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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

**SYNTHESIS OF BROMINATED PHENOL-FORMALDEHYDE  
RESIN AS PLYWOOD ADHESIVE**



**Miss Supattra Hanphichanchai**

**A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Petrochemistry and Polymer  
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งานวิจัยนี้เป็นการศึกษาการใช้โบรมิเนต ฟีนอล-ฟอร์มัลดีไฮด์ เรซิน เป็นกาวไม้อัดเพื่อ  
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น้ำเย็นและน้ำร้อนของไม้อัดตัวอย่าง

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ไม้อัดได้

สาขาวิชา.....ปีโคเรเคมีและวิทยาศาสตร์พอลิเมอร์.....ลายมือชื่อนิสิต.....สุภัทรา หาญพิชาญชัย

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## 4172504023 MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORD: PLYWOOD/ FLAME RETARDANT RESIN/ PHENOL-FORMALDEHYDE RESIN

SUPATTRA HANPHICHANCHAI: SYNTHESIS OF BROMINATED  
PHENOL-FORMALDEHYDE RESIN AS PLYWOOD ADHESIVE,  
THESIS ADVISOR: ASSOCIATE PROFESSOR DR. AMORN PETSOM,  
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The brominated phenol-formaldehyde resin was investigated as plywood adhesive in order to study the effect of bromine on physical and flammability properties of this resin. The effect of bromine content in brominated phenol-formaldehyde resin as plywood adhesive was studied. This research involves the use of this adhesive for preparation of 3-ply plywood from rubber wood veneer. Compressing temperature and compressing time were varied in preparation process. Flammability and resistance to cold and hot water of plywood samples were studied.

Result of this study showed that brominated phenol-formaldehyde resin of 10% bromine content by wt. of phenol-formaldehyde resin was suitable to be used as plywood adhesive. The optimum parameters for plywood preparation were compressing time of 30 min and compressing temperature of 110°C. Prepared plywood using brominated phenol-formaldehyde resin as adhesive under the optimum conditions gave moisture content 9.64%, shear strength 266.97 N/cm<sup>2</sup>, flame retardancy property which was studied by the limiting oxygen index value (LOI value) 27.16% and good resistance to cold and hot water. The plywood with brominated phenol-formaldehyde adhesive demonstrated that brominated phenol-formaldehyde resin could be used as plywood adhesive.

Department. Petrochemistry and Polymer Science ..... Student's signature..... *Supattra #*  
Field of study. Petrochemistry and Polymer Science. Advisor's signature..... *A. Petsom*  
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# CHAPTER I

## INTRODUCTION

The forests of the world are progressively dwindling as the countries of the world are rapidly developing and their populations are increasing very fast. Wood, the main product of the forests, is today the base material in the manufacture of the multiplicity of valuable products like rayon, paper, and fiberboard, etc. As a result of vast quantities of wood being used for these industries, there is a growing scarcity of wood and the price of wood is becoming increasingly prohibitive for the fields in which it is traditionally used. However, man is not too happy to dispense with the use of wood for certain traditional uses, and the result is that cheap and effective substitutes for wood panels, such as plywood, fiberboard and particleboard using cheap sources of wood, have emerged. They are made out of species of wood or wood waste, which are not acceptable for use in the traditional furniture and other industry [1].

The demand for wood is on the increase and the supply is unable to keep pace with it. Furthermore, the declining size of available logs (due to the use of younger trees) and the economic need to recover higher percentages of usable material from forest resources. Chemical modification is one of the attempts to demonstrate utility of wood [2,3]. New sources of wood supplies have to be exploited so as to maintain the industries in which wood is the starting material. In this respect the softwood,

small, and low-quality trees of wood are used as effective substitutes for wood panel industries, such as plywood, fiberboard, and particleboard [1].

Plywood has been defined as a product of balanced construction made up of veneers assembled by gluing. The greatest volumes of wood adhesives or binder for structural applications are thermosetting phenol-formaldehyde (PF) or urea-formaldehyde (UF) polymers or their derivatives. Plywood has many structural advantages. It has high uniform strength and can be made in large sizes.

Plywood has, however, several disadvantageous properties especially flammability. Wood, because of its high carbon and hydrogen contents, is combustible. There is no known means of making it incombustible. The rate of burning of wood and the spread of fire can be reduced by either surface fire retardant coatings or impregnation with fire retardant chemicals [4]. Unfortunately, once the coating is broken it tends to peel away from the wood, thus losing its protective power and impregnation with fire retardant chemicals is an expensive procedure and a complicated process [5]. Therefore, it has still been the problem to wood's user.

Chemical modification of phenolic resin has been undertaken to improve their thermal behavior and flame retardancy by introducing flame retardant elements such as bromine to phenol molecule. Therefore, the use of phenolic resin, which is synthesized from bromination of phenol-formaldehyde resin as plywood adhesive is one of the methods for improving fire retardant property of plywood.

## 1.1 Objectives of the Research Work

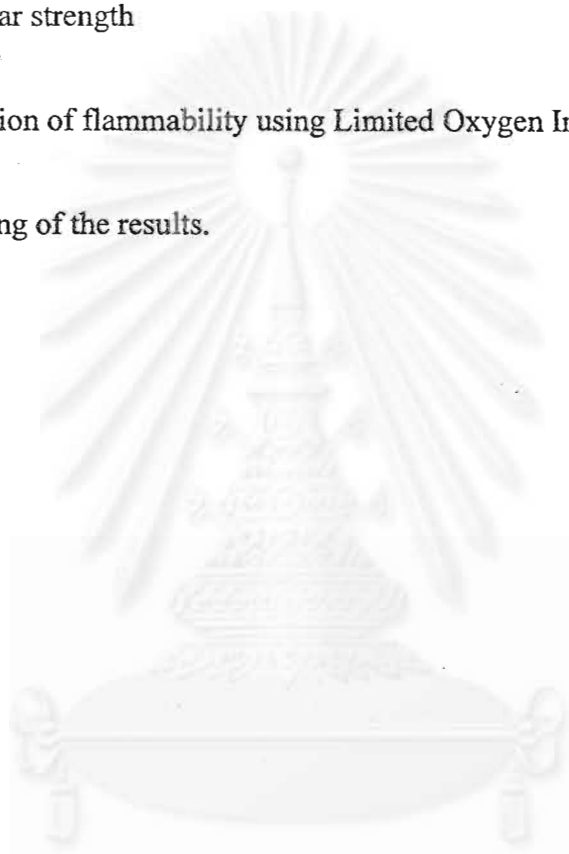
1. To synthesize brominated phenol-formaldehyde resin as plywood adhesive.
2. To study the preparation of plywood which uses brominated phenol-formaldehyde resin as plywood adhesive and to determine the properties of prepared plywood.

## 1.2 Scopes of the Research Work

In this work, the plywood from rubber wooden veneer with brominated phenol-formaldehyde resin was prepared. Three-layer plywood was fabricated and tested under normal and vigorous conditions. The effects of bromine content on flammable property and mechanical properties are investigated. Scopes of the study are as follows:

1. Literature survey of the relevant research works.
2. Preparation of chemicals and equipments.
3. Preparation of brominated phenol-formaldehyde resin as plywood adhesive with different bromine concentration.
4. Preparation of plywood from rubber wooden veneers with brominated phenol-formaldehyde resin, which was obtained by changing the following parameters:
  - a. Compressing temperature

- b. Compressing time
5. Determination of the following physical and mechanical properties:
  - a. Moisture content
  - b. Shear strength
6. Determination of flammability using Limited Oxygen Index (LOI)
7. Summarizing of the results.



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## CHAPTER II

### THEORY AND LITERATURE REVIEWS

Wood is a preferred building and engineering material because wood is valued as a building material which is a renewable abundance of supply with a wide variety of types. Wood is a durable, strong, attractive, easily worked, and versatile material.

#### 2.1 Plywood

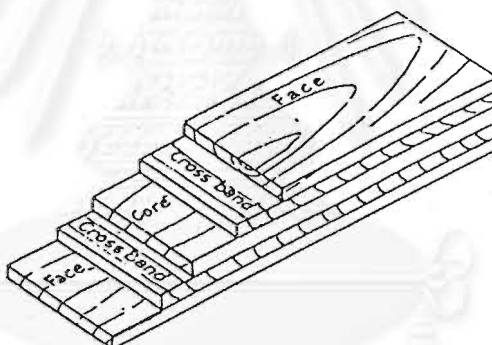
Plywood has been defined as a product of balanced construction made up of veneers assembled by gluing. The chief characteristics are the crossing of alternate plies to improve the strength properties and minimize movement in the plane of the board.

Plywood is manufactured by bonding together layers (plies) of thin sheets of wood (veneer). The layers are glued together with the grain direction of adjacent layers at right angles. The veneer is usually rotary-peeled from logs, but may also be sliced or sawn. After trimming, drying and grading, the veneers go to glue spreaders, where adhesive is applied and the plywood panel is laid up. The plywood is generally hot-pressed in large multi opening heated hydraulic presses. The application of both heat and pressure cures the glue [5].

### 2.1.1 General Definitions [4,6,7]

Plywood is normally defined as an assembly of an odd number of layers of wood joined together by means of adhesive. In most cases, the grain direction of each layer or ply is at right angles to the grain of the adjacent ply or layer. In recent years this definition has been modified slightly.

As illustrated in Figure 2.1, plywood consists of two outer sheets known as the faces, a center sheet known as the core, and possibly one or more pairs of cross sheets called the cross-bands. They are all glued together with one of type of adhesive.

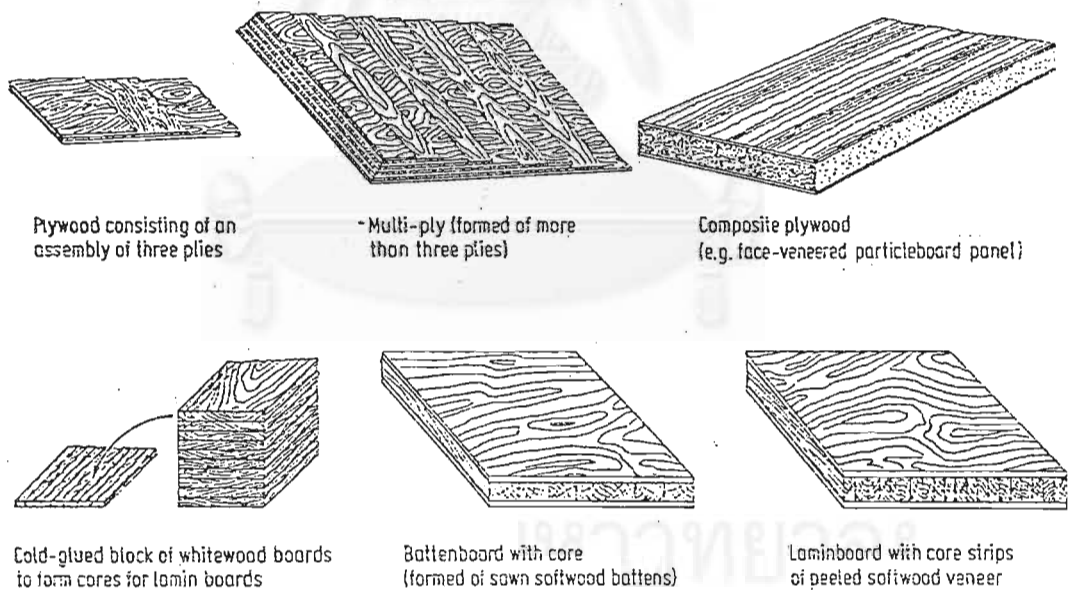


**Figure 2.1** Essentials of plywood structure showing faces, core, and one pair of cross-bands.

The terminology for plywood is as follows:

- 1) Plywood: a panel consisting of an assembly of plies bonded together with the direction of the grain, in alternate plies usually at right angles.
- 2) Veneer plywood: a panel in which all the plies and possibly the core made of veneers orientated parallel to the plane of panel.
- 3) Core plywood:

- Wood core plywood: core of solid wood or veneers.
- Batten-board: core made of strips of solid wood more than 30 mm wide, glued or not be glued together.
- Block-board: as above strips 7 mm. To 30 mm wide.
- Lamin-board: core made of strips of solid wood or veneer not wider than 7 mm.
- Cellular board: core consists of a cellular construction.
- Composite plywood: core made of materials other than wood.



**Figure 2.2** Principal types of plywood



## 2.1.2 Principles of Manufacture [8]

### 2.1.2.1 Veneer

Veneers are thin sheets of wood manufactured by various knife-cutting methods or by sawing. They are used as decorative facings or are combined either with other veneers to form plywood or with lumber to form various combinations having desirable properties of stiffness and strength, as well as non-shrinking and non-splitting characteristics not available in plain wood.

In manufacturing plywood, green logs are first crosscut to a length that suitable for the veneer lathe. At present, there are few if any longer than 380 cm (12 ½ ft), and 240 to 270 cm (8 ft to 9 ft) is a very common size. With some species of timber, the billet can be peeled or converted to veneer without further treatment. But many timbers require first to be softened in steam or hot water before and billet is debarked and cleaned.

For plywood, veneer is almost without exception rotary cut, that is produced in a continuous sheet by feeding a knife mounted parallel to axis into the billet as it rotates in the lathe. The proper combination of pre-treatment and the setting of its lathe results in smooth veneer uniform in thickness to within  $\pm 0.075$  mm ( $\pm 0.003$  in). Under good conditions the veneer is delivered at speeds up to 225 meters/minute (750 ft/minute) and re-wound on spools or led to multi-deck conveyers for storage. It is then clipped to size defects such as knots and splits being cutout in the process.

### **2.1.2.2 Preparation of Veneers for Gluing**

Depending on the type and quantity of plywood to be produced, the steps to be taken in preparing the veneer stock for gluing and pressing may range from direct transfer of dry veneer to the glue spreader, and then a series of operations (redrying, grading and matching, dry clipping, jointing taping and splicing, inspecting and repairing, conditioning) as required in the manufacture of high quality furniture plywood.

In general, however most veneers whether rotary cut or sliced, are cut to size and squared by a dry clipper, edge jointed, taped or sliced and graded into cores, cross bands, or face veneers prior to being assembled for gluing and pressing.

Sliced veneers are processed, basically the same as rotary cutting. However, usually greater working lengths aggravate difficulties. Also more waste and loss are more serious when working with expansive material and large sized veneers.

### **2.1.2.3 Applying the Adhesive**

#### **a. Glue and Gluing Procedures**

Synthetic resin glues replaced protein and starch glues for plywood manufacture, with urea formaldehyde predominating because of price, properties and ease of application.

- Urea formaldehyde glues are extensively used for interior and intermediate grade bonding, which covers the majority of hardwood plywood produced. Formulas differ somewhat and can be adapted to meet specific conditions.

- Polyvinyl acetate glues and also polyvinyl acetate/urea formaldehyde glues are used for edge jointing and veneering. Polyvinyl acetate glues resistant to boiling water are available.

- Melamine formaldehyde glues are not extensively used for plywood gluing but are used where a high-grade bond is required, and where black phenolic glues cannot be tolerated. They are used to fortify urea formaldehyde glues to increase the weathering resistance of the bond. The largest application of the melamine formaldehyde resin is in the production of decorative overlays.

- Phenol-formaldehyde glues are standard for exterior bonds. With a glue properly formulated for exterior use and suitably employed, no exposure conditions or laboratory tests are known which will degrade hot-pressed phenolic glue bonds without destroying the adjacent wood layers. [Baldwin 1981] Phenolic glues are also used for impregnating veneers and paper overlays for plywood.

- Resorcinol-formaldehyde and phenol/resorcinol-formaldehyde glues are similar to phenolic glues in quality of performance but being more reactive, can be cured at room temperature. They are more expensive than phenolic glues, and therefore limited in use to special applications.

## **b. Application of Adhesives**

Application may be by brush, spray gun, doctor blade, roller spreader or film, and depends upon the viscosity of the glue and the speed and flexibility required of process. Brushing is perhaps the most flexible but also the slowest and least uniform method of applying an adhesive and is used for field application or for assembly work such as furniture or aircraft manufacture. For application to large surfaces roller spreading and the other more rapid and uniform method are employed.

The amount of spread depends upon the glue and the surface usually is specified in terms of pounds of solution or pounds of solid per thousand square feet of surface (or in term of kilograms of solution or kilograms of solid or square meter of surface).

### **2.1.2.4 Plywood Pressing**

Prior to pressing the veneers, the veneers are assembled together to form plies consisting of unglued and glued veneers laid alternatively, with their grains mutually perpendicular. The assembled plywood panels may then be grouped together and pressed in pressing.

#### **a. Hot Pressing**

Hot pressing is carried out in hydraulic press incorporating multiple heated platens between which each individual panel assembly is subjected to

heat and pressure. Hot press pressure for softwood pine plywood usually range between 1242 to 1380 kPa. Platen temperatures of around 120 °C are used and pressing times for panels 3.5 and 22 mm are 2.75 and 9.5 minutes respectively. Very accurate control to pressing times, temperatures and pressure are necessary to ensure adequate adhesive bond development.

#### **b. Cold Pressing**

Cold pressing is carried out at room temperature with either mechanical (screw type) or hydraulic presses. The glues employed are low temperatures curing synthetic resin adhesives such as urea formaldehyde. Cold presses are usually single opening and a complete bundle of uncured panels are held together by clamps between top and bottom retainer boards and I-beams and is pressed at one time. As pressure is applied, the retainer clamps are taken up until full pressure has been obtained. The press is then opened and the entire bundle or package held under pressure by the clamps is removed. After a curing period, which ranges from 4 to 24 hours depending upon the glue used, the retainer clamps, retainer boards, and I-beams are removed and the panels sent for further processing.

#### **2.1.2.5 Conditioning of Plywood**

In hot pressing, a considerable amount of water, but not all, the water in the glue line escapes in the form of steam. Moreover, hot pressed panels are often dipped or sprayed with water immediately after removal from the press in order to restore the moisture in the face plies. Consequentially, a conditioning or redrying

period is necessary and hot pressed plywood is usually hot stocked in solid plies for a period ranging from one or two hours to overnight. In this way the glue joints attain full cure and the moisture content of the panels is reduced and equalized through out the panels before further processing is carried out.

In cold pressing, particularly all of the water from the glue line is taken up by the wood layers and redrying is mandatory. Usually the panels are plied with tiers separating the panels at regular intervals to permit air circulation throughout the plies. Conditioning rooms are often used where panels are dried from 8 to 24 hours at temperatures up to 49 °C.

## **2.2 Phenolic Resin [9,10,11]**

Phenolic resins, which can be called phenol-formaldehyde resins, are synthetic polymers that conclude of wide range variety of products resulting from the reaction of phenol or substituted phenol with aldehyde, especially formaldehyde, under various conditions. Phenolic resins possess many good properties, such as heat resistance, chemical resistance, moisture resistance, etc. Thus the most important uses of phenolic resins relate to the wood working industry, thermal insulation and molding compounds. Moreover, phenolic resins are now employed in wide range of applications from commodity construction materials to high technology applications in electronics and aerospace.

