SYMBOLS

$\eta$	response
$\mu$	Micron
$\varepsilon$	Extinction coefficient
$\alpha$	alpha
$\beta$	beta
kPa	Kilo pascal
$\Delta$	enthalpy
$T_c$	Crystalline temperature
$T_m$	Melting point

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## SINTESIS DAN PENCIRIAN KERTAS KALIS API MELALUI FOSFORILASI

### ABSTRAK

Kajian ini dijalankan untuk menghasilkan kertas yang mempunyai sifat ketahanan api daripada bahan mentah tempatan iaitu pulpa kayu keras (*Acacia mangium*) dengan menggunakan kaedah fosforilasi. Terdapat tiga peringkat utama yang telah dijalankan. Peringkat pertama melibatkan perawatan pulpa di dalam campuran cecair yang mengandungi bahan DMF, urea dan asid fosforus di dalam aliran gas nitrogen pada jangka waktu yang tertentu dan pada suhu antara 140 °C sehingga 145°C. Kaedah respon permukaan, (Response Surface Method, RSM) telah digunakan untuk menetapkan nilai-nilai faktor yang ingin dikaji. Bagi rawatan peringkat kedua, faktor yang dikaji ialah faktor waktu rendaman, suhu rendaman dan kepekatan  $\text{Ca(OH)}_2$ . Manakala bagi rawatan peringkat ketiga, faktor yang dilihat pula ialah faktor waktu dan suhu rendaman, serta kepekatan bahan  $\text{Ca(OH)}_2$  dan  $\text{H}_3\text{PO}_4$  telah digunakan. Respon utama yang dikaji untuk ketiga-tiga peringkat rawatan ialah peratusan kandungan fosforus yang terikat bersama bahan selulosa dan tahap kalis api bahan yang dikaji melalui ujian indeks oksigen. Daripada kajian yang telah dijalankan, didapati bahawa peringkat rawatan pertama telah memberikan nilai peratusan kandungan fosforus tertinggi iaitu 1.71% dan peratusan indeks oksigen tertinggi iaitu pada kadar 30.95%, berbanding dengan hanya 17.90% bagi bahan selulosa yang tidak dirawat. Namun begitu, peratusan kandungan fosforus yang terikat pada pulpa SFI telah berkurangan bagi rawatan peringkat kedua dan ketiga iaitu masing-masing hanya 1.62% dan 1.13%. Nilai peratusan indeks oksigen juga didapati

menurun iaitu hanya pada kadar 26.75% bagi rawatan peringkat kedua dan sekitar 20-22% sahaja bagi rawatan peringkat ketiga. Ujian-ujian lain seperti DSC, FTIR, SEM dan EDX turut dijalankan untuk mengesahkan kehadiran bahan fosforus dan kalsium di atas pulpa bagi mengesahkan keberkesanan rawatan yang dijalankan.

# **SYNTHESIS AND CHARACTERIZATION OF FIRE RETARDANT PAPER VIA PHOSPHORYLATION**

## **ABSTRACT**

This study was undertaken to produce a fire retardant paper from the nation's local raw material, *Acacia mangium* using the phosphorylation process. There are three main stages conducted in this study. The first stage of the treatment requires the pulp to be treated in an aqueous solution containing DMF, urea and phosphorus acid, swept by nitrogen gas at a temperature range of 140°C to 145°C. Response surface method (RSM) was used to determine the factor range required for this study. The factors used in the second stage treatment are the period of immersion, the immersion temperature and the concentration of Ca(OH)<sub>2</sub>. While for the third stage treatment, the factors required are the immersion period, temperature of treatment and the concentration of Ca(OH)<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>. The main responses determined from all the three treatment stages are the percentage of the phosphorus content bound with the cellulosic material and the fire retardant ability of the material by using limited oxygen index. From the study, it has been shown that the first stage treatment has the highest percentage of the phosphorus content which is 1.71%, and the percentage of the oxygen index also shows the highest value which is 30.95% compared to the untreated SFI pulp which is only 17.90%. However, the percentage of the phosphorus content bound to the SFI hardwood decreased in the second and third stage treatment with only 1.62% and 1.13% of the phosphorus content. The percentage of the oxygen index was also found to decrease with values for

both stages were 26.75% and 20-22% for the second and third stage treatment respectively. Other analyses using DSC, FTIR, SEM and EDX have been conducted to verify the presence of phosphorus and calcium substance on the SFI hardwood pulp to confirm the effectiveness of the treatment conducted.

# CHAPTER 1

## INTRODUCTION

### 1.1 General

The uses and applications of paper and paper products are undeniably important. Paper had been made as early as 3000 B.C by the Egyptian using pressed pith tissue of papyrus for writing. In China, strips of bamboo or wood were used for drawing and writing until the discovery of paper, which is attributed to Tsai Lun in A.D 105. The original paper was made in China from rags, bark fiber and bamboo. The papermaking technology was spread to the Islamic world in the 8<sup>th</sup> century where the hardness and laborious process of papermaking was refined and paper starts to be manufactured in bulk using machine. The development transforms the papermaking process from an art into a major industry (Mahdavi, 2003).