### 2.2.1 History

The formation of resins based on the linkage between phenol and formaldehyde has been observed by Baeyer as early 1872. In 1909, an industrial application of these products was announced by Baekeland who mentioned in his early patents the possibility of using condensation products of phenol and formaldehyde for the gluing wood. Approximately 10 years later, 1919, McClain applied for a patent of gluing wood with paper or similar sheets impregnated with phenolic resins. In 1935, water-soluble phenolic resins came into use for impregnation and as binding agents for veneer, plywood, and (compresses) laminated wood. During World War II liquid phenolic resin glues were developed.

### 2.2.2 Classification of Phenolic Resins

There are many factors, which can be deliberately varied to introduce special characteristics of phenol-aldehyde reaction products. The ones which divide phenolic resins into two great classes, novolaks and resoles, are the type of catalyst-specifically whether it is acid or alkaline and the ratio of phenol to formaldehyde-specifically whether there is more or less than one mole of formaldehyde per mole of phenol.

### 2.2.2.1 Novolaks

Novolaks are prepolymers which prepared by the reaction of phenol and formaldehyde in a strongly acidic pH region. The reaction is carried out at a molar ratio of 1 mole phenol to 0.5-0.85 mole of formaldehyde. Novolaks are linear or slightly branch condensation products linked with methylene bridges of a relatively low molecular weight approximately 2,000. So these resins are thermoplastic which are soluble, permanently fusible and can be cured or crosslinked only by addition of hardener (curing agent), almost exclusively hexamethylenetetramine, to form insoluble, infusible and crosslinked thermosetting products.

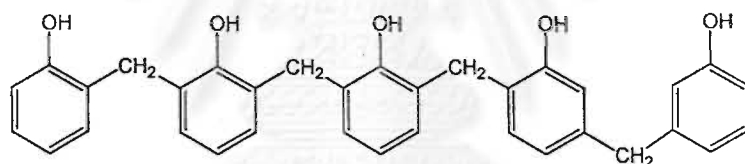


Figure 2.3 Example of novolak resin molecule

The typical acid catalyst used for novolak resins is sulfuric acid, sulfonic acid, oxalic acid, or occasionally phosphoric acid. Hydrochloric acid, although once is widely used, has been abandoned because of the formation of toxic chloromethyl ether by-products. The novolak properties are generally within the ranges shown in Table 2.1



**Table 2.1** Properties of Novolak compound

Compressing time on 150°C. hot plate, sec:	45-110
Inclined plate flow, mm	15-60
Nitrogen analysis, %	3-7
Hexamethylenetetramine, calculated from %N	7.5-17.5
pH	6-9
Free phenol, %	8-11
Soluble in:	Alcohol
	Esters
	Ketones
	Alkaline soluble

Source: David, F. G., *Phenolic Resins*, Reihold Publishing Corporation, New York [11]

#### 2.2.2.2 Resoles

Resoles are prepolymers, which are prepared by the reaction of phenol and formaldehyde under alkaline conditions, a pH above 8. The reaction is carried out at molar ratio of 1 mole phenol per 1-3 mole formaldehyde. The results are mono-, di-, tri-hydroxymethylphenols (HMP, a-e). These prepolymers are heat reactive and can

further react if apply heat, so the reaction must be stopped deliberately before completion.

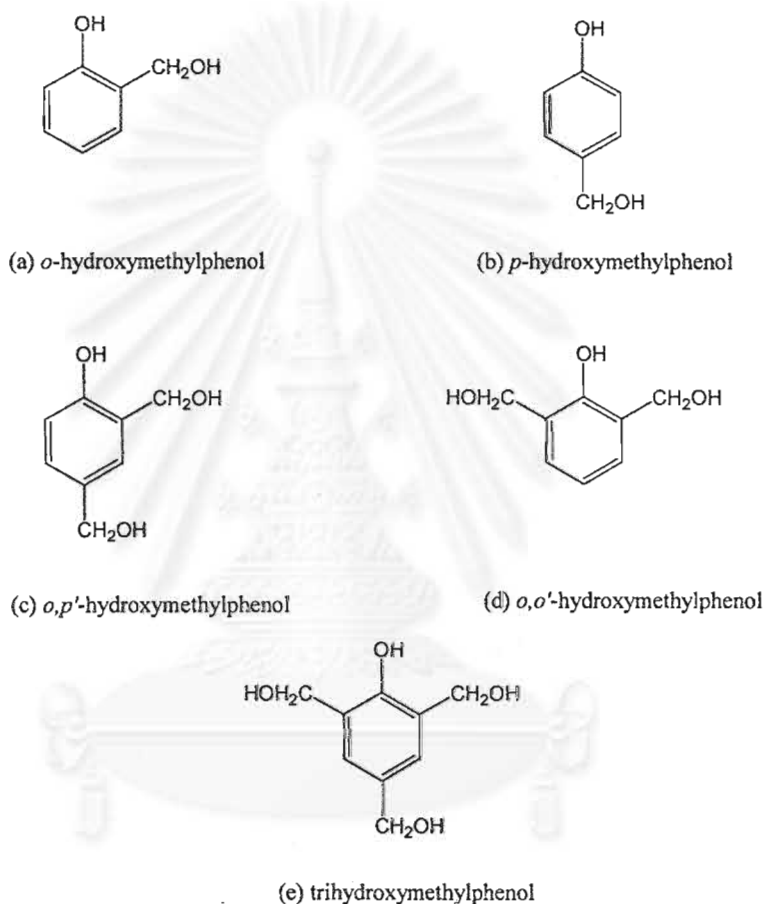


Figure 2.4 Species of resole resins

The typical basic catalyst used for resoless is sodium, barium, magnesium, potassium and calcium hydroxides, sodium carbonate, ammonia and organic amines. The resole properties are generally within the ranges shown in Table

Table 2.2 Properties of resoles

<b>Liquid Resins</b>	
Color	Reddish-brown
Specific gravity	1.15-1.30
pH	6-10
Viscosity, centipoises	35-5000
Water tolerance	Nil to infinite
Nonvolatile, %	55-75
Compressing time on 150°C hot plate, sec.	30-720
Free phenol, %	5-20
Free formaldehyde, %	2-5
<b>Solid Resins</b>	
Color	Tan to reddish-brown
Flow on incline plate, mm	5-150 plus
Capillary tube melting point, °C	55-85
Compressing time on 150°C hot plate, sec.	35-360
Free phenol, %	5-15

Source: David, F. G., *Phenolic Resins*, Reihold Publishing Corporation, New York [11]

The reaction network of resoles formulation is shown in Figure 2.5.

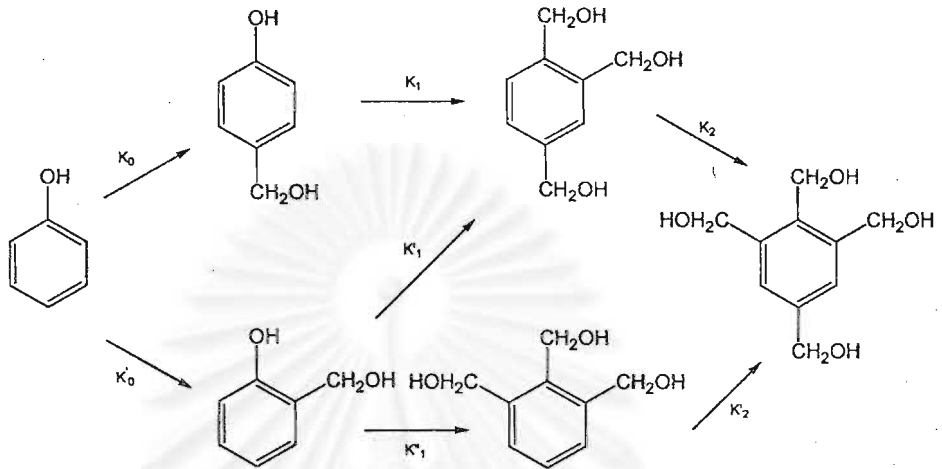


Figure 2.5 Reaction network of resoles

## 2.2.3 Uses of Phenolic Resins

### 2.2.3.1 Molding Materials

Phenolic molding materials are highly consolidated composites containing particulate and/or fibrous fillers, various additives, and a high concentration of resin binder. Resin functionality and curing conditions are such that a high cross-link density is developed in the finished part. Important properties of the cured product include temperature resistance, modulus retention at elevated temperature, good electrical properties, solvent resistance, and a high gloss surface. Cured products are applied to be electrical sockets, switch gear, circuit breakers, and many other devices where good electrical properties. Molding-material properties

depend not only on the type of resin but also on the fillers used and their concentrations.

The phenolic resins that are used in molding materials are predominately novolaks and hardening agent, which usually are hexmethylenetetramine. Resin/curing-agent content is 30-50 wt%. Oxalic acid-catalyzed novolaks are used in the greatest amount.

### 2.2.3.2 Coatings and Adhesives

Most coating and adhesive applications involving phenolic resins are based on combinations with other thermoplastic or thermosetting polymers. In the area of coating applications are, automotive primers, can coatings, drum linings, anticorrosion paints, printing links, wire enamels. In all cases, the phenolic is corrective with the second resin. Phenolic resin compositions' varying depends on the polymer with which the resin is to be combined. All modified phenolic resins that are used in coatings display one or more of the following properties: good solvent, abrasion and corrosion resistance, thermal stability, and insulating properties, etc.

### 2.2.3.3 Wood Composites

Wood composites include plywood, particleboard, fiberboard, wafer board, and macroscopic wood composites such as beam arches. Plywood manufacture involves adhering three or more layers of wood with a phenolic resin under heat and pressure. Caustic-catalyzed water-soluble resoles are employed. The resin generally is combined with fillers and diluents in order to control wetting and to avoid substrate penetration. Particleboard is based on wood chips, shavings, and wood flour rather

than wood sheeting. Liquid resoles are also the principal resin in particleboard manufacture.

#### **2.2.3.4 Fiber Bonding**

In fiber bonding the resin is used as a binder in such products as thermal- insulation batting, acoustical padding, and cushioning materials. All these materials consist of long fibers laid down in a randomly oriented loosely packed array to form a mat. They are bonded with resin to preserve the special insulating or cushioning quality of mat. Resole-based resins are the standard for the fiber-bonding industry. They have excellent curing properties and low content of solvent extractable after curing.

#### **2.2.3.5 Laminates**

A wide variety of applications that exist for phenolic-bonded laminates are based on papers, cotton, or glass substrates. Commercial items include electronic circuit boards, gears, rods, bearings, furniture, wall paneling, and home and office furnishings.

#### **2.2.3.6 Abrasives**

Phenolic-based abrasives are two types; bonded abrasives, including grinding wheels, snagging wheels and coated abrasives, including sandpaper disks, belts, etc. Bonded abrasives that are based on phenolic resins display greater strength and thermal-shock resistance than those based on ceramic or vitrified compositions.

Metal grinding is a principle application for phenolic-bonded abrasives for which surface temperatures are higher than 1000°C.

#### 2.2.3.7 Friction Materials

Phenolic resins are the principle-bonding agent for the asbestos used in friction materials. The major categories are automotive brake lining, clutch facings and automatic transmission discs.

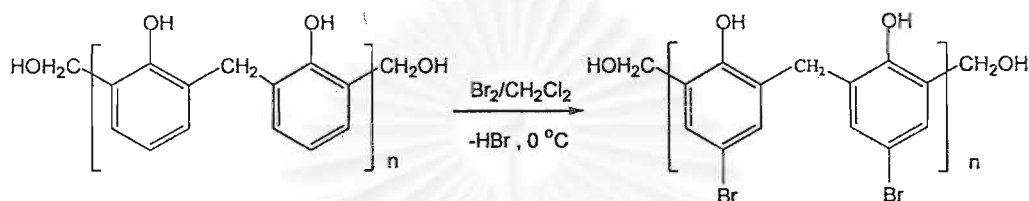
### 2.3 Flame Retardancy of Phenolic Resins [12,13,14,15,16]

In general, phenolics are considered to have moderate non-flammability characteristics. However, early investigators found that various simple materials could be used to improve the fire retardancy of phenolic resins. These include  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{H}_3\text{BO}_4$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

The objectives in flame retarding phenolic resin are to increase the resistance of a product to ignition and to reduce the rate of flame spread. The use of a flame retardant may thus prevent a small fire from becoming a major catastrophe.

Halogen compounds make phenolic resins more flame resistant. Bromine is believed to perform most of its flame-retardant function in the gaseous phase, by means of two mechanisms: redirection or termination of the chemical reactions involved in combustion, and the evolution of heavy bromine-containing gases which tend to protect the condensed phase by inhibiting access of oxygen and transfer of heat.

Brominated phenol-formaldehyde resin was prepared by the bromination of phenol-formaldehyde resin according to Rosy and Pillai's work [12] through the ortho/para position available after polymerization. The bromination of phenol-formaldehyde resin is shown in Figure 2.6



**Figure 2.6** Bromination of phenol-formaldehyde resin

The combustion of gaseous fuels produced by decomposition of an organic material proceeds via a free radical mechanism. For example, a hydrogen radical will be produced during the combustion of an organic polymer, which in turn reacts with oxygen to form oxygen and hydroxy radicals. A number of propagating and chain branching reactions take place which are critical for maintaining the combustion mechanism [17].

In the radical trap theory of flame inhibition by halogen, it is believed that halogen halide (HBr) competes for the radical species (H, OH, O) that are critical for flame propagation. The active chain carriers are replaced with the much less active halogen radical, showing the rate of energy production and helping flame extinguishment. The most important flame inhibiting reaction of halogens are shown in Figure 2.7 [18]



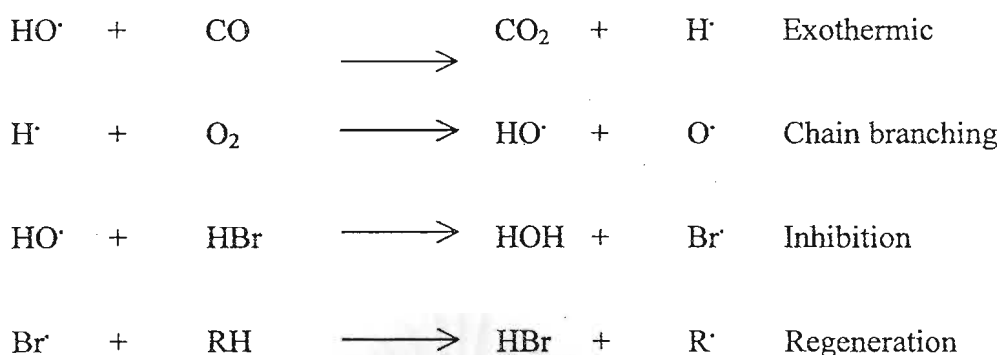


Figure 2.7 Flame inhibiting reactions of halogens

## 2.4 Literature Reviews

Although plywood as a material of construction has many desirable properties, some of its shortcomings, such as its lack of strength in thin layers, and its inherent combustibility, have restricted the scope of its application. Most of the glues used are flammable, although some are self-extinguishing. They impart little fire resistance to the plywood. This is the case with plywood and various types of phenol-formaldehyde resin used as adhesive for plywood. In this literature survey, the various types of phenol-formaldehyde resin and plywood are summarized as follow:

L.B. Manfredi, O. de la Osa, N. Galego Fernandez and A. Vazquez [19] studied the relationship between the structure and the viscoelastic properties of resole resins. Six phenolic resins were synthesized with different molar ratios of the formaldehyde to phenol. These resols were cured by means of temperature and without catalyst. The characterization of the resole was done by means of infrared spectroscopy and chemical methods. From the viscoelastic properties of the fully cured resin, characteristic properties such as: storage modulus ( $E'$ ), width of tan ( $T$ )

and damping peak were obtained. The compression modulus and the void content were also determined. A maximum in the methylene bridge and the result of the viscoelastic properties allow us to say that the resole with F/Ph between 1.3 and 1.4 has the highest crosslinking density.

A. Rosy and C.K.S. Pillai [12] studied the phenolic resins with improved/alterd thermal stability and flame retardancy. These phenolic resins were prepared by introducing flame retardant elements such as phosphorus and bromine at the monomer stage, followed by condensation with formaldehyde and hexamethylene tetramine (HTMA). Thermal stability and flammability of monophenyl phosphoric acid (HPPA), monophenyl phosphoric acid-formaldehyde resin (MPPAF), brominated phenol-formaldehyde resin (BrPF) and 2,4,6-tribromophenyl phosphoric acid-formaldehyde (BrMPPAF) were evaluated by TGA and LOI, respectively. In this study, it shows that the addition of phosphorus to PF resins at the monomer stage enhances their thermal stability and LOI significantly over that obtained by the addition of phosphorus at the polymer stage. Addition of bromine, on the other hand, while raising the LOI value, brings down the thermal stability.

T. Hidekazu, M. Toshiharu and N. Kazuhiko [20] invented flame-retardant phenolic resin. A flame-retardant phenolic resin which comprises the product obtained on reacting at least one halogenated compound (chlorine or bromine) and reacting the resulting reaction product with at least one phosphorus acid ester compound containing a phenolic OH group. These flame-retardant phenolic resins have excellent electrical and mechanical properties, impart resistance and punchability and a process for producing the same.

A.C. Norman [21] invented phenolic resole plywood resin, for manufacture and use. Aqueous phenol-formaldehyde resin solution with formaldehyde-phenol had mol ratio in the range of 1.8 to 2.8, polymerization catalyze of 3% to 9% by wt., measured as NaOH equivalent, with about 0.1% to about 1.75% by wt. potassium carbonate. This was added after the catalytically activated polymerization reaction subsided while the resin was both soluble and fusible. Adhesive binders exhibit tolerance for variables in veneer moisture content from 0% to around 25% and in production timing from delivery of the veneer for assembly to curing of around 10 minutes to about 2 hours without significant degradation of bonding quality.

E. Harold [5] invented fire-barrier plywood. A novel method was presented for converting plywood, wall paneling, and laminated sheeting, used in construction, into a fire barrier which not only decreases the spread of flame along the surface, but prevents the penetration of flame into the interior of the product and through to the opposite side. The method consists of substituting a non-combustible, high temperature-resistant coating, which it has adequate adhesive properties to substitute for the presently used adhesives in the laminated wood. The cited examples consist of a synergistic combination of two and three non-combustible inorganic bonding systems: magnesium "oxychloride" or magnesium "oxysulphate" cements, along with high alumina calcium aluminate cement and with or without colloidal silica. These non-combustible formulations are compatible with some of the currently used plywood phenolic, urea and resorcinol adhesives and may be mixed together so that only one application and curing cycle is required and still imparts the fire-barrier properties inherent in the coating and coating laminate.

## CHAPTER III

### APPARATUS AND EXPERIMENTAL PROCEDURES

#### 3.1 Materials and Chemicals

##### 3.1.1 Rubber Wood Veneer

The wood veneer in this study was all rubber wood, obtained from wood industry. Dimension of veneer is 3 x 130 x 130 mm (thickness x width x length) and its color is light brown.

##### 3.1.2 Chemicals

1. Phenol : Fluka
2. Formaldehyde solution : Lab scan
3. Sodium hydroxide : Carlo Erba
4. Bromine solution : Fluka
5. Methylene chloride : Merck
6. Acetone : Merck
7. Hydrochloric acid : Merck

### 3.2 Apparatus and Equipment

1. Reflux apparatus
2. Compressing molding : Lab Tech. Engineering Co., Ltd.
3. X-ray fluorescence: Oxford E.D. 2000
4. Infrared spectrophotometer: Perkin Elmer, Nicolet (Impact 410)
5. Nuclear Magnetic Resonance spectrometer: Bruker, ACF 200 MHz.
6. Testing shear strength machine: Otto Wolpert-Werke G.m.b.H.  
Ludwigshafen amRh.
7. Limiting Oxygen Index machine: Polymer Laboratories.