Traditionally, paper has been defined as a material formed on a fine screen as a felted sheet from a water suspension of fibers. This traditional paper making process is still been used in the paper industries except that, most of the paper product nowadays contain non-fibrous additives, and new methods also been applied for the manufacture of a few paper specialty products (Smook, 1992).

All materials used to make paper have to be in the form of pulp. Pulp is the raw material used to make paper in a form of fibers. Pulp fibers are usually of plant origins, but other types of fiber such as animal, mineral or synthetic fibers can still be used for some special applications. One of the most important and basic material use to make pulp

is hardwood. Hardwood trees are also known as angiosperms or broad leafed trees, which either evergreen in tropics region or mostly deciduous in temperate and boreal latitudes.

Until now, the significance of paper and paper products in modern life is obvious to everyone and plays meaningful role in every area of human activity. Paper provides the means of recording, storage and dissemination of information which is virtually all writing and printing process is done on paper. Also, paper has been widely used as wrapping and packaging material and very important for structural applications.

The uses and applications for paper and paper products are virtually limitless. New specialty products are continually being developed which include heat resistant papers, water or humid resistant paper and other enhanced quality products of paper which is restricted to construction utilization such as wall paper. To date, there is no thorough study record on a specialty paper made for documentation purposes when it is urgently and very much needed.

With the increasing of public awareness, it is acknowledged that nothing replace papers better in documentation such as in recording news, historical events, mapping and the recent interest is recording will. These essential documents however are exposed to vast demolishing factors. Paper is a product which made from the cellulosic materials. There are many special properties which are ingrained in paper nowadays to enhance the quality of certain paper used for certain industry. Many of these properties are classified as resistance properties which are related to the properties of the cellulose fibers used to manufacture the paper such as oil and grease resistance, water and writing ink resistance and others. Among these many factors that affect paper properties, fire seems the most disastrous; if a document catches fire it is almost impossible to retain it in anyway. Fire

retardant is one of the most important properties of paper and research is still being carried out to develop better fire resistant paper.

The furthest step that had been taken to protect a document from fire is to laminate, but the process is not only tedious, un-user-friendly but also costly.

Thus to lessen the risks on these valuable documents there is an urgent call upon an in depth study to research a production of new generation of papers that is ingrained with special characteristics such as fire retardant.

The word fire retardant had been used to explain about basic flammability of some polymers which had been reduced by some modification as measured by one of the accepted method. A fire retardant is a material used as a coating on or incorporated in a combustible product to raise the ignition point or to reduce the rate of burning of the product. The product to which fire retardant are applied include apparel, carpets and rugs, construction materials, electrical materials, paper and wood products, transportation vehicle interior components, apparel fabrics and home furnishings. The materials involved in the products to be protected include fibers, fabrics, sheets, panels, structural forms, foams, insulation (thermal and electrical), padding and much more materials which made of natural or synthetic organic polymers (Mark *et al*, 1980 and Cavendish, 1989).

There are many types of fire retardants used in plastics and textiles industries. However, the main fire retardant currently used in these fields are alumina trihydrate, halogenated compounds which usually used together with antimony oxide, borax and boric acid, and the phosphorus compounds. In this study, phosphorus was picked as the main material to be used for the cellulose fire retardant treatment.

Many thousands of phosphorus compounds have been described as having flame retardant utility since the report made by Gay Lussac in 1821, which found the use of ammonium phosphate as a flame retardant. Phosphorus had been picked as the main material used for a fire retardant treatments on SFI hardwood pulp as it had been widely known that any phosphorus-containing material are by far the easiest and most important compound which can be used to impart durable flame retardance to cellulose and any cellulosic materials (Mark *et al*, 1980).

In this study, the phosphoric acid-based system had been chosen to impart phosphorus in the cellulose, and the treatment can be attained by using the phosphorylation process. Phosphorylation is a kind of treatment which can be accomplished by heating and impregnate any cellulosic materials such as cotton and pulp, by using phosphoric acid in the presence of basic compound such as urea, at a certain degree of temperature. By using the phosphorylation process, we can still manage to maintain the origin of paper, and the treatment done on the cellulose does not make the paper made afterwards to be in the form of plastics, which makes the paper not user-friendly for any documentation purposes, or too weak which lead the paper into further complicated treatments. This is because, the phosphorylation treatment itself permits the phosphorus to be part of the cellulose and make the whole paper making process become easier.

However in Malaysia, there are still lack of effort to improve our own paper quality especially involving a kind with fire retardant specialty. This study will serve as a first step towards fire retardant paper making thus enhance the use of science knowledge. The success of this research will also means as a production of a fire retardant paper that

will serve as a good documentations material thus protect the documents from any perils especially fire. Therefore, this study stressed on a fire retardant treatment for paper product made by using hardwood pulp from Sabah Forest Industry (SFI).

### **Objectives**

The objectives of this study are:

- To produce fire retardant paper from Sabah Forest Industry (SFI) hardwood fibers using urea-dimethylformamide method.
- To study the effectiveness of various stage of treatment in phosphorylation process to ingrain phosphorus as a fire retardant material.
- To characterize the optimal fire retardant paper by using various stage of treatment in the urea-dimethylformamide phosphorylation method to ingrain phosphorus as a fire retardant material.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Fiber chemistry**

More than 95% of the base material in the manufacture of paper products is fibrous and more than 90% originates from wood (Kroschwitz and Howe-Grant, 1995). Wood is a complex polymeric structure and contains many different chemical substances, which can be divided into four major groups; cellulose, hemicellulose, lignin and extractive. Cell walls of wood are composed of cellulose and hemicellulose bound together by lignin. The combination of cellulose and hemicellulose is called holocellulose and generally account for 65-70% of a plant's dry weight (Leh, 2002). The cell wall in every wood usually contains a small amount of various extraneous substances which are organic such as fatty acid, resin, wax, triglycerides and etc., and all of these substances are called extractives and can be removed from wood with various neutral organic solvents and usually can be done using a pulping process.

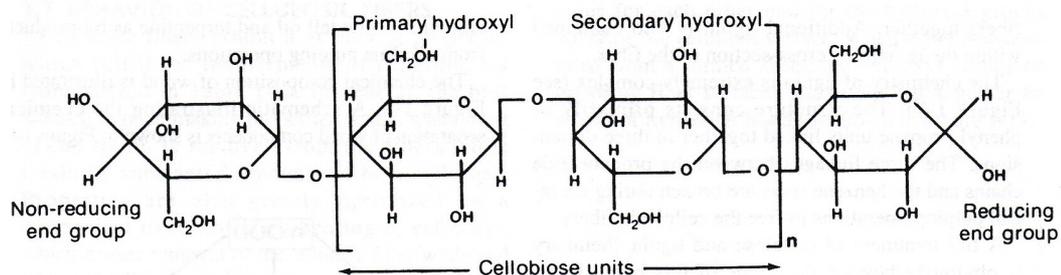
The chemical compositions of wood are varies from plant to plant, and also within different parts of the same plant. Furthermore, the same wood species may have different chemical composition influenced by all sorts of factors including geographical location, age, soil and climatic condition. (Leh, 2002)

##### **2.1.1 Cellulose**

Cellulose is the main part of the cell walls of wood (Mimms *et al*, 1990). In plant fibers it is the substance cellulose that determines the character of the fiber and allows its use in papermaking. Cellulose is a carbohydrate, meaning that it is composed of the three

main elements; carbon, hydrogen and oxygen, with the latter two elements in the same proportion as in water (Smook, 1992). In its natural form, cellulose is the easiest found organic chemical in the world. It is the major constituent of plant matter and billions of tons of it are made each year through photosynthesis mechanism. It is the skeletal or framework substance of all wood cell walls and mainly located in the secondary cell wall, typically 40-50% by weight of oven-dry wood (Leh, 2002).

Cellulose is a complex polymeric carbohydrate having the same percentage composition as starch, which yields glucose on complete hydrolysis by acid. It consists of a long chain of identical molecules bound together which is also can be known as homopolysaccharide of  $\beta$ -D-glucose in pyranose form linked together (1 $\rightarrow$ 4)-glycosidic bonds (Mimms *et al*, 1990 and Sjöström, 1993). The repeating units of two consecutive glucose anhydride (anhydroglucose) units form a cellobiose unit as shown in Figure 2.1. The anhydroglucose units are almost exclusively in their lower-energy chair form with all pendent groups equatorially disposed. Neighbouring anhydroglucose units are rotated almost 180° relative to each other to achieve chain extension.



**Figure 2.1: The structure of cellulose**

The chemical formula for cellulose is  $(C_6H_{10}O_5)_n$  where  $n$  is the number of repeating sugar units or the degree of polymerization (DP) (Smook, 1992). The DP of cellulose varies from 700-10 000 or more depending on the different origins and the treatment received such as hydrolysis, oxidation, photochemical degradation, or even mechanical action which may lead to chain scission and lowering of the DP (Leh, 2002). Most fibers used for paper making have a weight-averaged DP in 600-1500 range. Table 2.1 lists the average DP of a number of native and treated cellulose. The properties of cellulosic material are principally related to the DP of the cellulose molecules. Decreasing the molecular weight below a certain level will cause the strength to be deteriorated.

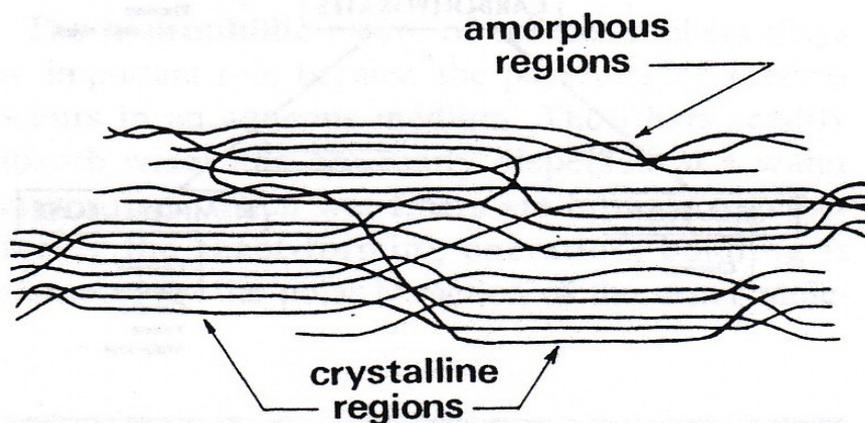
**Table 2.1: Degree of polymerization for different sources of cellulose (Smook, 1992; Hans, 1986).**