### 3.3 Experimental Procedures

#### 3.3.1 Preparation of Wood Veneer

The size of rubber wood veneer was determined by using an electric saw. The rough surface was polished by sandpaper in order to remove the woolly fiber and to make the surface smooth. Thus, the precise measurement of the dimension could be made. The veneer sheets were dried by the dryer to control moisture content at  $10 \pm 2.5\%$ .

### 3.3.2 Preparation of Synthetic Adhesive

#### 3.3.2.1 Synthesis of Phenol-Formaldehyde Resin (PF)

Phenol 50 g, 37% aqueous formaldehyde 100 ml and 40% sodium hydroxide 6 ml were placed in a 250-ml 3-necked flask fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated under constant stirring at 80-90°C for 60-75 min. To stop the reaction, the reaction mixture was cooled and then adjusted to pH 7-8. Phenol-formaldehyde resin (PF) was obtained.

#### 3.3.2.2 Synthesis of Brominated Phenol-Formaldehyde Resin (BrPF)

PF was brominated to obtain brominated phenol-formaldehyde resin (BrPF). PF 100 g and methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) 100 ml were taken in 500-ml round bottom flask that was kept in an ice bath and 50 ml of bromine (1,5,10,15% wt of PF) in methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was added dropwise with vigorous stirring. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was evaporated.

### 3.3.3 Characterization of Brominated Phenol-Formaldehyde Resin

The brominated phenol-formaldehyde resin was characterized by x-ray fluorescence (XRF), infrared spectrophotometer (IR), nuclear magnetic resonance (NMR) and Limiting Oxygen Index (LOI).

### 3.3.4 Preparation of Plywood

#### 3.3.4.1 Applying of Adhesive

For each application, the amount of adhesive transferred to the veneer was controlled. The appropriate quantity of resin was weighed as follows:

$$\text{Weight of adhesive} = 220 \text{ (g)} \times \text{area of veneer (m}^2\text{)}$$

The prepared resin was brushed onto the surface of the veneer.

#### 3.3.4.2 Pressing

Prior to pressing, the veneers were assembled together to form 3-ply consisting of glued veneers alternatively laid, with their grains mutually perpendicular. The assembled plywood panels were pressed in a hot-press. The hot press pressure was 1400-1600 psi . The plywood was pressed for a selected time and temperature.

#### 3.3.4.3 Cooling and Trimming

After being pressed, the plywood was cooled. After that, the finish product was trimmed to precise size.

### **3.3.5 Factors Affecting on Plywood Properties**

#### **3.3.5.1 Effect of Bromine Concentration on the Properties**

The plywood was prepared as follows: compressing temperature of 120°C, compressing time of 30 min, pressed pressure 1400-1600 psi (110-130 kg/cm<sup>2</sup>). Brominated phenol-formaldehyde resins, which had different bromine concentration (0,1,5,10,15% wt of PF) were used.

#### **3.3.5.2 Effect of Compressing Time on the Properties**

The plywood was prepared as follows: 10% (wt of PF) bromine in the phenol-formaldehyde resin, compressing temperature of 120°C, pressed pressure 1400-1600 psi (110-130 kg/cm<sup>2</sup>). Different compressing time (10,20,30,40 min) was studied.

#### **3.3.5.3 Effect of Compressing Temperature on the Properties**

The plywood was prepared as follows: 10% (wt of PF) bromine in the phenol-formaldehyde resin, compressing time of 30 min, pressed pressure 1400-1600 psi (110-130 kg/cm<sup>2</sup>). Different compressing temperatures (100,110,120,130,140°C) were studied.



Table 3.1 Processing parameters of the plywood

Plywood	Bromine content in BrPF (%)	Compressing temperature (°C)	Compressing time (min)	Pressed pressure (psi)
A	0	120	30	1400-1600
B	1	120	30	1400-1600
C	5	120	30	1400-1600
D	10	120	30	1400-1600
E	15	120	30	1400-1600
F	10	120	10	1400-1600
G	10	120	20	1400-1600
H	10	120	30	1400-1600
I	10	120	40	1400-1600
J	10	100	30	1400-1600
K	10	110	30	1400-1600
L	10	120	30	1400-1600
M	10	130	30	1400-1600
N	10	140	30	1400-1600

### 3.3.6 Testing

The properties of the rubber wooden plywood were measured by following the test methods:

The moisture content and strength property of adhesive by shear were determined according to TISI 178-2538. The minimum oxygen concentration to support combustion of plywood (LOI value) was determined according to ASTM D2863-95.

**Table 3.2** Dimension of testing specimens

Standard	Testing Method	Dimension of Specimens (mm)
TISI 178-2538	Moisture content	25±0.25 x 70 x 4±1 (width x length x thickness)
	Strength property of adhesive	25±0.25 x 150 x 4±1 (width x length x thickness)
ASTM D2863-95	LOI value	6.5±0.5 x 4±1 (width x thickness)

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### 3.3.6.1 Moisture Content

The testing specimens were randomly taken from each plywood. Each specimen was weighed accurately to 0.1 g, and then put in an air drier at  $103 \pm 2^\circ\text{C}$  to obtain dry weight. Then, the specimens were taken from the drier and cooled in a desiccator. Each specimen was weighed again. The specimen was dried and cooled again until constant dry weight was obtained. The moisture content in each specimen was calculated as follows:

$$\text{Moisture content (\%)} = \frac{W_0 - W_1}{W_1} \times 100$$

where,  $W_0$  = weight before drying  
 $W_1$  = weight after drying

### 3.3.6.2 Strength Property of Adhesive in Plywood (Shear Strength)

The testing specimen was cut as shown in Fig.3.1. The specimen was placed in the jaws of the grips in the testing machine such as those in Fig. 3.2 so that the specimen is perfectly aligned and parallel to the centerline of the jaws. Testing specimens from each plywood were numbered in a sequence and placed in

the jaws alternately. The load was applied at a rate of 6mm/min-12mm/min. The failing loads were expressed in  $N/cm^2$  of shear area.

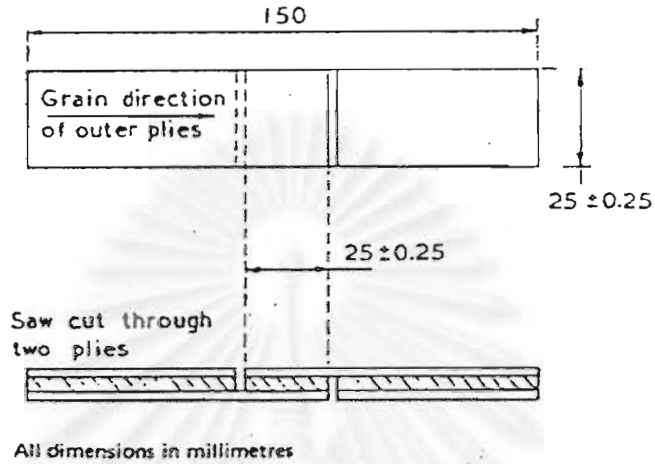


Figure 3.1 Testing specimen

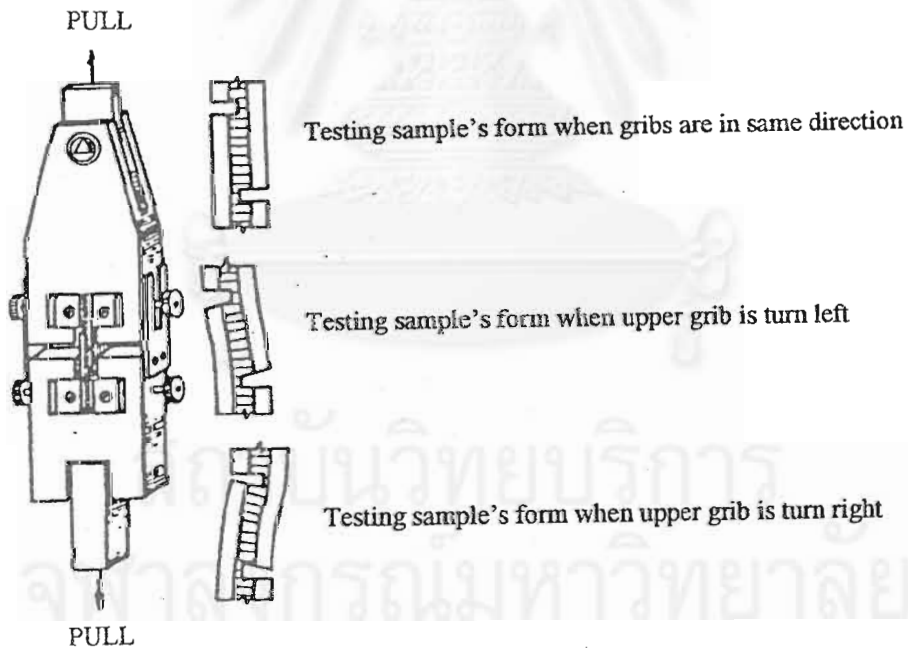
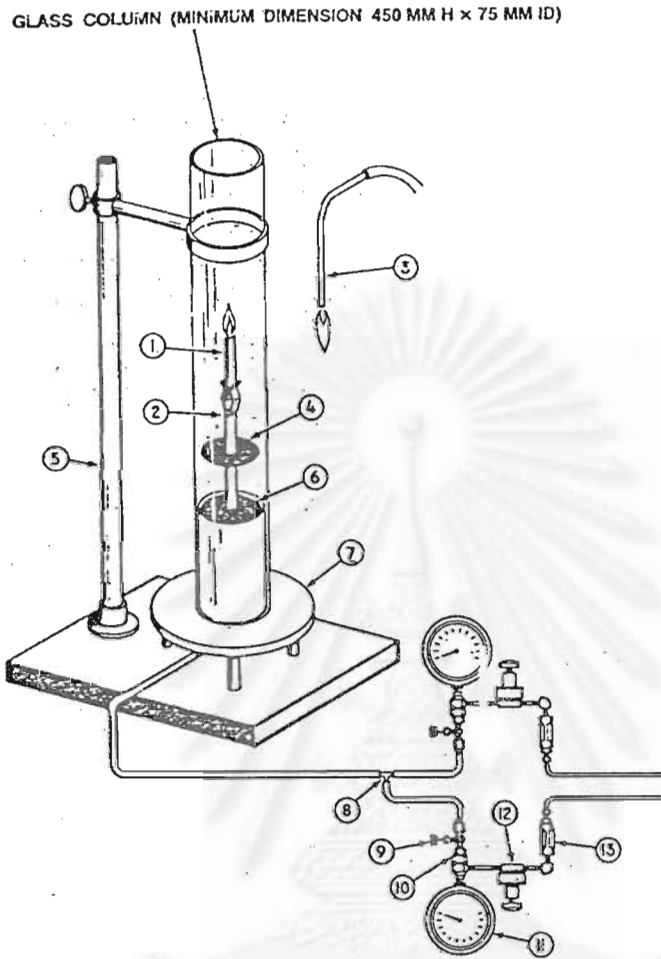


Figure 3.2 The jaws of grips in testing machine

### 3.3.6.3 Minimum Oxygen Concentration to Support Combustion of Plywood (Limiting Oxygen Index (LOI) Value of Plywood)

The limiting oxygen index equipment layout is shown in Figure 3.3. The testing specimen was cut according to the determined specimen dimension. The specimens were clamped vertically in the center of the column. The flow valves were set so that the desired initial concentration of oxygen flowed through the column. The gas flow rate in the column was  $4 \pm 1$  cm/s. The gas was allowed to flow for 30 s to purge the system. The entire top of the specimen was ignited with the ignition flame so that the specimen was well lighted. The ignition flame was removed and the timer was started. The concentration of oxygen was too high and need to be reduced if the specimen burned in accordance with criteria for burning at least 3 min or 50 mm. The concentration of oxygen need be raised if the flaming of the specimen extinguished before meeting the criteria. All values were expressed in % of LOI value.



- |                           |                                  |
|---------------------------|----------------------------------|
| 1. Burning Specimen       | 8. Tee                           |
| 2. Clamp with Rod Support | 9. Cut-Off Valve                 |
| 3. Igniter                | 10. Orifice in Holder            |
| 4. Wire Screen            | 11. Pressure Gage                |
| 5. Ring Stand             | 12. Precision Pressure Regulator |
| 6. Glass Beads in a Bed   | 13. Filter                       |
| 7. Brass Base             |                                  |

**Figure 3.3** Typical limiting oxygen index (LOI) equipment layout

### **3.3.7 Determination of Resistance to Cold Water**

The testing specimens were immersed completely in water at  $27\pm 2$  °C for 16 hr. to 24 hr. During the treatment, it was ensured that the water had full access to the surfaces and edges of every specimen. The specimens were removed and immediately tested, without drying, by the method described in 3.3.6.

### **3.3.8 Determination of Resistance to Hot Water**

The testing specimens were immersed completely in water boiling under normal atmospheric conditions for 72 hr. By the use of suitable racks to hold the specimens, the water was ensured to have free access to all surfaces, and was kept at the specified temperature during the whole period for which the specimens were immersed. After the high temperature treatment, the specimens were cooled immediately to approximately room temperature. They were then tested by the method described in 3.3.6.

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## CHAPTER IV

### RESULTS AND DISCUSSION

The effects of various parameters on processing conditions and mechanical properties of plywood made from rubberwood, using phenol-formaldehyde resin (PF) and brominated phenol-formaldehyde resin (BrPF) as plywood adhesive, were studied. Plywood was manufactured by bonding together layers (plies) of thin sheets of wood (veneer). The layers were glued together along with the grain direction of adjacent layers are at right angles. In this work, the veneer was trimmed, dried and graded. After that, the veneer was brushed with glue (PF and BrPF resins). The 3-ply plywood was pressed in hot-press with the specified condition. After pressing, they were allowed to cool, trim and cut to the testing specimens. The plywood was tested according to the TISI 178-2538 standard of plywood.

#### 4.1 Preparation and Characterization of Brominated Phenol-Formaldehyde

##### Resin (BrPF)

BrPF resin was synthesized from the bromination of PF resin [12] and characterized by infrared spectrophotometer (IR), nuclear magnetic resonance (NMR), x-ray fluorescence (XRF) and Limiting oxygen index (LOI).



### 4.1.1 Infrared Spectra

The IR spectra of PF and BrPF resins are shown in Appendix A. Table 4.1 lists the important absorption peaks and their assignments. When the IR spectrum of BrPF was compared with PF, the absorption peak at approximately  $740\text{ cm}^{-1}$  of BrPF was observed due to the presence of C-Br bonds, while it is absent in the case of phenol-formaldehyde resin.

**Table 4.1** Infrared spectral data of phenol-formaldehyde resin (PF) and brominated phenol-formaldehyde resin (BrPF)

Vibration Assignments	Absorption Frequency ( $\text{cm}^{-1}$ )	
	PF resin	BrPF resin
C-Br (stretching)	-	740
C=C aromatic (stretching)	1600	1600
C-H aliphatic (stretching)	2980	2980
C-H aromatic (stretching)	3050	3050
C-OH (stretching)	3500	3500

## 4.1.2 NMR Spectra

Nuclear magnetic resonance spectrometer was used for the characterization of PF and BrPF resins. The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of PF and BrPF resins are shown in Appendix B.

### 4.1.2.1 $^1\text{H}$ -NMR Spectra

The  $^1\text{H}$ -NMR spectrum of PF in acetone- $d_6$  revealed the signal at  $\delta_{\text{H}}$  7.09, 6.98, 6.95, 6.91, and 6.78 ppm, which all of chemical shifts referred to the protons in aromatic ring. Signals at between  $\delta_{\text{H}}$  4.73 and  $\delta_{\text{H}}$  4.28 ppm referred to  $-\text{CH}_2\text{-OH}$  protons. Signals at  $\delta_{\text{H}}$  3.78 ppm and  $\delta_{\text{H}}$  3.71 ppm referred to Ar- $\text{CH}_2$ -Ar protons and at between  $\delta_{\text{H}}$  3.24 and 3.39 ppm referred to phenolic (Ar- $\text{OH}$ ) protons.

For BrPF resin in acetone- $d_6$ , the  $^1\text{H}$ -NMR spectrum revealed the signals at  $\delta_{\text{H}}$  7.09, 6.98, 6.95, 6.90 and 6.78 ppm, which all referred to the protons in the aromatic ring. Signals at between  $\delta_{\text{H}}$  5.50 and  $\delta_{\text{H}}$  4.72 ppm referred to  $-\text{CH}_2\text{-OH}$  protons, which were effected by the presence of Br at the *para*-position.  $^1\text{H}$ -NMR spectrum also indicated the presence of Ar- $\text{CH}_2$ -Ar protons at between  $\delta_{\text{H}}$  3.83 and  $\delta_{\text{H}}$  3.68 ppm.

### 4.1.2.2 $^{13}\text{C}$ -NMR Spectra

The  $^{13}\text{C}$ -NMR spectrum of PF resin in acetone- $d_6$ , shown in  $\delta_{\text{C}}$  from 133.5 to 126.9 ppm, attributed to carbon at *meta* -free sites. The free sites of the

phenolic resin was substituted and already reacted. The signal at  $\delta_C$  119.9-ppm referred to carbon of phenolic ring at *para*-free sites. Signals at  $\delta_C$  116.1, 115.8 and 115.6 ppm referred to carbon of phenolic ring at *ortho*-free sites. Signals between  $\delta_C$  65.9 and 61.0 ppm referred to carbons at methylol groups. Signals at  $\delta_C$  41.0 and 35.3 ppm referred to carbon of methylene bridge groups at *para-para* position and methylene bridge groups at *ortho-para* position, respectively.

For BrPF resin in acetone- $d_6$ , its  $^{13}C$ -NMR spectrum was nearly the same as the spectrum of PF resin; but the signal, which referred to carbon at *para*-free sites on phenolic resin, was decreased due to the displacement of bromine atom at *para*-position.

#### 4.1.3 X-Ray Fluorescence (XRF) and Limiting Oxygen Index (LOI) Value

Bromine content was determined by using Oxford E.D 2000, x-ray fluorescence. LOI data, which exhibited flammability behavior of these polymers, was determined by using Polymer Laboratories, LOI equipment. In this study, in PF and BrPF resins the bromine concentration was varied from 0 % to 15 % by wt. of PF. All of the samples, both the bromine content and LOI value, were characterized. The XRF graphs of PF resin and BrPF resin are presented in Appendix A. The results of characterization are shown in Table 4.2.