Type of cellulose	DP
Native cellulose	3500
Raw cotton	7000
Purified cotton linters	1000-3000
Commercial wood pulp	600-1500
$\alpha$ -cellulose (isolated from wood fibers)	800-1100
Regenerated cellulose (e.g., rayon)	200-600

The polymeric linkages during cellulose synthesis are such that the chains form in an extended manner. As a consequence, cellulose molecules fit snugly together over long

segments, giving rise to powerful associative forces that are responsible for the great strength of cellulosic materials (Smook, 1992).

Cellulose in plant fibers is found in several ordered levels of orientation, as shown in the Figure 2.2 (Smook, 1992). Cellulose has strong tendency to form intra and intermolecules hydrogen bonds. Bundles of cellulose molecules are thus combined together in the form of microfibril, which contain two distinctly different regions; the high ordered crystalline region and less ordered amorphous region (Leh, 2002). The regions of crystallinity consist in the long segments of the cellulose molecules are more difficult to be penetrated by any solvents or reagents. By contrast, the relatively more amorphous regions are readily penetrated and therefore are more susceptible to be hydrolyzed (Smook, 1992). Subsequently, microfibrils build up fibril and finally cellulose fiber. Different origin and treatment history of cellulose influenced the relative amount of ordered and disordered region contains in any cellulose fiber (Leh, 2002).



**Figure 2.2: A schematic structure that shows an amorphous and crystalline region between cellulose microfibrils**

Cellulose is a very highly insoluble material in water and in non-concentrated acid even though it is relatively hygroscopic material. This is because, the strength of the hydrogen bonds between each cellulose molecule is the same or stronger than the bonds existed between cellulose and water molecules, hence it is impossible for water molecules to penetrate or solvate the individual cellulose molecules particularly in the crystalline region. However, cellulose may be can still dissolved in concentrated strong acid such as 72% sulfuric acid, 40% hydrochloric acid and 85% phosphoric acid under severe degradation (Leh, 2002). Most of the cellulosic material is used in its original fibre form, with only partial removal of non-cellulosic constituents for paper, board and non-woven industries.

#### **2.1.1.1 Reactivity of cellulose**

The commercially important cellulose derivatives are prepared by reactions typical of compounds containing hydroxyl groups. The uniqueness of the reactions of cellulose is not influenced by any characteristic difference between the natural internal reactivities of the hydroxyl groups of cellulose and those of other types of compounds. The problems encountered are mainly because of two factors. The first factor is because of the access of the reagent to the hydroxyl groups are hindered by the crystallinity or insolubility of the cellulose, and interrupt any possible reactions between cellulose.

The second factor of the problem is because the excessive amounts of degradative side reactions must be avoided because cleavage of the cellulose chain would result, giving products with unsatisfactory properties. Fortunately, the degradation reactions can be controlled, usually by temperature, and held within acceptable bounds. So, it is very

important to have any particular cellulose in a good form or state that consist a maximum number of hydroxyl groups which are available for any reactions. This can be brought about by a decrease in hydrogen bonding between the chains. Non-uniform products can result because of differences in accessibility of different portions of the cellulose.

### **2.1.2 Hemicellulose**

Hemicellulose is also polymer mainly built of sugar units (Mimms *et al*, 1990). Hemicellulose is an amorphous branched chain heterogeneous polysaccharide consisting of five-carbon and six-carbon ring sugar, with low DP in the range of 50-300. Besides, hemicellulose is generally water insoluble, alkali soluble substances that are more readily hydrolyzed by acid to their monomeric components than is cellulose (Leh, 2002). Hemicellulose is not linear and cannot form crystalline structures and microfibrils as cellulose does (Mimms *et al*, 1990). In contrast to cellulose, which is a polymer of only glucose, the hemicellulose is polymer of five different sugars which are glucose, mannose, galactose for the five-carbon type of sugars, and xylose and arabinose for the six-carbon type of sugars (Smook, 1992). Figure 2.3 below shows structure of two different sugars of hemicellulose.



**Figure 2.3: The example structure of hemicellulose sugars, (a) mannose and (b) xylose**

There are different kinds of hemicellulose. The type of hemicellulose is usually referred to by the sugar they contain, for example, galactoglucomannan, arabinoglucuronoxylan, arabinogalactan, glucuronoxylan, glucomannan and etc (Leh, 2002). Different wood species contain hemicelluloses of slightly different composition. Hardwoods have more Xylan, while softwoods have more glucomannan. The type of hemicellulose also varies depending on the within the wood structure (Mimms *et al*, 1990). Furthermore some hemicelluloses are present in very large amounts when the tree is under stress, for example a wood which had been compressed has a higher D-galactose content as well as higher lignin content. However the type of hemicellulose in softwood is much more varied than in hardwood (Leh, 2002).

In wood, the hemicelluloses are mostly found around the cellulose microfibrils, which they support (Mimms *et al*, 1990). The hemicelluloses are more easily degraded and dissolved than cellulose, so their percentage is always less in the pulp than in the original wood (Smook, 1992). In papermaking, the hemicellulose will aid in making the paper stronger, so for the paper-grade pulp, hemicelluloses are retained as much as possible to maintain pulp yield and to enhance final paper properties by promoting internal lubrication of the fiber, leading improve flexibility, ease of mechanical refining

and increase sheet density. Hemicelluloses also act as an interfiber bonding agents or adhesive to strengthen paper (Leh, 2002).

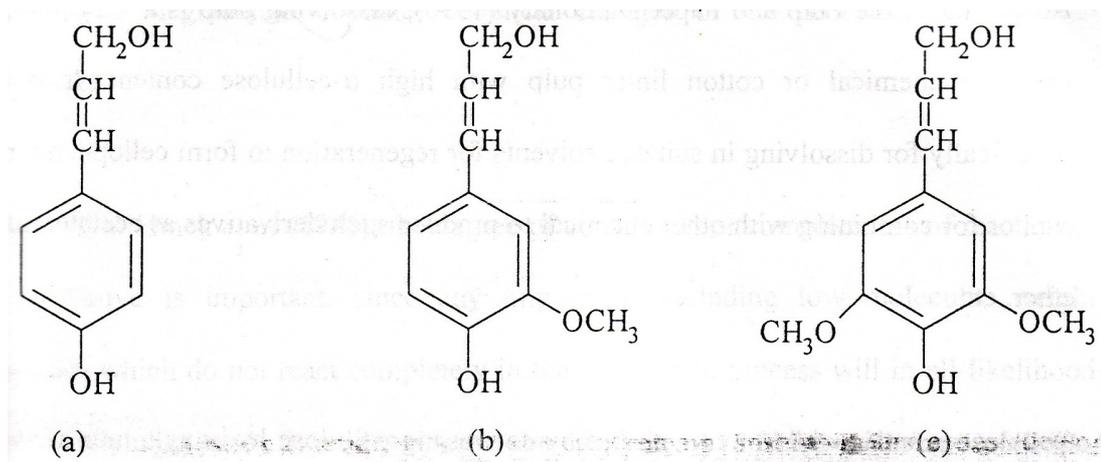
### **2.1.3 Lignin**

The term “holocellulose” is used to describe the total carbohydrate content of fibers. In addition to holocellulose, woody plant material contained lignin (Smook, 1992). The word lignin is derived from the Latin word *lignum* meaning wood. It is a main component of vascular plants. Indeed, lignin is second only to polysaccharides in natural abundance, contributing 24-23% and 19-28%, respectively to dry wood weights of normal softwoods and temperate-zone hardwoods. Lignin is an amorphous substance that together with cellulose forms the woody cell wall of trees. Lignin is also known as the cementing material between the cells and thus, provides added mechanical strength to the wood (Mimms *et al*, 1990). In addition lignin is also contained within the remaining cross section of the fiber (Smook, 1992).

Lignin is a highly branched, mainly aromatic and three-dimensional polymer. The basic molecular unit in lignin is phenyl propane. A lignin molecule is large with a high degree of polymerization. Because of its size and three-dimensional structure, the lignin in wood functions as a glue, or cement (Mimms *et al*, 1990).

Lignin is manufactured by maturing fiber (of other wood cells) and permeates the fiber wall and intercellular regions (middle lamellae, which cements fiber together). Lignin imparts a woody, rigid structure to the cell walls and distinguishes wood from other fibrous plant material of lesser lignin content. Furthermore, it also acts protectively for carbohydrates against bacterial composition (Leh, 2002).

According to a widely accepted concept, lignin may be defined as a polyphenolic material arising from enzymatic dehydrogenative polymerization of three phenylpropanoid monomers as shown in Figure 2.4, namely coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol.



**Figure 2.4: Chemical precursors of lignin.(a) *p*-coumaryl alcohol, (b) coniferyl alcohol, and (c) sinapyl alcohol.**

Normal softwood lignins are usually referred to as guaiacyl lignins because the structural elements are derived principally from coniferyl alcohol (more than 90%), with the remainder consisting mainly of *p*-coumaryl alcohol-type units. Normal hardwood lignins, termed guaiacyl-syringyl lignins, are composed of coniferyl alcohol and sinapyl alcohol type units in varying ratios. In hardwood lignins, the methoxyl content per phenylpropanoid unit is typically in the range of 1.2-1.5. Grass lignins are also classified as guaiacyl-syringyl lignins. However, unlike hardwood lignins, grass lignins additionally contain small but significant amounts of structural elements derived from *p*-coumaryl alcohol. Grass lignins also contain *p*-coumaric, hydroxycinnamic and ferulic acid residues attached to the lignin through ester and ether linkages (Mark *et al*, 1982).