**Table 4.2** Bromine content and LOI of brominated phenol-formaldehyde resin (BrPF)

Sample	Bromine content (wt%)	LOI value (%)
PF	0.00	28.10
Br1	12.93	29.33
Br5	41.32	33.00
Br10	75.53	35.70
Br15	84.36	38.80

Where,

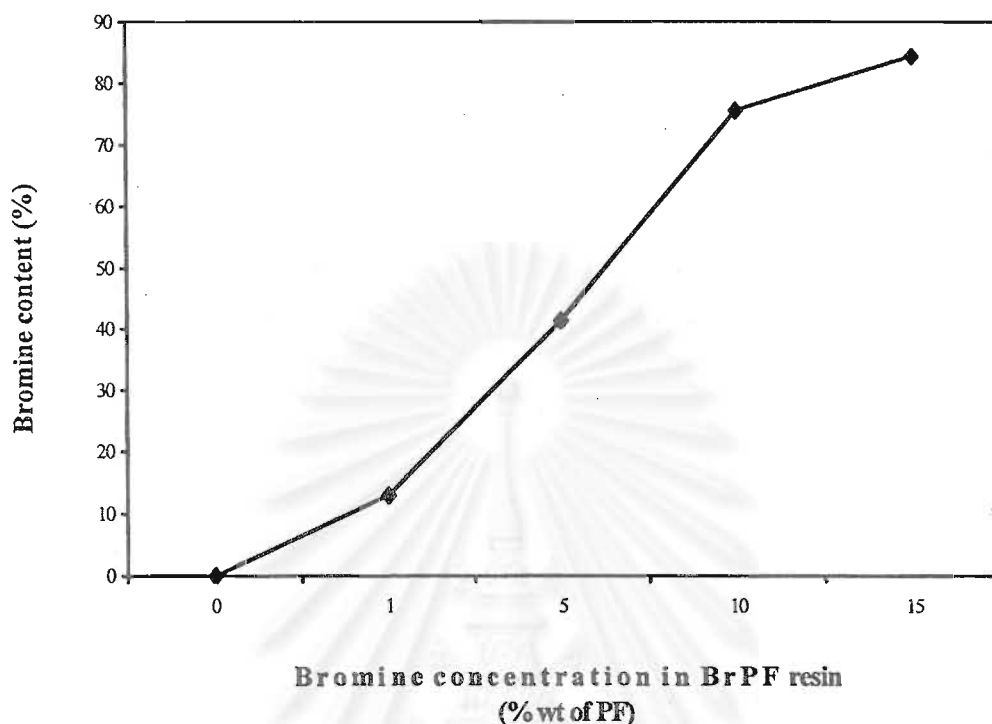
Br1 = bromine 1% by wt of PF

Br5 = bromine 5% by wt of PF

Br10 = bromine 10% by wt of PF

Br15 = bromine 15% by wt of PF

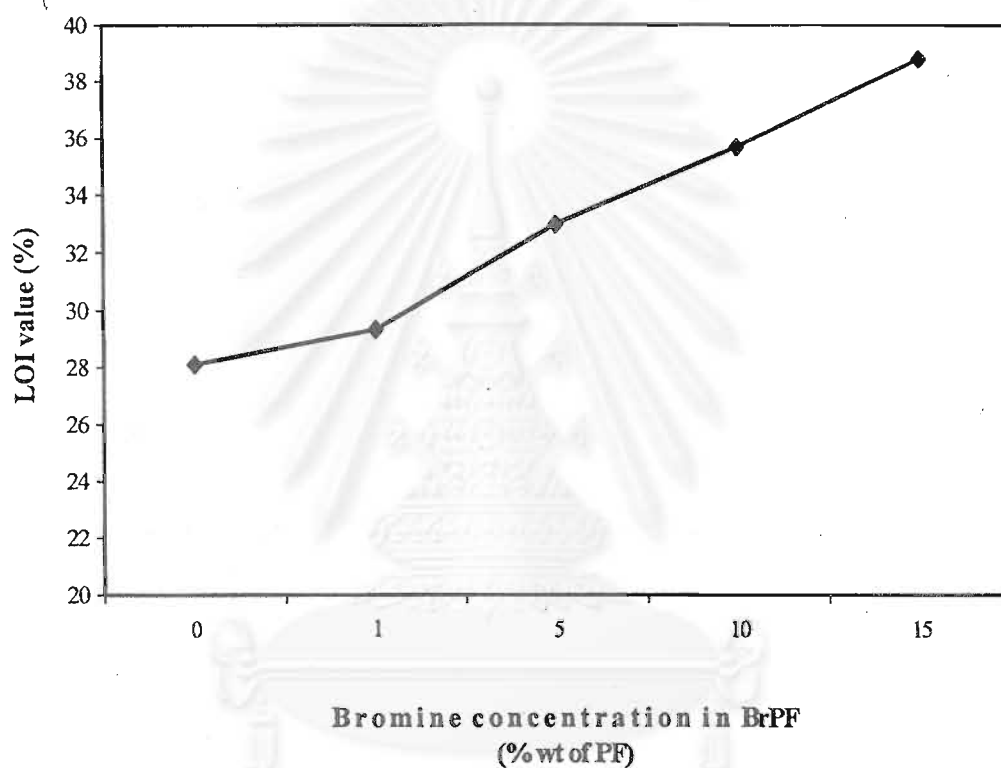
From Table 4.1, the bromine content of 0 wt% and LOI value of 28.10% of PF resin were detected. For BrPF resins, which were prepared from the bromination of PF resin by varying the bromine concentrations from 1-15 % by wt. of PF, it indicated that the bromine content was increased accordingly when the amount of bromine concentration in prepared BrPF resin was increased, as shown in Figure 4.1.



**Figure 4.1** Bromine content of the brominated phenol-formaldehyde resin (BrPF)

Introduction of bromine into PF brought about a reduction in flammability behavior. Table 4.2 and Figure 4.2 showed that the LOI values of Br1, Br5, Br10, and Br15 increased from 28.10% of PF to 29.33, 33.00, 35.70, and 38.80%, respectively. This was the general behavior of bromine-containing flame retardant. The flame-retardant effect on BrPF could result from vapor phase, which was generated from the decomposition of bromine-containing products, which might interfere or poison with the flame-propagating reactions and prevent a movement of heat flux from flame to fuel [18]. Therefore, the bromine content was increased accordingly when the amount

of bromine concentration in prepared BrPF resin was increased, thus, resulting in the increasing of LOI value of BrPF resin.



**Figure 4.2** LOI values of prepared brominated phenol-formaldehyde resin (BrPF)

In the study of Rosy and Pillai [12], they reported that the addition of bromine to PF resin effected a reduction in its flammability behavior. The LOI values of PF and BrPF resins are presented in Table 4.3.

**Table 4.3** Comparison between LOI values of PF and BrPF resins with Rosy and Pillai's work [12]

Samples	LOI value (%)	
	Rosy and Pillai's work	This research
PF	25	28.1
BrPF	48	38.8

From Table 4.3, the LOI value of BrPF resin, in Rosy and Pillai's work, was increased from 25% of PF resin to 48%. For this research, the LOI value of BrPF resin was increased from 28.1% of PF resin to 38.8%. The LOI value of this research was less than in Rosy and Pillai's work because the amount of bromine was used in the synthesis of BrPF resin as a plywood adhesive, was less than in Rosy and Pillai's work.

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## 4.2 Effect of Bromine Content of BrPF Resin on the Properties of Plywood

The BrPF resins were used for preparation of plywood in order to reduce the flammability behavior of the prepared plywood. The LOI values of BrPF resins treated plywood are shown in Table 4.4. It indicated that the introduction of bromine into PF brought about a reduction in the flammability behavior of resins. Therefore, the use of BrPF resins, as plywood adhesive could reduce the flammability behavior of plywood. At 10% wt of bromine in BrPF resin, the LOI value could be increased at approximately 3 unit of LOI from untreated plywood.

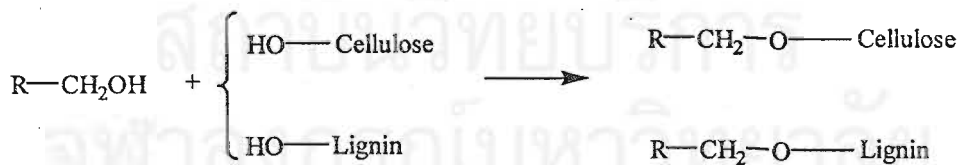
**Table 4.4** Effect of bromine concentration in BrPF resin on the properties of plywood

Bromine concentration in BrPF resin (% wt of PF)	Properties		
	Moisture content (%)	Shear strength (N/cm <sup>2</sup> )	LOI value (%)
0 (PF)	11.96±0.36	186.93±2.66	24.63±0.05
1	10.59±0.09	192.93±0.02	24.79±0.29
5	11.03±0.47	249.83±7.38	26.15±0.13
10	10.72±0.10	275.07±4.19	27.23±0.08
15	10.99±0.52	309.50±3.38	27.85±0.11



Plywood with BrPF resins were used as plywood adhesive, by which the amount of bromine concentration in the BrPF resin samples were varied from 0% to 15% by wt. of PF. The moisture content of the prepared plywood was controlled between 10 and 12 % and it was not significantly different from untreated plywood. These moisture content values of tested samples were in the range of TISI 178-2538 standard.

The shear strength of the prepared plywood, having PF resins, was 186.93 N/cm<sup>2</sup>. The shear strength of plywood increased with the increasing amount of bromine content in BrPF resins, as shown in Figure 4.4. This result might be due to the reactive site of PF resin, which was an oxymethylene group (-CH<sub>2</sub>OH groups). Thus when PF resin was polymerized by heating, the resin would form a long chain polymer with oxymethylene groups at the end of PF resin chain forming covalent bonds with wood. The covalent oxymethylene bridges were formed by condensing the oxymethylene groups of adhesive with hydroxyl groups of cellulose or lignin (Figure 4.3).

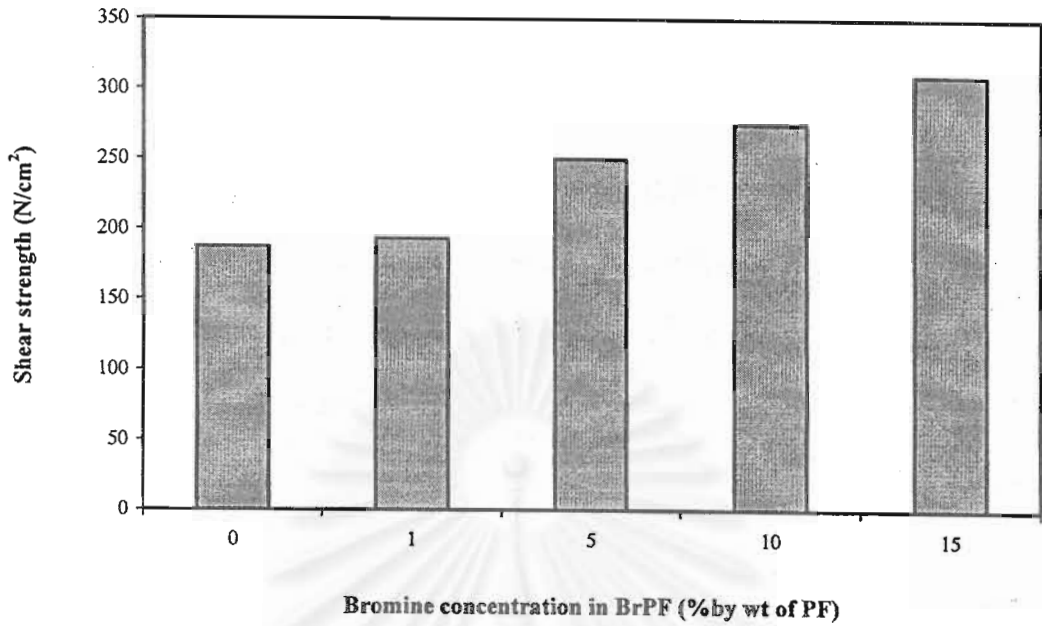


**Figure 4.3** The covalent bonds between adhesive and wood [6]

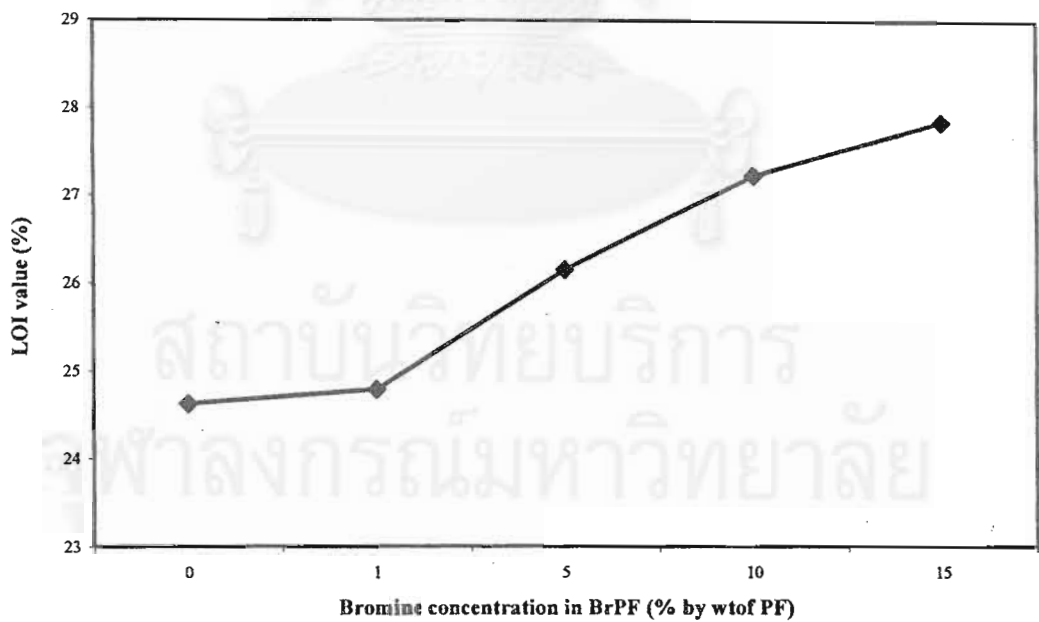
The reactive site of BrPF resin was hydroxyl group (-OH group) which was replaced with an oxymethylene group and the substituent Br affected the aromatic ring by resonance of the Br element. When BrPF resin was polymerized by heating, the polymer was formed and most of the oxymethylene groups formed covalent bonds with wood. Therefore, when the Br content of BrPF resin increased, shear strength of plywood increased significantly and shear strength of plywood using BrPF adhesive, was better than the shear strength of plywood using common PF adhesive.

Moreover, the LOI values of the plywood were increased accordingly with the increasing amount of bromine content of BrPF resins, as shown in Figure 4.5. This result suggested that the action of bromine-containing compounds appears to be principally effective in the ignition of plywood, by blocking the access of oxygen from the flame, in plywood combustion, in order to retard the combustion reaction. It was necessary for the burning process to be proceeded through the decomposition of plywood and to release bromine-containing compounds into the gaseous phase, which was the action of flame retardant.

From this experiment, the values of shear strength and LOI were increased accordingly with the increasing amount of bromine content of BrPF resins. The values of shear strength were especially higher than the standard values. When viscosity of BrPF resin was considered, it was found that viscosity of BrPF resin increased with the increasing amount of bromine content. The BrPF resin with a high viscosity was not suitable for use with plywood adhesive. Therefore, bromine content at 10% wt of PF resin was used for all of the following experiments.



**Figure 4.4** The bromine content effect in BrPF resin on the shear strength plywood property



**Figure 4.5** Effect of bromine concentration in BrPF on the LOI value of plywood

### 4.3 Effect of Compressing Time on the Properties of Plywood

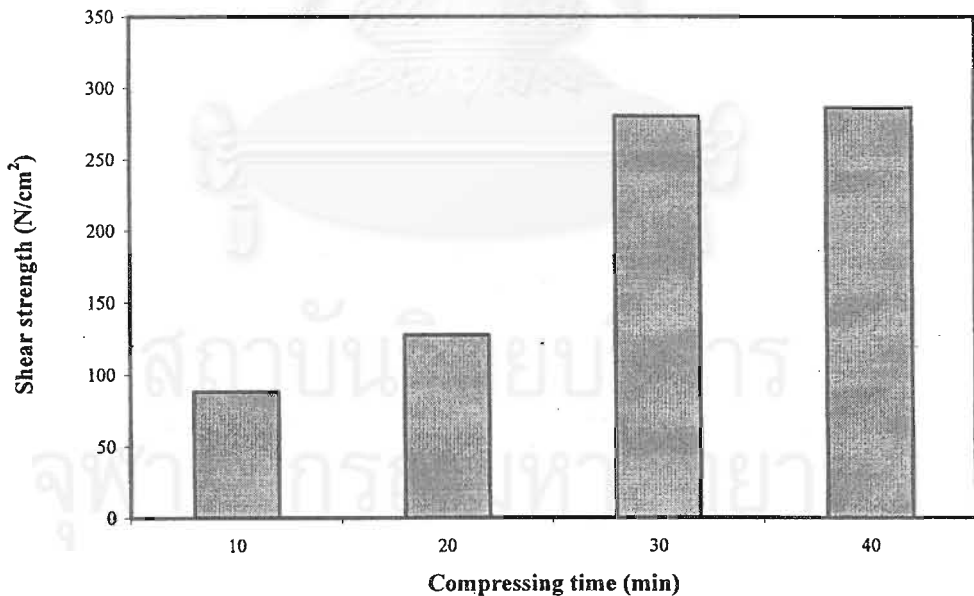
Compressing time was one of the major factors, which was considered. In this study, BrPF with 10% wt of bromine, pressure of 1400-1600 psi and compressing temperature of 120 °C were used. The effect of compressing time on the properties of plywood is presented in Table 4.5.

**Table 4.5** Effect of compressing time on the properties of plywood

Compressing time (min)	Properties		
	Moisture content (%)	Shear strength (N/cm <sup>2</sup> )	LOI value (%)
10	10.51±0.05	88.24±7.67	27.18±0.02
20	10.56±0.02	127.48±0.99	27.22±0.02
30	10.97±0.51	280.27±1.53	27.22±0.01
40	11.35±0.00	285.73±0.98	27.23±0.00

From Table 4.5, it is shown that the moisture content of plywood was between 10-11%. The moisture content was within the range of TISI 178-2538 standard.

The effect of compressing time on plywood shear strength is shown in Figure 4.6. Shear strength of plywood corresponded with the compressing time. Shear strength of plywood using BrPF (bromine concentration 10% wt of PF), which was prepared by varying compressing time showed that shear strength increased with increasing compressing time. At a compressing time of 30-40 min, shear strength of the plywood showed no significant different values. Moreover, a compressing time of 30-40 min gave the highest values. These could be explained by the short compressing time for preparation of plywood, the BrPF resin was not completely cured. When increasing the compressing time for the preparation of plywood, BrPF resin was cured better.



**Figure 4.6** Effect of compressing time on the shear strength property of plywood

For LOI value of plywood, the effect of compressing time did not have an impact on the flammability behavior of plywood according to Figure 4.7. Because the same BrPF resin, with bromine concentration at 10% wt, was used as plywood adhesive. Therefore, the optimum compressing time, which resulted from the maximum shear strength and LOI value of 30 min, was observed.