In commercial chemical pulping of wood, the reverse process in nature is performed to isolate fibers for papermaking. In the process, wood is delignified by chemically degrading and/or sulfonating the lignin to water-soluble fragments. The industrial lignins thus obtained are used in many applications (Mark *et al*, 1982).

## **2.2 Hardwoods**

Botanically, woods are classified into two major groups. Softwoods or conifers are also commonly known as gymnosperms. The term hardwood is used to describe wood from non-monocot angiosperm trees and for those trees themselves. These are usually broad-leaved; in temperate and boreal latitudes they are mostly deciduous, but in tropics and subtropics they are mostly evergreen (Wilson and White, 1986).

Hardwood contrasts with softwood, which comes from conifer trees. On average, hardwood is of higher density and hardness than softwood, although there is an enormous variation in actual wood hardness in both groups, with the range in density in hardwoods completely including that of softwoods; some hardwoods are softer than most softwoods (Wilson and White, 1986).

The principal vertical structure of hardwoods is composed of both relatively long, narrow cells called libriform fibers, and much shorter, wider cells, called vessels. Vessels in a typical hardwood sample are often large enough in diameter to be seen easily with the naked eye, in cross-section as “pores” or on vertical surfaces as a series of long grooves. Hardwoods also have a vertical parenchyma system and a horizontal or ray parenchyma system (Smook, 1992).

Vessel diameter varies from earlywood to latewood within an annual ring. If this difference is extreme and abrupt, the rings become easy to distinguish, and the wood is termed ring-porous. In other species where the gradation in vessel diameter is small and gradual, the annual rings are more difficult to distinguish, and the wood is termed diffuse-porous (Smook, 1992).

### **2.3 Pulp**

Pulp is the fibrous raw material for papermaking. Pulp fibers can be extracted from almost any vascular plant found in nature. However, a high yield of fibers is necessary if the plant is to have economic importance. Wood is far and away the most abundant sources of papermaking fibers (Smook, 1992). Many varieties of wood, eg, hardwood and softwood, are used to produce pulp. In addition to the large number of wood types, there are many different manufacturing processes, by which only mechanical energy is used to separate the fiber from the wood matrix, to chemical processes, by which the bonding material such as lignin is removed chemically. Many combinations of mechanical and chemical methods also are employed. Pulp properties are determined by the raw material and manufacturing process, and must be matched to the needs of the final paper product (Kroschwitz and Howe-Grant, 1995).

In order for fibers to be useful for papermaking, they must be conformable, i.e. capable of being matted and pressed into a uniform sheet. Strong bonds must also develop at the points of contact. For some applications, the fiber structure must be stable over long periods of time (Smook, 1992).

The properties of paper are dependent on the structural characteristic of the various fibers that compose the sheet. Undoubtedly the two most important of these characteristic are fiber length and cell wall thickness. A minimum length is required for interfiber bonding, and length is virtually proportional to tear strength (Smook, 1992).

## **2.4 Paper**

### **2.4.1 Paper and modern technology**

The significance of paper and paper products in modern life is obvious to everyone. No manufactured products play more meaningful role in every area of human activity. Paper provides the means of recording, storage and dissemination of information; virtually all writing and printing is done on paper. The uses and application for paper and paper products are virtually limitless. New specialty products are continually being developed. At the same time, the industry is aware of inroads and competition from other sectors, notably plastics and electronic media, for markets traditionally served by paper. As never before, new technology and methodology is being adopted so that the industry can remain competitive in existing markets and be receptive to new opportunities (Smook, 1992).

Paper has traditionally been defined as a felted sheet formed on a fine screen from a water suspension of fibers. Current paper products generally conform to this definition except that most products also contain non-fibrous additives. A sheet of paper is fundamentally a structure that exhibits the same general attributes as other structures encountered by the engineer in the field of materials of construction. Thus a paper

structure displays tensile strength, elasticity, resistance to compression and the usual strength moduli in bending (Willels, 1963).

A paper structure as bounded by its surfaces is composed broadly of fibers and voids between fibers. The fibers form a definite self-supporting structure or matrix by virtue of being felted and bonded, fiber surface to fiber surface, locally where the surfaces of two fibers cross or meet (Willels, 1963).

Starting from the early age of modern paper technology era, there are so many researches have been done to increase the quality of paper properties. It had been noted that starting from the preparation of the fiber for the paper making process; whether the fibers are from the groundwood pulp, semichemical, chemical or mechanical processed pulp is just to bring some added value to the fibers to ensure the best quality of paper to be made.

For example, the mechanical action shortens, splits, and bruises the fiber. At the same time the ends of the fibers become frayed, fibrils are loosened on the surface and the fiber becomes much more flexible. The number of fibers that are affected, the degree of cutting and the amount of mechanical action applied, the type of equipment used, and the concentration of the pulp in water (Willels, 1963).