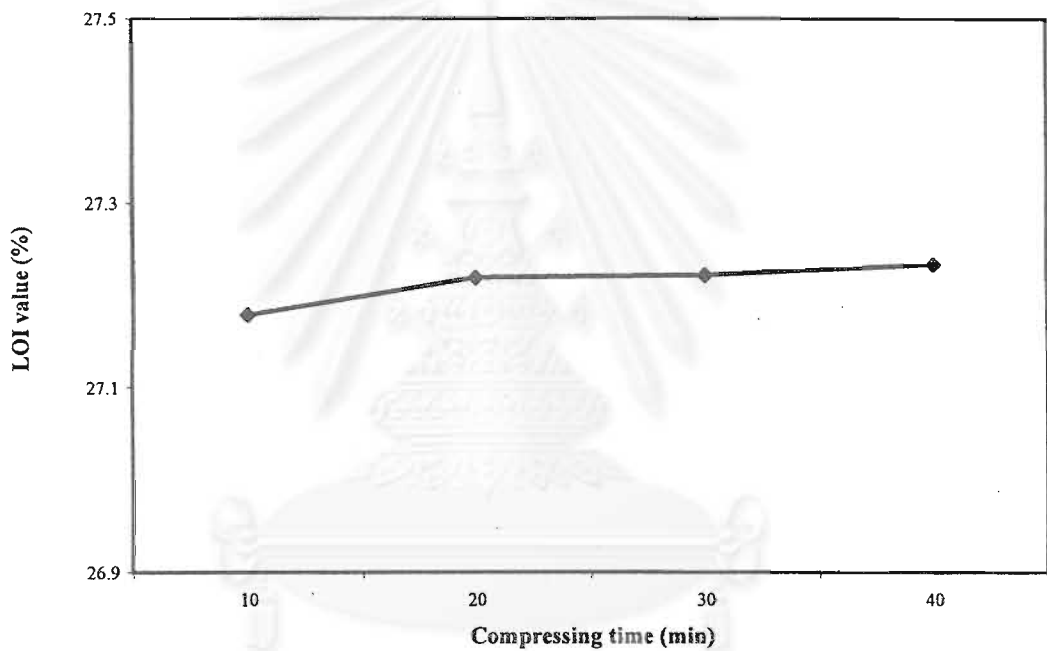


Figure 4.7 Effect of compressing time on the LOI value of plywood

#### 4.4 Effect of Compressing Temperature on the Plywood Properties

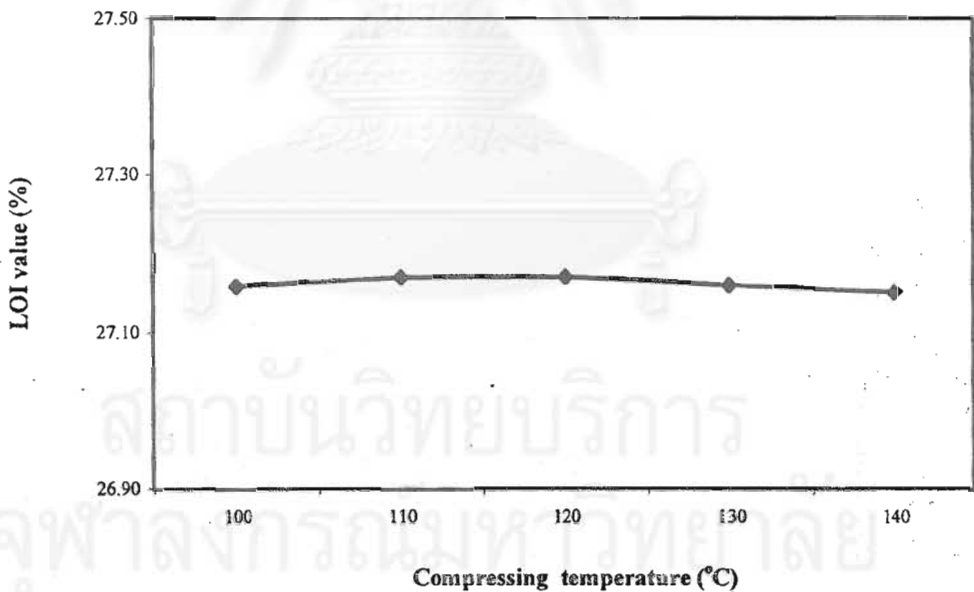
In this study, BrPF resin with 10% wt. bromine, pressure of 1400-1800 psi and compressing time 30 min were used. The effect of compressing temperature on the properties of the plywood is shown in Table 4.6.

**Table 4.6** Effect of compressing temperature on the properties of plywood

Compressing temperature (°C)	Properties		
	Moisture content (%)	Shear strength (N/cm <sup>2</sup> )	LOI value (%)
100	10.02±0.01	158.42±11.22	27.16±0.004
110	9.64±0.08	266.97±0.32	27.17±0.035
120	9.38±0.10	302.59±0.38	27.17±0.003
130	10.03±0.02	292.69±6.37	27.16±0.00
140	9.37±0.09	305.26±7.05	27.15±0.03

The plywood, which was prepared from various compressing temperatures of 100-140 °C, had moisture content between 9-10%. These moisture contents were in agreement with the range of TISI 178-2538 standard.

The effect of compressing temperature on LOI value of plywood is shown in Figure 4.7. The plywood at various compressing temperatures showed that there were no significant differences in the flammability behavior of plywood. As a result, the LOI values of plywood were similar for all the compressing temperatures. Because, the same BrPF resin with bromine concentration at 10% wt, was used as a plywood adhesive.

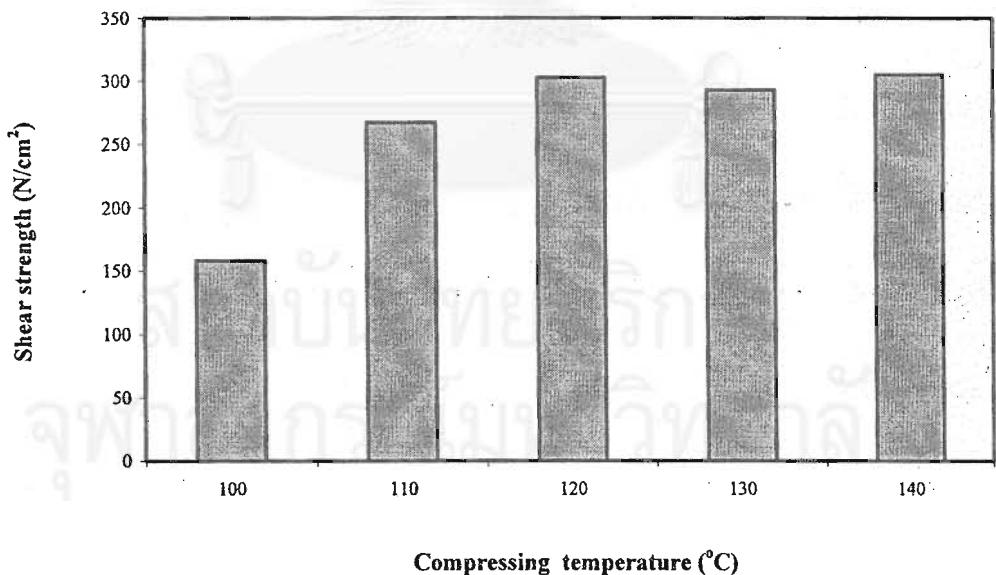


**Figure 4.8** Effect of compressing temperature on the LOI value of plywood



In the case of shear strength, the effect of compressing temperature on the properties of plywood is also shown in Figure 4.8. The plywood was pressed at 100 °C resulting in significantly lowest shear strength. But when the compressing temperature was increased to 110, 120, 130 and 140 °C, the shear strength of plywood increased with the increasing compressing temperature.

Considering the shear strength property of plywood and the compressing temperature, it showed that when the compressing temperature increased, the shear strength of plywood had nearly the same value of each compressing temperature, from 110 °C to 140 °C. Therefore, compressing temperature of 110 °C was selected for this experiment.



**Figure 4.9** Effect of compressing temperature on the shear strength property of plywood

#### 4.5 Determination of Resistance of Cold Water and Hot Water of Prepared Plywood

In this part of the work, BrPF resin with 10% wt bromine concentration in PF resin, compressing time of 30 min, compressing temperature of 110 °C, and pressure of 1400-1600 psi, were used. The prepared plywood, which was immersed in cold water and hot water, was compared with the plywood using PF as plywood adhesive and plywood, which was not immersed in water. The results are shown in Table 4.7.

**Table 4.7** Results of resistance to cold water and hot water of prepared plywood

Samples	Properties		
	Moisture content (%)	Shear strength (N/cm <sup>2</sup> )	LOI value (%)
PF	11.96±0.36	186.93±2.66	24.63±0.05
PF in cold water	13.62±0.00	141.29±0.94	24.08±0.05
PF in hot water	13.75±0.00	114.81±6.56	24.03±0.03
BrPF	9.64±0.08	266.97±0.32	27.16±0.085
BrPF in cold water	12.59±0.04	243.12±2.67	25.90±0.06
BrPF in hot water	13.75±0.01	218.59±1.14	25.59±0.07

Where, PF = plywood using PF resin as an adhesive

BrPF = plywood using BrPF resin as an adhesive

Table 4.7 showed the moisture content of plywood using PF resin adhesive was 11.96%, when the plywood samples were immersed in cold water and hot water, and it was found that the moisture contents were higher than in the original plywood (13.62 and 13.75 % respectively). When BrPF resin was used as an adhesive, the moisture content was 9.64%. After it was immersed in cold water and hot water, the moisture contents were increased to 12.59% and 13.75%, respectively.

The shear strength property of plywood using PF resin as an adhesive was 189.93 N/cm<sup>2</sup>. After it was immersed in cold and hot water, the shear strength values were decreased to 141.29 and 114.81 N/cm<sup>2</sup>, respectively. When using BrPF resin as an adhesive, the shear strength was 266.97 N/cm<sup>2</sup>. After it was immersed in cold and hot water, the shear strength values decreased. However, the shear strength values of plywood using BrPF resin as an adhesive, which after being immersed in water, had higher shear strengths than when PF resin was used as an adhesive.

The LOI value of plywood using PF resin as an adhesive was 24.63% and after being immersed in cold and hot water, the LOI values were slightly decreased. When using BrPF resin as an adhesive, a LOI value of 27.16% was observed. After the samples were immersed in cold and hot water, the LOI values were decreased to 25.90% and 25.59%, respectively. However, the LOI values of plywood using BrPF resin as an adhesive, after immersing in water, were still higher than those using PF resin as adhesive.

It was found that both of PF adhesive and BrPF adhesive were dissolved in hot water more than cold water, nevertheless properties of plywood after being immersed in water still gave better properties than standard requirement.

#### **4.6 The Comparison of the Properties of Plywood using PF resin and BrPF resin as Plywood Adhesive with TISI (Thai Industrial Standard Institute) Standard**

In this observation, the BrPF resin was used as plywood adhesive. Some properties were better than in the case of using PF resin as a plywood adhesive. The properties met the industrial requirements for commercial plywood. The comparisons of general plywood properties are presented in Table 4.8.

Table 4.8 indicated that plywood using BrPF as an adhesive had better properties than plywood using PF resin as an adhesive. When comparing with TISI standard, the plywood using BrPF resin as an adhesive had a moisture content of  $10(\pm 0.5)\%$  which in the range of standard of TISI 178-2538. The shear strength value was higher than the established standard value. For the resistance property to cold water and hot water, the properties of the plywood using BrPF resin as an adhesive was also better than the standard requirements.

For the LOI values, the property of plywood using BrPF resin as an adhesive was higher than the plywood using PF resin as an adhesive. Therefore, using BrPF

resin as a plywood adhesive was well suited for the reduction of flammability behavior of the prepared plywood.



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**Table 4.8** Comparison of the properties of plywood using PF resin and BrPF resin as adhesive with TISI

Properties	TISI (178-2538 and 360-2523)	PF	BrPF
1. Moisture content (%)	7-15	11.96±0.36	9.64±0.08
2. Shear strength (N/cm <sup>2</sup> )	≥77	186.93±2.66	266.97±0.32
3. LOI value (%)	-	24.63±0.05	27.16±0.085
4. Resistance to cold water			
• Moisture content (%)	-	13.62±0.00	12.59±0.035
• Shear strength(kg/cm <sup>2</sup> )	17 (166.6 N/cm <sup>2</sup> )	14.45 (141.29 N/cm <sup>2</sup> )	24.89 (243.12 N/cm <sup>2</sup> )
• LOI value (%)	-	24.08±0.05	25.90±0.06

**Table 4.8** Comparison of the properties of plywood using PF resin and BrPF resin as adhesive with TISI (continued)

Properties	TISI (178-2538 and 360-2523)	PF	BrPF
5. Resistance to hot water			
• Moisture content (%)	-	13.75±0.00	13.76±0.01
• Shear strength (kg/cm <sup>2</sup> )	7-13 (68.6-127.4 N/cm <sup>2</sup> )	11.70 (114.81 N/cm <sup>2</sup> )	22.29 (218.59 N/cm <sup>2</sup> )
• LOI value (%)	-	24.03±0.03	25.59±0.07

## CHAPTER V

### CONCLUSION

From this research work, brominated phenol-formaldehyde resin (BrPF) was synthesized from the bromination of phenol-formaldehyde resin. BrPF resin from the reaction was characterized by infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), x-ray fluorescence and Limiting Oxygen Index (LOI) techniques.

The manufacture of plywood from rubber wood-veneers using BrPF resin, as adhesive appears to be technically feasible. The plywood preparation meets the industry-level requirements for commercial plywood. The optimum conditions for the plywood preparation were as follows:

Bromine concentration in PF resin (% wt. of PF resin)	10
Compressing temperature (°C)	110
Compressing time (min)	30

Under this condition, high performance plywood was achieved with the highest shear strength, high LOI value, which indicated high flame retarding property of plywood, and high resistance to cold and hot water.

The plywood samples, which were prepared using BrPF resin and PF resin as adhesive under the same condition, showed significantly different values of properties



of plywood. BrPF resin as an adhesive had higher performance than PF resin. It affected the shear strength and LOI value.

The flame retardancy property of plywood could be confirmed via the observation of LOI value. The LOI value of the plywood prepared using BrPF resin as adhesive under optimum conditions, which increased from 24.63% to 27.23% of plywood using PF and BrPF resin, respectively showed a better flame retardancy property than the plywood prepared using PF resin. This result indicated that the introduction of bromine into PF resin brought about a reduction in flammability behavior of resin and also of plywood.

It could be concluded that the BrPF resin can be synthesized from the bromination of phenol-formaldehyde resin and used quite well as adhesive with rubber wood-veneers and gave the plywood with moisture content 9.64%, shear strength  $266.97 \text{ N/cm}^2$ , LOI value 27.16% and good resistance to cold and hot water. These properties of plywood were better than the one using conventional adhesive. Because of the major drawbacks of plywood is its flammability. Therefore, the use of phenolic resin, which improved the thermal behavior and flame retardancy by the introduction of bromine in PF resin as a plywood adhesive, is one of the methods for improving the fire retardant property of plywood by themselves without the need of other structural chemical coating. This present investigation demonstrates that the rubber wood plywood with BrPF resin adhesive might also be used for structural applications.

## SUGGESTIONS FOR FURTHER WORK

The use of rubber wood –veneers for plywood production using BrPF resin, as plywood adhesive should be further studied in the following aspects:

1. The new type of flame retardant elements, such as phosphorus, should be investigated. The industrial production of the high flame retardancy of plywood adhesive should be used.
2. The preparation of BrPF resin impregnated wood and the effect of the impregnation on mechanical and physical properties, especially on flammability of wood-polymer composite products should also be studied.

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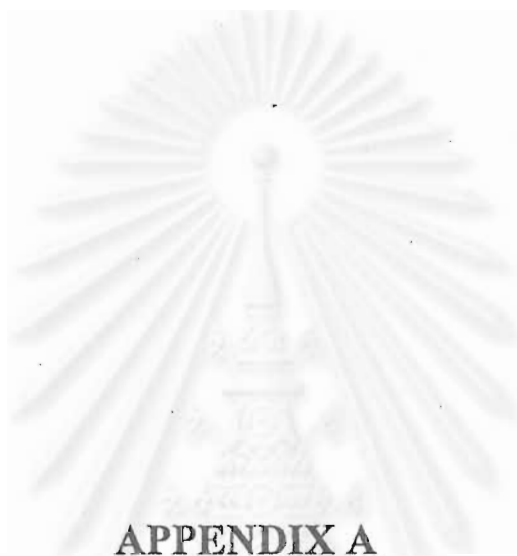


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**APPENDICES**



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## APPENDIX A

### IR SPECTRA OF PF RESIN AND BrPF RESIN



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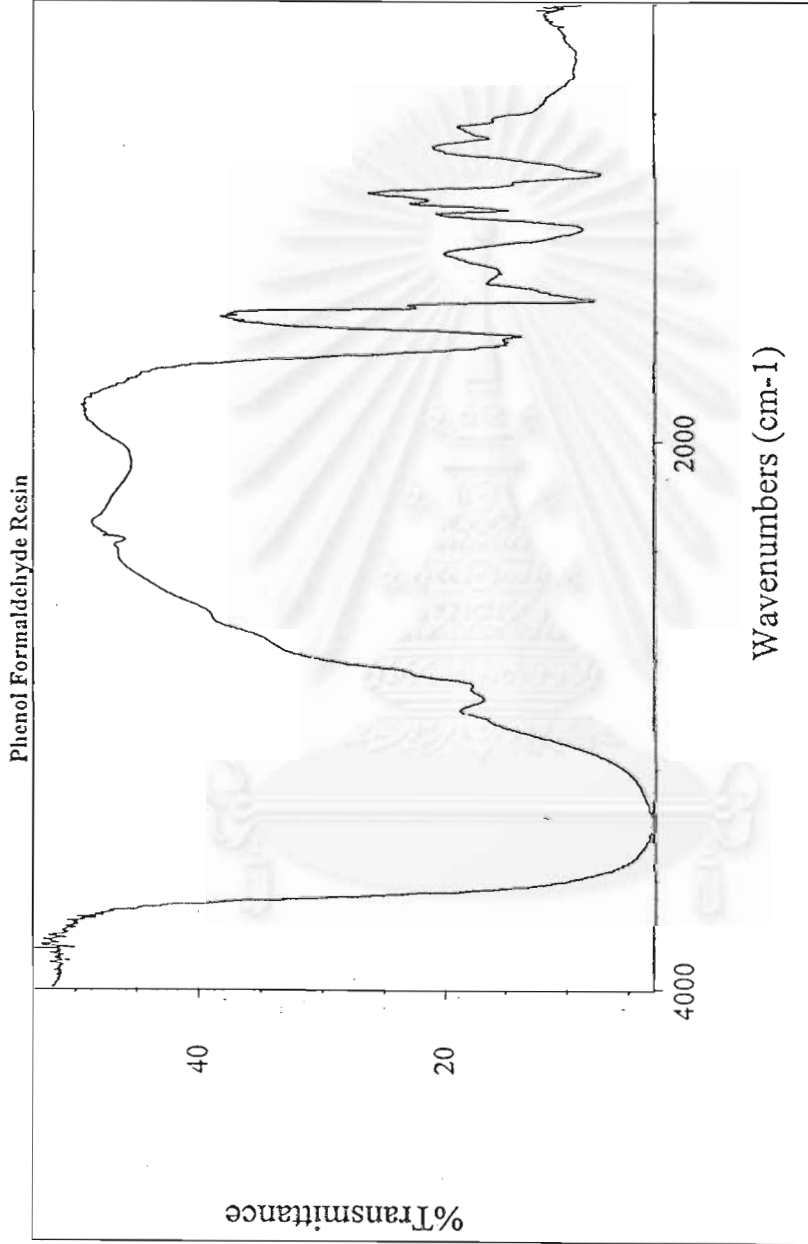


Figure A-1 IR spectrum of phenol-formaldehyde resin (PF)



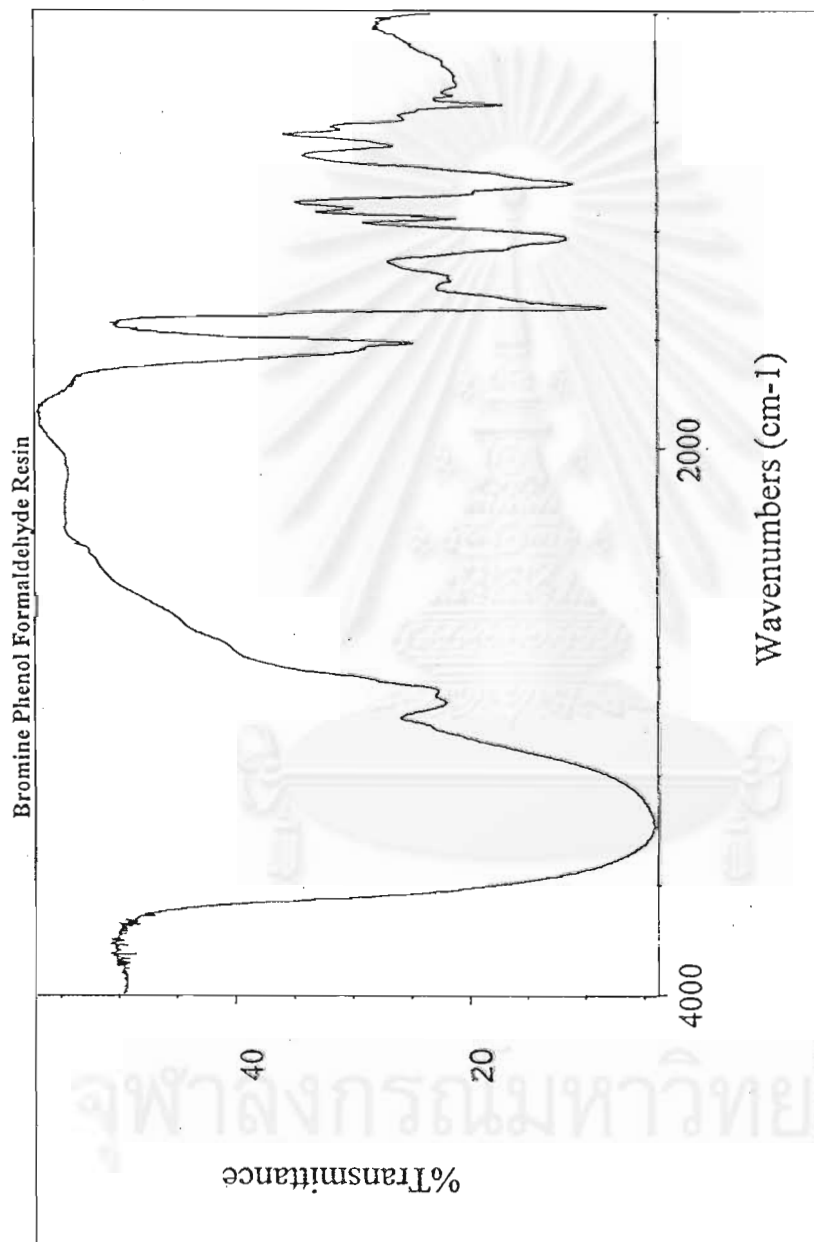
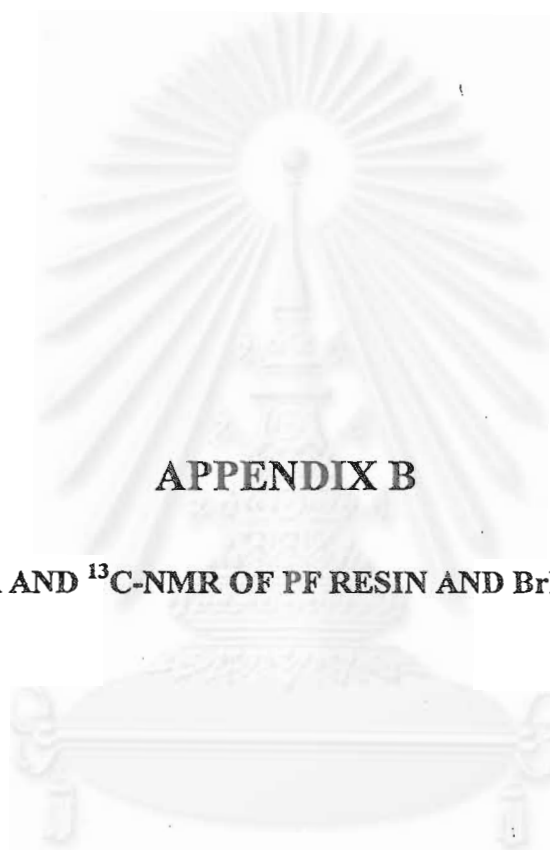


Figure A-2 IR spectrum of brominated phenol-formaldehyde resin (BrPF)



## APPENDIX B

**$^1\text{H-NMR}$  AND  $^{13}\text{C-NMR}$  OF PF RESIN AND BrPF RESIN**

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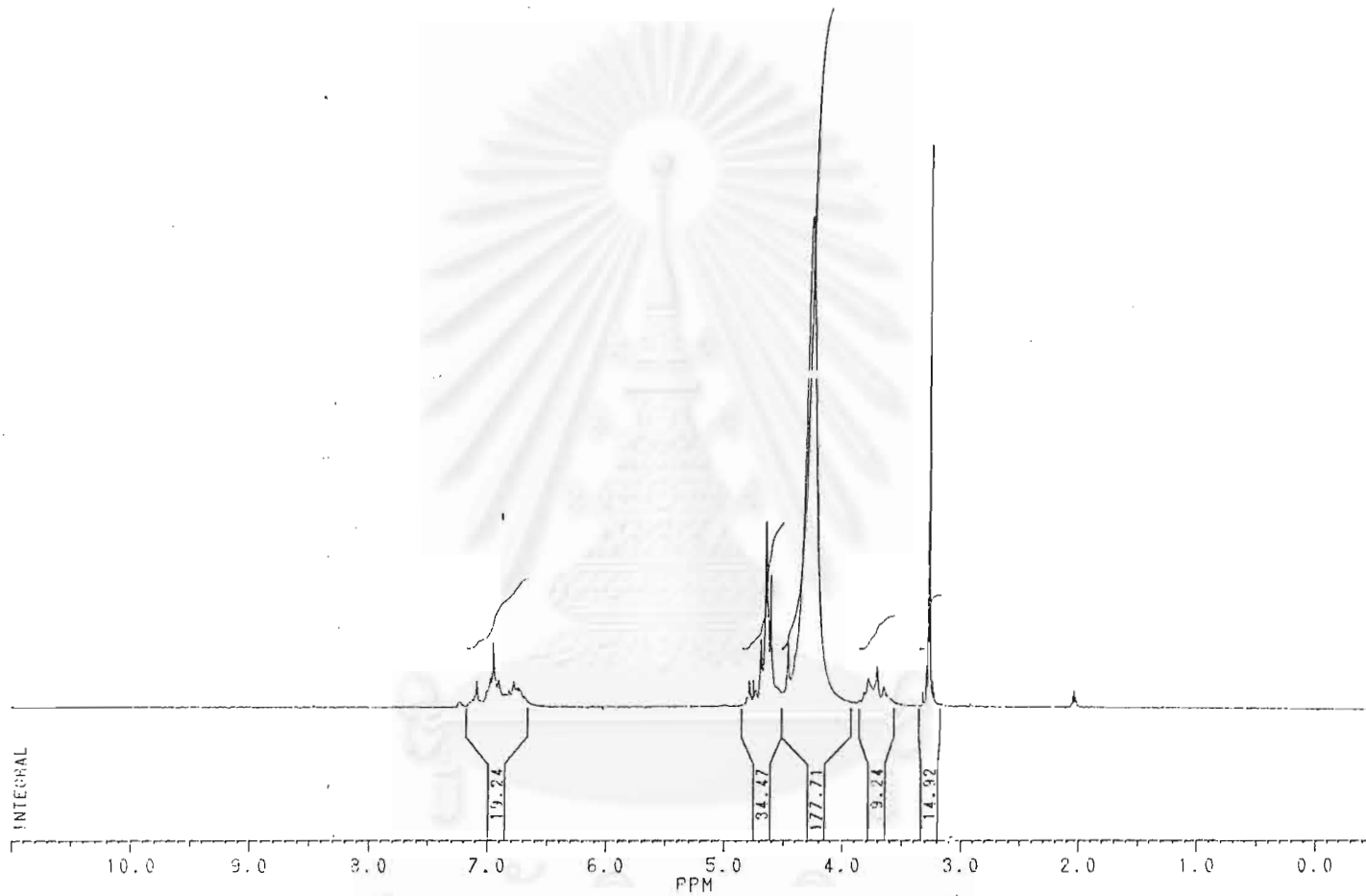


Figure B-1  $^1\text{H-NMR}$  of phenol-formaldehyde resin (PF)

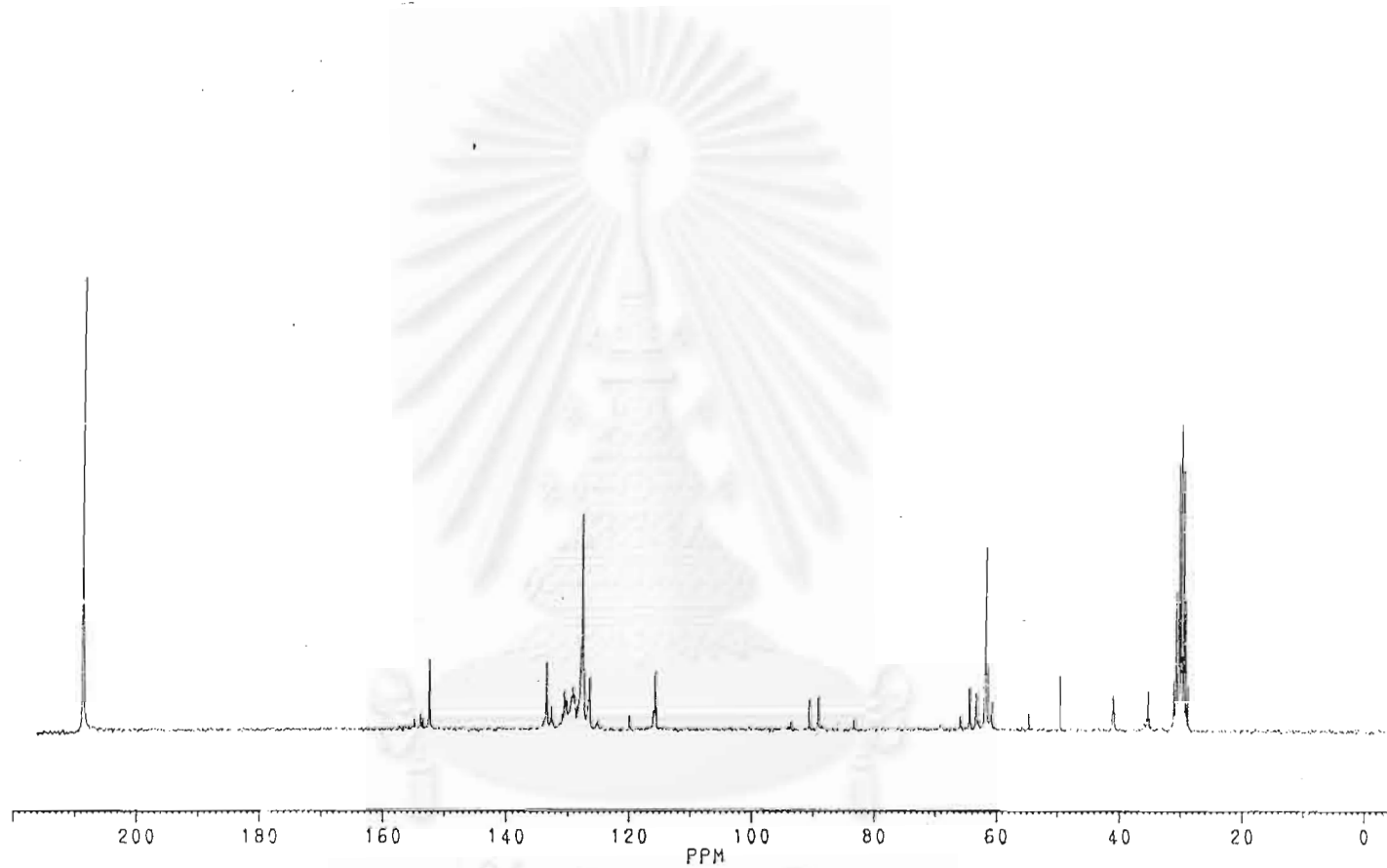


Figure B-2  $^{13}\text{C}$ -NMR of phenol-formaldehyde resin (PF)

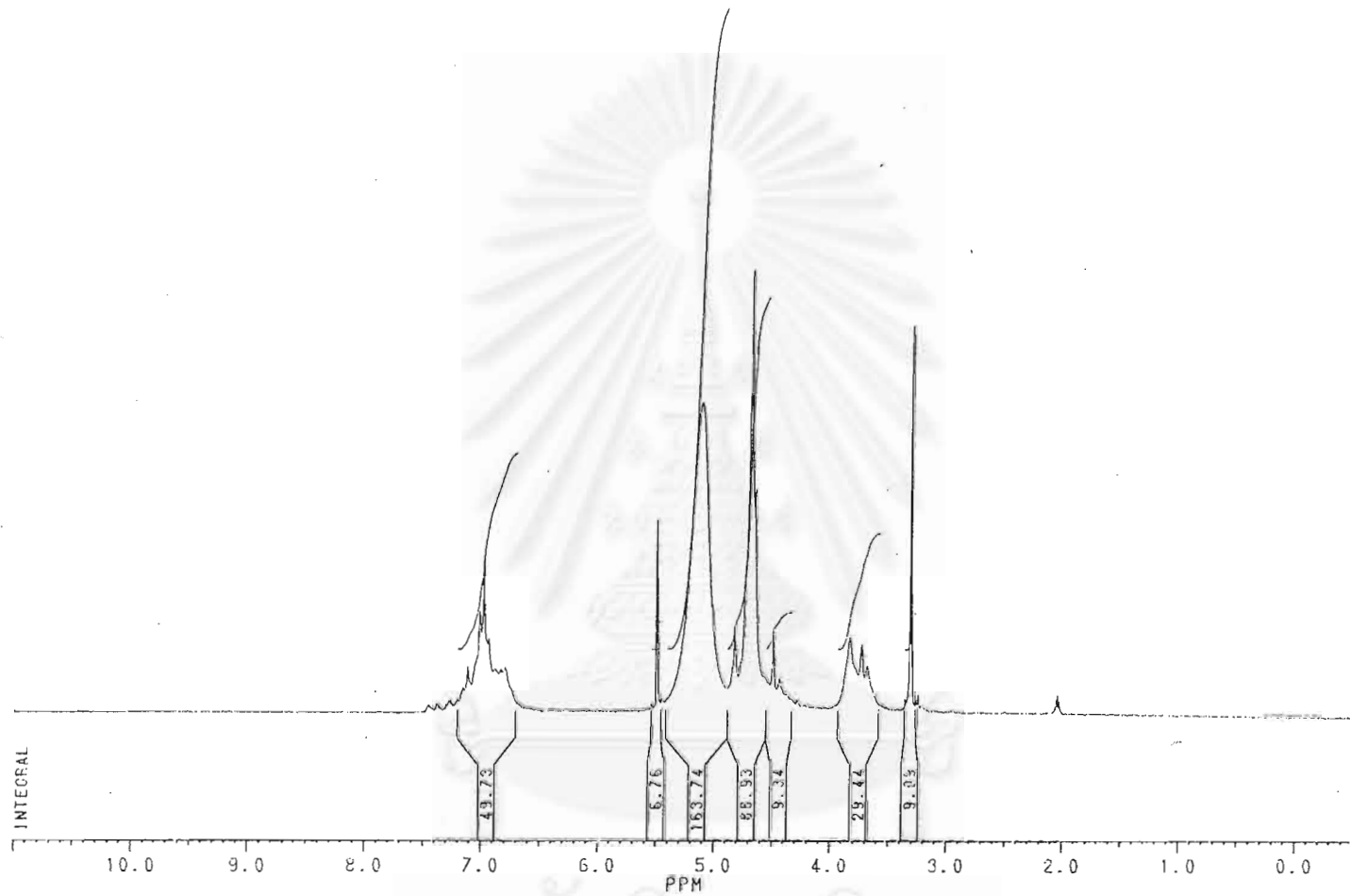


Figure B-3  $^1\text{H-NMR}$  of brominated phenol-formaldehyde resin (BrPF)