In the other hand, chemical pulps have greatly reduced lignin and hemicellulose contents compared to the native wood, as these components are dissolved during chemical digestion. Because the lignin is removed, much less mechanical energy is needed to separate the fibers from the wood matrix, and the resulting pulp fibers are undamaged and strong. Chemical pulps are used principally for strength and performance in a variety of paper and paperboard products (Mark *et al*, 1980).

Above all this, we understood that the paper maker has many methods available for developing specific properties in paper. These include the selection of fibers to be used, addition of non-fibrous materials, variation in mechanical treatment of stock, variation in conditions during sheet formations, variations in pressing, drying, calendaring and many more (Willels, 1963).

In papermaking, chemicals can be added either to the pulp slurry prior to sheet formation, such as internal addition, or to the resulting sheet after complete or partial drying. Which method is used depends primarily on the desired effects. For example, strength additives usually are added internally if uniform strength throughout the sheet is wanted, but they are applied to the surface if increased surface strength is needed. If an additive cannot be retained efficiently from dilute pulp slurry, then it is better to apply it to the surface of the sheet (Mark *et al*, 1980).

Functional internal additives improve specific properties of the paper, for example sizing, dry strength, wet strength, and optical properties, which those that are affected by the presence of light-scattering particulate additives such as clay and titanium dioxide (Mark *et al*, 1980).

Functional surface treatments involve many of the same chemicals that are used internally. However, since retention of the chemical by pulp fibers is not important to surface treatment, many other materials may be used that are ineffective or, at best, inefficient when added internally (Mark *et al*, 1980).

Over the years, many scientists in paper making technology have thoroughly doing research as the demand for paper starts to increase. New special properties are

applied for certain kind of paper to enhance the quality and to make it as a multi-purpose material.

There are many properties of paper that are classified as resistance properties. Many of these are related to the properties of the cellulose fibers used to manufacture the paper. Cellulose does not conduct electricity; therefore, paper has high electrical resistance but can be made to conduct an electrical current by special treatment. There are many other resistance properties such as insect resistance, mildew resistance, and resistance to biological degradation, but most resistance properties refer to the resistance to the penetration of liquids or gases; the balance of this discussion is devoted to this subject:

- *Oil and grease resistance* are important in many types of paper. As we know that, most printing inks oil based; therefore, the oil resistance is a measure of the degree to which the printing ink will penetrate into the paper. Grease resistance is important for papers that are used to package foodstuffs containing oil (Casey, 1981).
- *Water and writing-ink resistance* is a kind of resistance which is quite different from the resistance to oil and oil based inks. Oil resistance is controlled primarily by the formation of the sheet and is related to the air resistance. Water resistance is obtained by adding sizing materials that reduce the ability of the water to wet the sheet. These sizing agents have little effect on the rate of oil penetration (Casey, 1981).
- *Water-vapor permeability* is a very important property of packaging papers. Packages for dry hygroscopic materials such as crackers and breakfast cereals must resist the penetration of water vapor or the food will become soggy and

unappetizing. Water-vapor resistance and water resistance are two different properties. Water resistance is developed by adding sizing materials, but sizing has little effect on water-vapor transmission. Water vapor is a gas, and a good water-vapor resistance is obtained by adding a material such as wax that fills all the pores of the paper, thus leaving no passageway for the gaseous water vapor. Some will be transmitted by being absorbed on the fibers exposed on one surface, migrating through the fiber as water and then being released on the other side of the paper or board (Casey, 1981).

Another resistance property for paper which is still running actively under research is *fire and heat resistance*. As we know, cellulose is a poor conductor of heat; therefore, paper is a good heat insulator; shredded paper can be used for home insulation if properly treated to make it fire resistant. Cellulose burns; therefore, untreated paper burns. The fact that paper burns is a very important property of paper frequently overlooked. It permits the disposal of solid waste, a large part of which is paper, by burning and recovering energy. However, this is a very undesirable property when the paper is being used for insulation, for clothing, for draperies, or for other uses where it might catch fire. No paper manufactured from cellulose fiber can be made fireproof; it will burn if sufficient heat is applied. Paper can be made fire resistant so that it will not support combustion; it will burn if it is brought in contact with a flame, but, it will cease to burn when the flame is removed (Casey, 1981).

The test for this property consists of bringing paper in contact with a flame produced by burning gas with specified energy content in a burner with specified

characteristics. After certain seconds the flame is removed and the time that it continues to glow is measured along with the length of the char that is produced (Casey, 1981).

## **2.5 Flame retardant and flame retardant agents**

### **2.5.1 Flame retardant in general**

Most of the immediate surroundings are combustible – clothes, furnishings, and much of the construction material in dwellings and work places, the interiors of cars, buses, airplanes and etc. Wood, paper, textiles and synthetic polymers all burn under the right conditions; many burn vigorously and ignite readily. Human have always been plagued by unwanted fire.

Early chemists tried a variety of concoctions to reduce the flammability of textiles. Starting on the 19<sup>th</sup> century, when a scientist Gay Lussac found out that ammonium salts of sulfuric, phosphoric and hydrochloric acids were effective as a fire retardant as well as certain mixtures of these with borax. Later then, the dye chemist Perkin discovered that certain complex heavy metal ions (stannates and tungstates) helped make the treatment with ammonium salts water-resistant. In the 1930s the effect of mixing antimony oxide with organic halogen compounds was discovered. These three efforts represent the major discoveries on which modern flame-retardant chemicals are based and have become far more sophisticated in recent years (Mark *et al*, 1980).