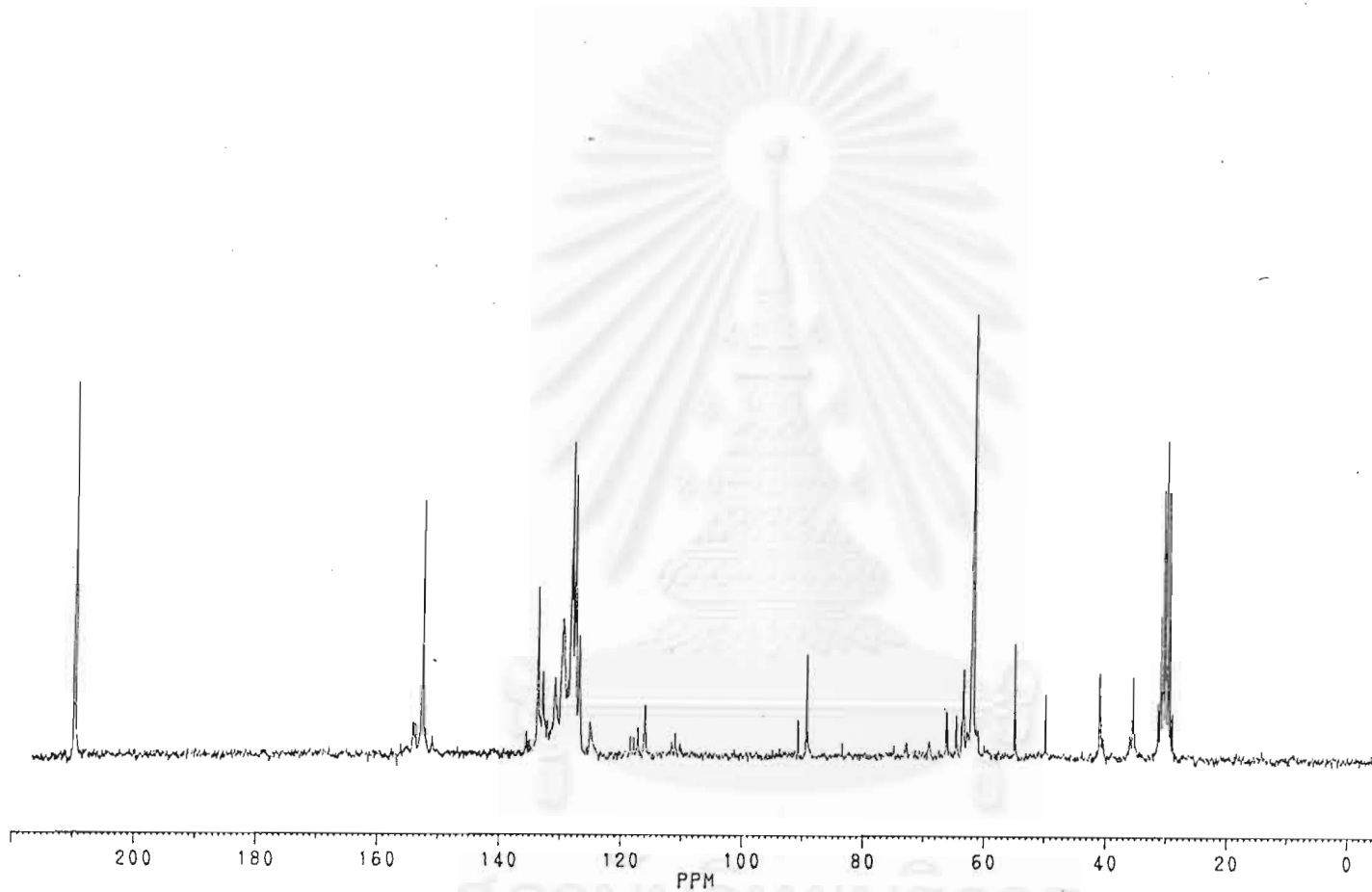


Figure B-4  $^{13}\text{C}$ -NMR of brominated phenol-formaldehyde resin (BrPF)



**APPENDIX C**

**A PLOT OF X-RAY FLUORESCENCE DATA OF PF RESIN  
AND BrPF RESIN**

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Sample: PF  
Fri 1/04/80 at 5:19:24 PM  
Method Name: Supattra

Analyte Concentration Units  
Br 230.44 ppm

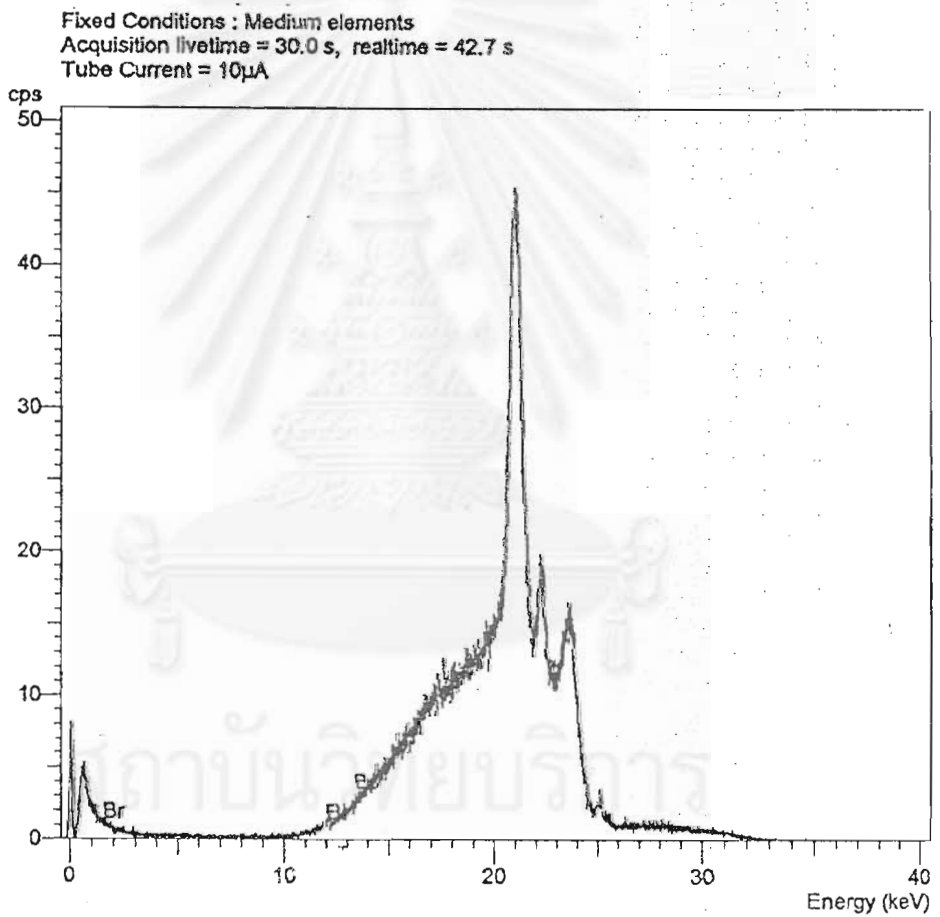


Figure C-1 A plot of x-ray fluorescence (XRF) data of phenol-formaldehyde resin (PF)



Sample: Br1  
Fri 1/04/80 at 5:56:59 PM  
Method Name: Supattra

Analyte Concentration Units  
Br 12.93 Wt %

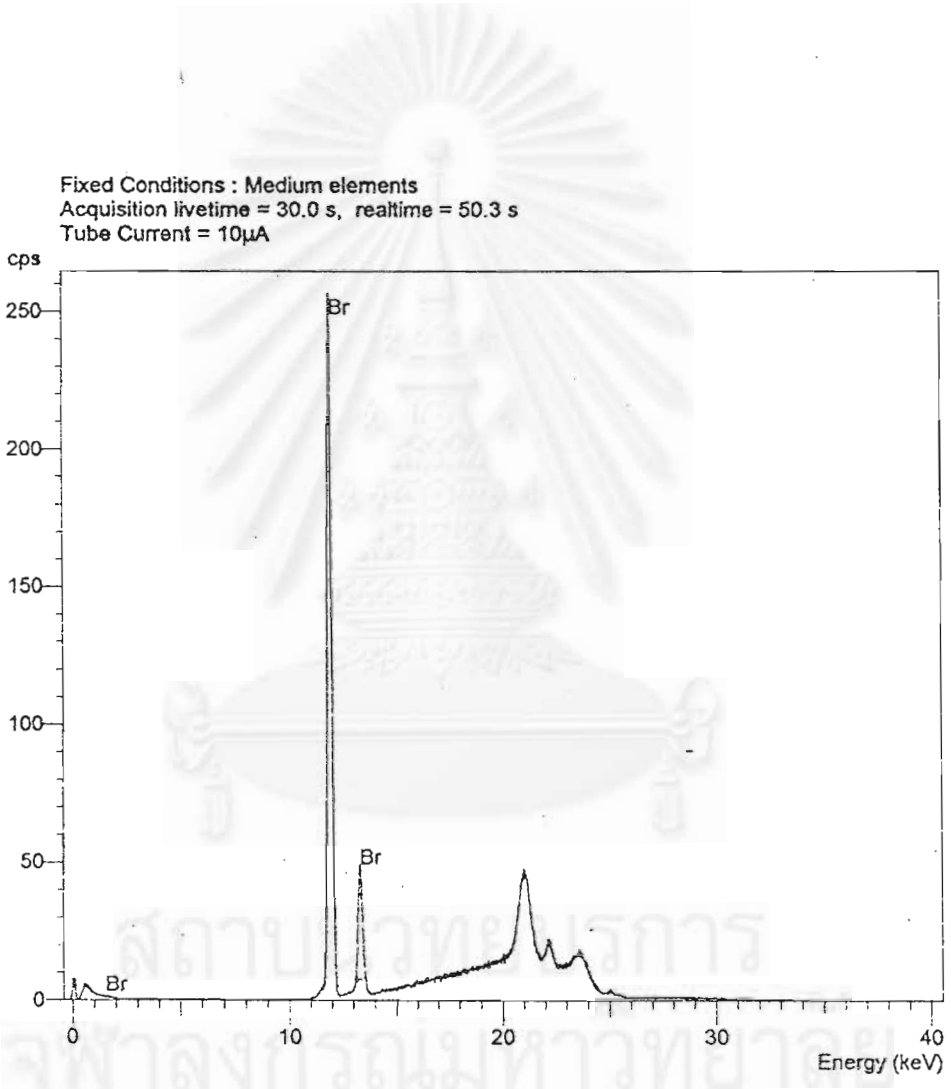


Figure C-2 A plot of x-ray fluorescence (XRF) data of brominated phenol-formaldehyde resin (BrPF) at 1% bromine

Sample: Br5  
Fri 1/04/80 at 5:22:52 PM  
Method Name: Supattra

Analyte            Concentration Units  
Br                    67.85 Wt %

Fixed Conditions : Medium elements  
Acquisition livetime = 30.0 s, realtime = 70.5 s  
Tube Current = 10 $\mu$ A

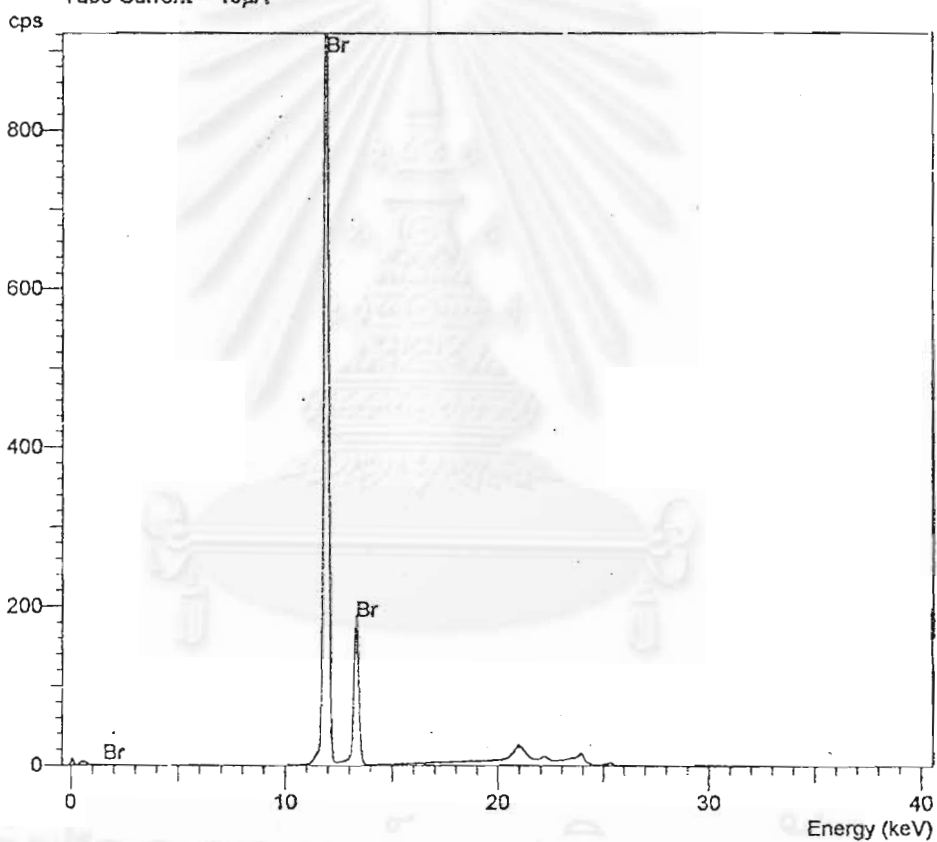


Figure C-3 A plot of x-ray fluorescence (XRF) data of BrPF resin at 5% bromine

Sample: Br 10  
Fri 1/04/80 at 5:31:31 PM  
Method Name: Supattra

Analyte Concentration Units  
Br 75.53 Wt %

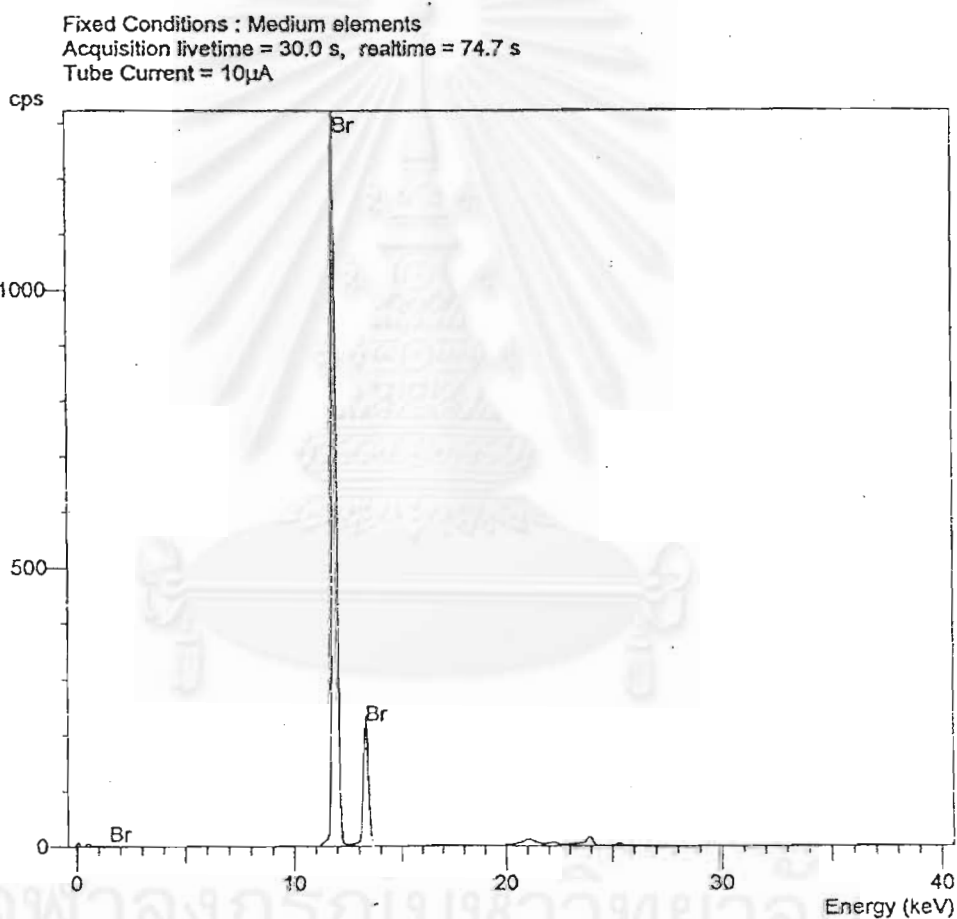


Figure C-4 A plot of x-ray fluorescence (XRF) data of BrPF resin at 10% bromine

Sample: Br15  
Fri 1/04/80 at 5:25:44 PM  
Method Name: Supattra

Analyte            Concentration Units  
Br                    84.36    Wt %

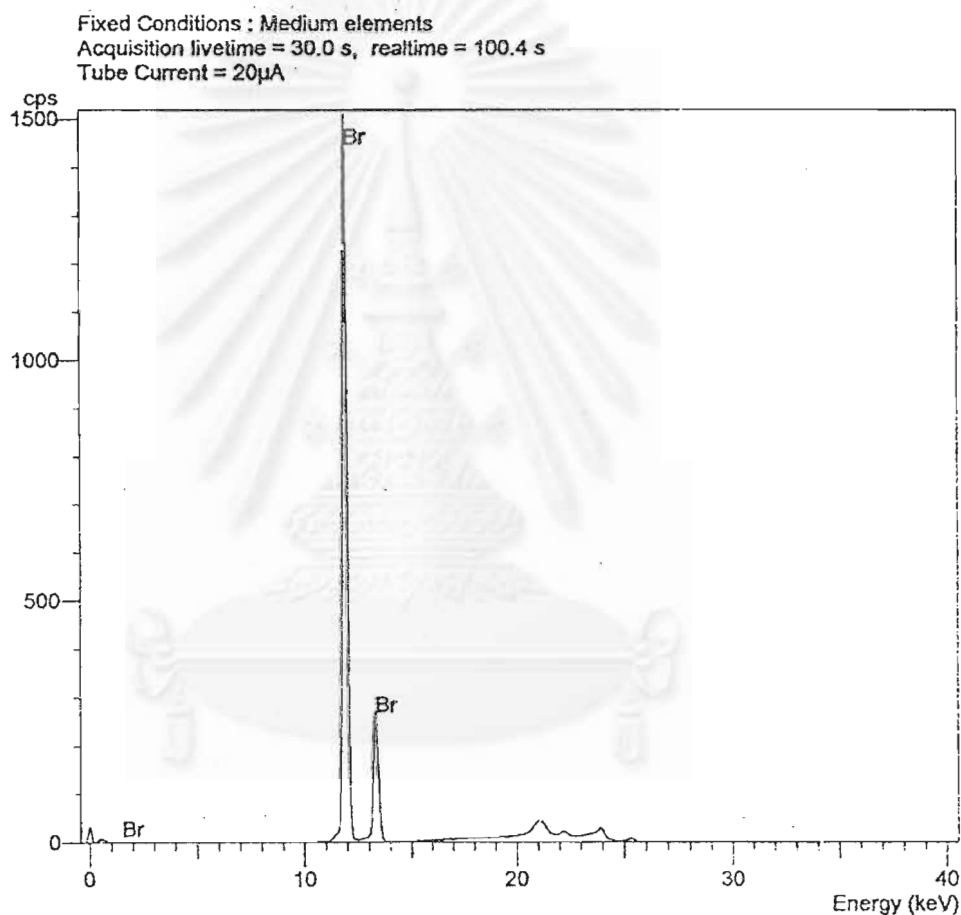
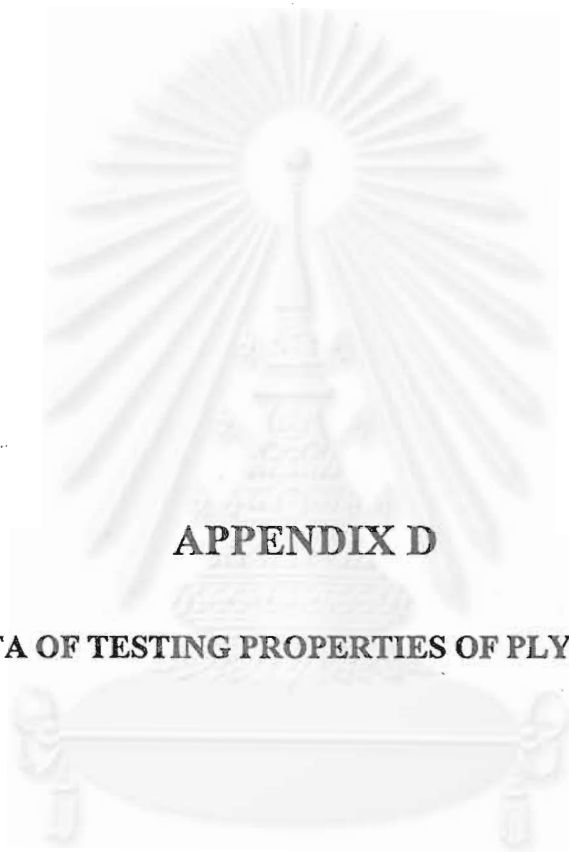


Figure C-5 A plot of x-ray fluorescence (XRF) data of BrPF resin at 15% bromine



**APPENDIX D**

**DATA OF TESTING PROPERTIES OF PLYWOOD**

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**Table D** Processing parameters of plywood using PF resin and BrPF resin as plywood adhesive

Plywood	Plywood adhesive	Bromine content in BrPF (%)	Pressed temperature (°C)	Pressed time (min)	Pressed pressure (psi)
A	PF	0	120	30	1400-1600
B	BrPF	1	120	30	1400-1600
C	BrPF	5	120	30	1400-1600
D	BrPF	10	120	30	1400-1600
E	BrPF	15	120	30	1400-1600
F	BrPF	10	120	10	1400-1600
G	BrPF	10	120	20	1400-1600
H	BrPF	10	120	30	1400-1600

**Table D** Processing parameters of plywood using PF resin and BrPF resin as plywood adhesive (continued)

Plywood	Plywood adhesive	Bromine content in BrPF (%)	Pressed temperature (°C)	Pressed time (min)	Pressed pressure (psi)
I	BrPF	10	120	40	1400-1600
J	BrPF	10	100	30	1400-1600
K	BrPF	10	110	30	1400-1600
L	BrPF	10	120	30	1400-1600
M	BrPF	10	130	30	1400-1600
N	BrPF	10	140	30	1400-1600

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Table D-1 Testing properties of plywood A

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	12.30	6.174	120	190.476	24.60
1/2	10.89	6.185	121	191.722	24.60
1/3	11.60	6.198	118	186.561	24.70
1/4	11.51	5.971	125	205.158	24.50
1/5	11.42	6.175	110	174.574	24.50
$\bar{x}_1$	11.60	6.186	119.67	189.592	24.58
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.21	6.174	102	161.905	24.30
2/2	10.78	6.125	110	176.000	24.30
2/3	13.84	6.175	114	180.920	24.80
2/4	13.65	6.275	134	209.270	24.70
2/5	12.50	6.503	130	195.910	27.70
$\bar{x}_2$	12.31	6.267	118.00	184.276	24.67
average	11.96	6.227	118.84	186.934	24.625
SD	0.355	0.041	0.835	2.658	0.047



Table D-2 Testing properties of plywood B

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	10.45	6.503	130	195.91	25.0
1/2	10.28	6.527	158	237.23	24.8
1/3	10.76	6.401	101	154.632	24.7
1/4	11.63	6.200	125	197.580	24.7
1/5	10.27	6.425	122	179.460	24.8
$\bar{x}_1$	10.50	6.376	125.67	193.134	24.78
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.89	6.174	108	176.00	24.60
2/2	10.10	6.300	111	172.667	24.80
2/3	10.76	6.275	134	209.27	24.80
2/4	11.14	6.075	131	211.325	24.80
2/5	10.41	6.148	121	192.875	24.50
$\bar{x}_2$	10.67	6.199	121.00	192.715	24.80
average	10.59	6.288	123.34	192.925	24.79
SD	0.093	0.088	2.335	0.209	0.290

**Table D-3** Testing properties of plywood C

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	10.67	6.173	134	212.726	26.00
1/2	10.44	6.100	153	245.803	26.20
1/3	10.56	6.349	201	310.250	25.20
1/4	10.32	6.120	171	273.824	26.40
1/5	11.24	6.175	159	252.340	26.30
$\bar{x}_1$	10.56	6.132	161.00	257.212	26.02

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	11.24	6.503	130	195.91	26.30
2/2	11.23	6.527	158	237.23	26.20
2/3	11.11	6.477	214	323.792	26.10
2/4	12.01	6.213	159	250.82	26.60
2/5	12.25	6.225	152	239.29	26.30
$\bar{x}_2$	11.49	6.322	156.33	242.446	26.27

<b>average</b>	11.03	6.227	158.67	249.829	26.15
<b>SD</b>	0.465	0.095	2.335	7.383	0.125

**Table D-4** Testing properties of plywood D

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	12.04	6.024	164	266.800	27.20
1/2	10.80	6.275	190	296.733	27.10
1/3	9.57	6.400	133	203.656	27.30
1/4	9.52	6.225	212	333.750	27.40
1/5	12.33	6.250	176	275.968	27.30
$\bar{x}_1$	10.81	6.183	176.67	279.258	27.25

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	11.33	6.100	145	232.951	27.00
2/2	10.27	6.348	202	311.850	27.60
2/3	10.30	6.225	212	333.750	27.40
2/4	10.06	6.502	168	253.214	27.20
2/5	11.28	6.452	163	247.582	27.00
$\bar{x}_1$	10.62	6.342	177.67	270.882	27.20

average	10.72	6.263	177.17	275.070	27.225
SD	0.095	0.080	0.500	4.188	0.077

**Table D-5** Testing properties of plywood E

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	11.35	6.349	201	310.250	27.40
1/2	9.64	6.452	211	320.489	28.00
1/3	10.49	6.275	190	296.733	28.30
1/4	10.60	6.144	192	306.250	28.20
1/5	11.45	6.477	214	323.792	27.90
$\bar{x}_1$	10.47	6.315	201.33	312.394	27.96
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.51	6.144	194	309.440	28.00
2/2	11.04	6.150	173	275.675	27.70
2/3	12.87	6.348	202	311.850	27.60
2/4	12.57	6.423	212	323.460	27.50
2/5	11.51	6.401	195	298.547	27.90
$\bar{x}_2$	11.71	6.298	197.00	306.612	27.74
average	10.99	6.307	199.17	309.503	27.85
SD	0.52	0.008	2.165	3.383	0.110

Table D-6 Testing properties of plywood F

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	11.50	6.554	53	79.249	27.0
1/2	10.61	6.502	55	82.898	27.4
1/3	10.49	6.528	53	79.565	27.2
1/4	10.55	6.452	56	85.059	27.2
1/5	10.53	6.527	52	78.076	27.2
$\bar{x}_1$	10.55	6.528	53.67	80.571	27.20
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.55	6.197	97	153.397	27.1
2/2	10.47	6.148	121	192.875	27.2
2/3	10.51	6.450	60	91.163	27.0
2/4	10.40	6.165	57	90.608	27.3
2/5	10.35	6.401	51	78.082	27.2
$\bar{x}_2$	10.46	6.270	61.33	95.908	27.16
<b>average</b>	10.51	6.399	57.50	88.240	27.18
<b>SD</b>	0.045	0.129	3.830	7.668	0.020

Table D-7 Testing properties of plywood G

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	10.51	6.452	85	129.107	27.20
1/2	10.65	6.250	79	123.872	27.10
1/3	10.62	6.321	70	108.527	27.20
1/4	10.53	6.300	81	126.000	27.30
1/5	10.55	6.426	90	137.255	27.50
$\bar{x}_1$	10.58	6.334	81.67	126.490	27.23
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.54	6.244	70	109.865	27.10
2/2	10.60	6.003	76	124.071	27.30
2/3	10.43	6.250	85	133.28	27.20
2/4	10.47	6.401	90	137.791	27.30
2/5	10.63	6.199	81	128.053	27.10
$\bar{x}_2$	10.54	6.151	80.67	128.468	27.20
average	10.56	6.243	81.17	127.479	27.22
SD	0.020	0.092	0.500	0.989	0.015

**Table D-8** Testing properties of plywood H

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	10.98	6.300	184	286.222	27.50
1/2	11.38	6.299	179	278.489	27.10
1/3	11.39	6.250	173	271.264	27.10
1/4	10.40	6.426	240	366.013	27.30
1/5	11.38	6.244	171	268.386	27.30
$\bar{x}_1$	11.38	6.249	180.67	278.743	27.23

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.15	6.075	202	325.860	27.30
2/2	9.71	6.172	155	246.111	27.00
2/3	10.45	6.024	168	273.306	27.30
2/4	10.76	6.121	177	283.385	27.20
2/5	11.05	6.144	181	288.704	27.10
$\bar{x}_1$	10.453	6.096	175.33	281.793	27.20

average	10.97	6.173	178.00	280.268	27.22
SD	0.512	0.077	2.670	1.525	0.010

Table D-9 Testing properties of plywood I .

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	11.27	6.300	169	262.889	27.10
1/2	11.44	6.401	195	298.547	27.20
1/3	11.35	6.426	192	292.810	27.40
1/4	11.55	6.375	201	308.988	27.40
1/5	11.23	6.451	165	250.659	27.00
$\bar{x}_1$	11.35	6.375	185.33	284.749	27.23

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	11.30	6.553	184	275.172	27.20
2/2	10.97	6.476	158	239.098	27.20
2/3	11.45	6.451	194	294.714	27.00
2/4	11.33	6.375	188	289.004	27.30
2/5	11.43	6.325	191	295.937	27.40
$\bar{x}_2$	11.35	6.417	187.67	286.704	27.23

average	11.35	6.396	186.50	285.727	27.23
SD	0.000	0.021	1.17	0.977	0.000



**Table D-10** Testing properties of plywood J

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	10.02	6.072	101	163.011	27.10
1/2	10.03	5.976	101	165.629	27.20
1/3	10.05	6.197	114	180.281	27.20
1/4	10.02	6.120	97	155.327	27.30
1/5	10.01	6.051	120	194.348	27.10
$\bar{x}_1$	10.02	6.082	105.33	169.643	27.18
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.03	5.735	73	124.743	27.30
2/2	10.00	5.832	63	105.864	27.20
2/3	9.97	5.664	88	152.259	27.00
2/4	10.02	5.954	100	164.595	27.20
2/5	10.02	5.636	105	182.576	27.10
$\bar{x}_1$	10.01	5.784	87.00	147.199	27.17
average	10.02	5.933	96.17	158.421	27.17
SD	0.005	0.149	9.470	11.222	0.004

Table D-11 Testing properties of plywood K

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	9.27	6.051	149	241.327	27.10
1/2	9.28	6.075	220	354.897	27.20
1/3	9.50	6.148	129	205.628	27.30
1/4	9.61	6.002	223	364.112	27.20
1/5	9.60	6.125	125	200.00	27.20
$\bar{x}_1$	9.56	6.091	166.00	267.284	27.20

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	9.40	5.686	166	286.106	27.20
2/2	10.27	5.686	160	275.765	27.10
2/3	9.45	5.639	151	262.422	26.90
2/4	10.03	5.808	149	251.412	27.20
2/5	9.67	5.617	130	226.811	27.10
$\bar{x}_2$	9.72	5.711	153.33	266.647	27.13

average	9.64	5.901	159.67	266.966	27.17
SD	0.080	0.190	6.335	0.319	0.035

Table D-12 Testing properties of plywood L

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	10.10	6.075	200	322.581	27.00
1/2	9.05	6.097	179	287.715	27.10
1/3	9.73	6.120	209	334.673	27.20
1/4	9.38	6.098	211	339.095	27.30
1/5	9.29	6.350	173	266.992	27.20
$\bar{x}_1$	9.48	6.097	196.00	302.974	27.17

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	8.83	5.954	151	248.539	27.30
2/2	9.97	5.832	187	314.232	27.30
2/3	9.52	6.002	212	346.151	27.20
2/4	8.94	6.000	190	310.333	27.00
2/5	9.38	5.976	172	282.062	27.00
$\bar{x}_2$	9.28	5.936	183.00	302.209	27.17

average	9.38	6.017	189.50	302.592	27.17
SD	0.100	0.657	6.500	0.383	0.003

Table D-13 Testing properties of plywood M

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	9.94	6.273	207	323.386	27.10
1/2	10.06	6.120	180	288.235	27.20
1/3	10.01	6.075	177	285.530	27.00
1/4	9.91	6.144	211	336.555	27.10
1/5	10.11	6.125	169	270.400	27.40
$\bar{x}_1$	10.01	6.156	188.00	299.050	27.16

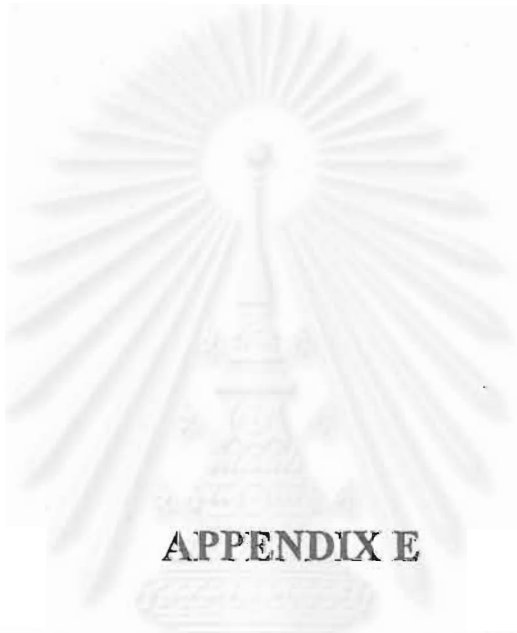
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	10.04	5.617	207	361.154	27.30
2/2	10.15	5.640	153	265.851	27.10
2/3	10.00	5.616	145	253.027	27.20
2/4	9.87	5.443	169	304.281	27.20
2/5	10.10	5.870	173	288.825	27.10
$\bar{x}_2$	10.05	5.651	165.00	286.319	27.16

<b>average</b>	10.03	5.904	176.50	292.685	27.16
<b>SD</b>	0.020	0.253	11.500	6.366	0.000

**Table D-14** Testing properties of plywood N

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	9.37	6.000	176	287.467	27.10
1/2	9.50	6.07	209	337.152	27.20
1/3	9.43	6.135	200	319.478	27.30
1/4	9.66	5.636	232	403.407	27.20
1/5	9.32	5.972	169	277.328	27.10
$\bar{x}_1$	9.46	6.070	195.00	312.309	27.17
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	9.83	5.734	174	297.384	27.20
2/2	8.96	5.764	181	309.348	27.40
2/3	8.66	5.808	217	366.150	27.20
2/4	8.95	5.616	165	287.927	27.00
2/5	9.35	5.617	160	279.153	27.00
$\bar{x}_2$	9.283	5.695	173.33	298.219	27.13
<b>average</b>	9.37	5.883	184.17	305.264	27.15
<b>SD</b>	0.089	0.188	10.835	7.045	0.020



**APPENDIX E**

**DATA OF RESISTANCE TO COLD AND HOT WATER**



จุฬาลงกรณ์มหาวิทยาลัย

## 1. RESISTANCE TO COLD WATER

Resistance to cold water was used to determine the retention in testing properties of plywood after immersing in cold water. The conditions of prepared plywood are shown as follows:

1. Plywood adhesive
  - phenol-formaldehyde resin
  - brominated phenol-formaldehyde resin at 10% wt bromine content of PF resin
2. Compressing temperature 110°C
3. Compressing time 30 min
4. Pressure 1400-1600 psi

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**Table E-1** Resistance to cold water data of plywood at using PF resin

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	13.46	6.300	111	172.667	24.10
1/2	13.77	6.325	101	156.240	24.00
1/3	13.62	6.098	75	120.531	24.20
1/4	13.40	6.123	84	134.44	24.10
1/5	13.79	6.452	90	136.702	23.90
$\bar{x}_1$	13.62	6.300	91.67	142.23	24.13
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	13.65	5.683	74	127.610	24.20
2/2	13.84	6.174	96	152.380	24.00
2/3	13.57	6.250	87	136.416	24.00
2/4	13.63	6.197	97	153.697	24.10
2/5	13.46	6.075	82	132.279	24.00
$\bar{x}_2$	13.62	6.166	88.33	140.358	24.03
<b>average</b>	13.62	6.233	90.06	141.294	24.08
<b>SD</b>	0.000	0.067	1.670	0.936	0.050



**Table E-2** Resistance to cold water data of plywood at using BrPF resin

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	12.83	6.300	170	164.444	25.80
1/2	12.28	6.553	130	194.415	25.90
1/3	12.55	6.350	158	243.843	26.10
1/4	13.00	6.502	170	253.214	26.10
1/5	12.26	6.300	155	241.111	25.70
$\bar{x}_1$	12.55	6.384	161.00	245.790	25.96
Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	12.67	6.003	136	222.022	25.70
2/2	12.53	6.172	155	246.111	25.50
2/3	12.70	6.075	145	233.909	26.20
2/4	12.31	6.051	149	241.327	26.00
2/5	12.65	6.300	169	262.889	25.80
$\bar{x}_2$	12.62	6.099	149.67	240.449	25.84
average	12.59	6.242	155.34	243.120	25.90
SD	0.035	0.143	5.665	2.671	0.060

## 2. RESISTANCE TO HOT WATER

Resistance to hot water was used to determine the retention in testing properties of plywood after immersing in hot water. The conditions of prepared plywood are shown as follows:

### 2. Plywood adhesive

- phenol-formaldehyde resin
- brominated phenol-formaldehyde resin at 10% wt bromine content of PF resin

- |                            |               |
|----------------------------|---------------|
| 2. Compressing temperature | 110°C         |
| 3. Compressing time        | 30 min        |
| 4. Pressure                | 1400-1600 psi |

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**Table E-3** Resistance to hot water data of plywood at using PF resin

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	13.65	6.018	84	136.789	24.20
1/2	13.84	6.120	78	124.902	24.10
1/3	13.75	6.297	64	99.603	24.00
1/4	13.87	6.273	74	115.607	24.10
1/5	13.63	6.250	79	123.872	23.90
$\bar{x}_1$	13.75	6.214	77.00	121.370	24.05

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	13.81	6.503	60	90.419	24.00
2/2	13.62	6.527	68	102.099	24.10
2/3	13.76	6.401	71	108.702	23.90
2/4	13.88	6.350	84	129.638	23.90
2/5	13.69	6.451	75	113.935	24.10
$\bar{x}_2$	13.75	6.459	71.33	108.246	24.00

<b>average</b>	13.75	6.337	74.17	114.808	24.03
<b>SD</b>	0.000	0.122	2.835	6.562	0.025

**Table E-4** Resistance to hot water data of plywood at using BrPF resin

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
1/1	13.42	6.300	145	225.556	25.80
1/2	14.07	6.553	130	194.415	25.50
1/3	13.75	6.350	155	239.213	25.30
1/4	13.25	6.452	163	247.582	26.00
1/5	14.13	6.553	120	179.460	25.60
$\bar{x}_1$	13.76	6.401	143.33	219.726	25.66

Piece/sample number	Moisture content	Shear strength			LOI value
		Shear area (cm <sup>2</sup> )	Load at failure (kg)	Shear strength (N/cm <sup>2</sup> )	
2/1	13.80	6.451	147	223.314	25.60
2/2	13.69	6.527	149	223.717	25.50
2/3	14.02	6.300	132	205.333	25.70
2/4	13.48	6.553	130	194.415	25.50
2/5	13.77	6.527	158	237.230	25.30
$\bar{x}_2$	13.75	6.426	142.67	217.455	25.52

<b>average</b>	13.76	6.414	143.00	218.591	25.59
<b>SD</b>	0.010	0.012	0.330	1.136	0.070

## VITA

Miss Supattra Hanphichanchai was born on April 30, 1977 in Bangkok. She received her Bachelor's degree in Chemistry from the Faculty of Science, Mahidol University in 1998. After that, she continued her Master study in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 1998 and she completed it in 2001.



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