In 1972, flammability standards for children's sleepwear were established in the United States. In an effort to confer fire retardant properties to the fabrics used, manufacturers began to use a number of chemical additives, notably organic halogens or

phosphate esters, or both. One of the most widely used fire retardant was tris-(2,3—dibromopropyl)phosphate, commonly called tris-BP. Other closely associated compounds were used. At a considerably later date, some researcher found that tris-BP and related compounds were carcinogenic, among other negative qualities. There is much room for further research into finding effective fire retardant that do not have adverse effects (Considine and Kulik, 2002).

Flame retardant is a material used as coating on or a component of a combustible product to raise the ignition point or to reduce the rate of burning (Considine and Kulik, 2002 and Hampel *et al*, 1973). But the protection provided by these fire retardant usually only partial, and because of that flameproofing and fireproofing are less accurate to be used as the terms since material and product treated with them will burn if the temperature is sufficiently high. The application of such terms as fireproof, flameproof, self-extinguishing, non-burning, non-combustible, etc, has often led to ambiguity about the relative flammabilities of different materials. These ambiguities eventually led the Federal Trade Commission to take action in the case to restrict the use of such terminology. This action, in addition to the prohibition placed on the use of certain terminology, requires the use of a caveat whenever the results of burning are cited. Much of the older literature, as well as some of the recent publications, uses this restricted terminology (Mark *et al*, 1980).

Flame retardant is used to describe polymers whose basic flammability has been reduced by some modification as measured by one of the accepted test method. Flame retardant chemical is used to denote a compound or mixture of compounds that when added to, or incorporated chemically into a polymer serves to slow up or hinder the

ignition or growth of fire. A flame retardant chemical technically is one that has the foregoing effect primarily in the vapor phase (Mark *et al*, 1980).

### **2.5.2 Flame retardants for textiles / fabrics/ cellulose**

The technique of imparting flame resistance to textile fabrics is relatively new. Among the earliest references is an article by Sabbatini published in 1638. Recognizing a need to prevent fire, he suggested that clay or gypsum pigments be added to the paint used for theater scenery to impart some flame resistance. Perhaps the first noteworthy recorded attempt to impart flame resistance to cellulose was made in England in 1735 when Obadiah Wyld was granted a patent for a flame-retardant mixture containing alum, ferrous sulfate, and borax .

In France in 1821, Gay Lussac developed a flame-resistant finish by treating linen and jute fabrics with a mixture of ammonium phosphate, ammonium chloride, and borax. Since World War II the flammability of textiles of all types has received greatly increased attention, spurred by the Conference on Burns and Flame Retardant Fabric in 1966, and by the 1967 amendment to the Flammable Fabrics Act of 1953. Flammability standards were established by the Department of Commerce and enforced by the Federal Trade Commission. The responsibility was taken over by the Consumer Product Safety Commission when it was created in 1973 (Mark *et al*, 1980).

Fibers are classified into natural fibers, eg, cotton, flax, silk, or wool; regenerated fibers, eg, rayon; synthetic fibers, eg, nylons, vinyls, polyester, acrylics; and inorganic fibers, eg, glass or asbestos. Combustibility depends on chemical makeup and whether the fiber is inorganic, organic, or a mixture of both (Mark *et al*, 1980).

The weight and construction of the fabric affect its burning rate and ease of ignition. Lightweight, loose-weave fabrics usually burn much faster than heavier-weight fabrics, therefore, flame retardant are mainly used on cottons and rayons. Fabrics made from wool, silk and protein like synthetic polymers are not considered sufficiently combustible, for the most part, to warrant the need for flame retardant finishes (Mark *et al*, 1980).

The terms used in connection with flame-resistant fabrics are sometimes confusing. Fire resistance and flame resistance are often used in the same context as the terms fire-proof or flameproof (Mark *et al*, 1980). Although the terms resistant and retardant have similar meanings, flame resistant is normally used when referring to that property of a material which prevents it from burning when an external source of flame is removed. Flame retardant is used when referring to the chemicals or chemical treatment applied to a material to impart flame resistance (Kroschwitz and Howe-Grant, 2001).

A textile that is flame resistant or fire resistant does not continue to burn or glow once the source of ignition has been removed, although there is some change in the physical and chemical characteristics (Mark *et al*, 1980). Flameproof or fireproof, on the other hand, refer to materials totally resistant to flame or fire. No appreciable change in the physical or chemicals property is noted (Kroschwitz and Howe-Grant, 2001).

Asbestos, steel and glass fibers are non-combustibles, but the yarns produced are suitable only for certain applications. Synthetic fibers designed for their flame retardant properties are now being manufactured from polyvinyl chloride (PVC), a copolymer of acrylonitril and polyvinylidene chloride, aromatic polyamide, or modified polyester. Fabrics produced from these synthetic fibers are similar in textile characteristics to