A Modified Starch Adhesive

Miss Pattama Sirichanya

Miss Prairaya Somanandana

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Name Miss Pattama Sirichanya Id.45050647
Miss Prairaya Somanandana Id.45050651

Faculty Science

Program Petrochemical Technology

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Special Project Advisor Asst.Prof.Dr. Vanchat Chuenchom

ABSTRACT

Wood adhesives were prepared from starch and PVA using glutaraldehyde as crosslinking agent. The starch and PVA were blended in the ratios of 0:100, 20:80, 50:50, 80:20, and 100:0. Adhesive solutions were then mixed with varied percentages of glutaraldehyde from 26.8%, 33.9% to 42.2% by weight of solid content. Siamese Sal was cut into 44.4 mm × 50.8 mm × 19 mm in dimension as wood blocks. Two wood blocks were used to make a wood specimen. One gram of adhesives was applied on one side of a wood block within the glue line then attached another block and placed in the oven. The curing time was 24 hours and curing temperature was 80°C. The crosslinking agent, glutaraldehyde (GA) is a sufficient crosslinker through condensation reaction between CHO-groups of GA and OH-groups of starch, PVA and wooden surfaces. Via this reaction, water is released. Wood specimens were subjected under compression loading. The appropriate blending ratio between starch and PVA is 20% to 80% by solid weight. Addition of starch into the solutions resulted in the reduction in adhesion strength of plywood joint. The optimal percentage of glutaraldehyde is 26.8% by weight of solid content. Increasing in the amount of crosslinking agent probably cause brittleness in adhesives matrix.

ACKNOWLEDGEMENT

We would like to say our words of gratitude to all those that means world to us.

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Pattama Sirijanya
Prairaya Somanandana

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Chapter I
Introduction

1.1 Motivations

At present, plywood industries are one of the major industries that value to the nation's trade. The region total consumption of plywood rose from about 11 million m^3 in 1982 to 19 million m^3 in 1992, an increase of 67%. Meanwhile, its world share also increases from 30% to 41% as a response of fast demographic and economic growth [1]. In South East Asia, especially Thailand, the production of wood in year 2001 was estimated at 41.3 million m^3 (1.46 billion ft^3). However, Thailand now exports primarily value-added wood products (mostly furniture, picture frames, utensils, and other items). Exports of wood products in 2000 totaled $805.9 million [2].

Plywood industry depends greatly on extremely large amount of adhesives. They play a prominent role in wood construction [3]. They are used for:

- The manufacture of laminated products
- As a mean of increasing the structural rigidity of sheathing/joist combinations in floors and of affixing non-structural panel products
- End joining dimension lumber
- Repair

Adhesives are divided into various types depend on the usage selection. Structural composites such as plywood, oriented strandboard (OSB) and wafer-board, prefabricated wood I-joists, laminated parallel strand lumber (PSL), laminated veneer lumber (LVL) and glulam are dependent upon adhesives to transfer the stresses between adjoining wood fibre [3].

There are two principle types of adhesive used for the manufacture of plywood. These are urea-formaldehyde (UF) which is suitable only for interior use products and phenol-formaldehyde (PF) which is used for exterior applications. The raw materials for UF adhesives are derived from natural gas through the intermediates of ammonia for urea and methanol for formaldehyde. UF adhesives are very economical and fast curing but are not suitable for damp conditions. For this reason, UF glues are used for panels intended for nonstructural use such as particleboard and hardwood plywood. UF adhesives are non-staining, and therefore have the further advantage of not blemishing the high quality expensive face veneers used for hardwood panels for interior finish applications. However, the release of formaldehyde is considered a priority pollutant and toxic to an environment [3].

Phenol-formaldehyde (PF) adhesives are a dark purple-brown colour and give the dark glue lines associated with products such as plywood and OSB. Known as the phenolics, they are a derivative of crude oil and the principle resins approved for the manufacture of wood products intended for exterior applications. PF adhesives are used for the manufacture of glulam, PSL, LVL, plywood, OSB/ waferboard and for fingerjoining stress graded lumber. PF adhesives are somewhat more expensive than UF adhesives and exhibit lower levels of formaldehyde emissions. Various types of extenders are used to moderate the cost of PF glues, control penetration into the wood fibre, and moderate strength properties to suit the materials being bonded [3].

According to the advantages and disadvantages of these commercial adhesives, the development of cheaper environmental friendly water-based adhesives that fit manufacture's demand would be of interest. The use of Tapioca starch as modified natural adhesives is one of the most promising choices, and has been studying by many researchers nowadays.

Starch is a renewable polymer derived from nature [6]. It is high purity carbohydrate, obtains from plant photosynthesis that main operators are carbon dioxide (CO_2), water, chlorophyll, and light [7]. According to this, starch would not cause further pollution since it begins with CO_2 which is the reduction of greenhouse effect. Since starch is soluble in water, it acts as a so called "water-based adhesive". The term means it is made up of materials or compounds that can be dissolved or dispersed in water and the carrier is primarily water [8]. This kind of adhesive generally develops a bond by losing water through evaporation or penetration into the substrates. So, at least one substrate must be absorbent or porous in order to form a strong bond [9]. For discarding, starch adhesive remains within furniture pieces and would burn into CO_2 that it started with. Because of this, starch out-advantages all commercial adhesives by its non-toxicity. This environmental friendly characteristic becomes crucial to the industry when consider mass production.

Apart from their advantages, natural adhesives are generally known to have low strength and high sensitivity to moisture and mould. Consequently, their use is restricted to the joining of low strength materials [5]. Moreover, under extreme conditions, these natural adhesives typically lack of durability especially for wood-to-wood bonding [6]. Chemical modifications of starches have been studied in great details. In recent years, there are numbers of authors reported on the variety of preparations of starch that can apply to many uses such as a thickener, gelling agent, bulking agent and water retention agent [4].

On previous research by Syed H. Imam and his co-workers, their wood adhesive was prepared by mixing starch with PVA and crosslinking agent, Cymel 323 (hexamethoxymethylamine). This Cymel 323 is effective through tranesterification reaction between methoxy groups in Cymel 323 and hydroxy groups in starch, PVA and wood where hydroxy groups replaced methoxy groups forming ether bonds with the crosslinker [6]. Their results exhibited high strength of wood joint samples with water-resistance and no visible growth of fungi.

In this work, we investigated on similar basis. The experiments were carried out using a different crosslinking agent, component percentages and conditions. Our study concerned on improved properties of studied adhesives to match the commercial latex, with comparable price. Crosslinking was done by mixing PVA or starch with glutaraldehyde, instead of cymel 323 (hexamethoxymethylamine), for price reduction. All components proportion was also varied to study an adhesion trend, and to adjust wood adhesion ability.

1.2 Objectives

1) Investigate the strength of wood joint samples using commercial latex, PVA, and starch solution as adhesives.

2) Investigate the effect of starch/PVA ratios in adhesives to the strength of wood joint samples.

3) Investigate the effect of the percentages of crosslinking agent, glutaraldehyde, in starch adhesives to the strength of wood joint samples.

4) Study on an appropriate amount of PVA and crosslinking agent to be blended in adhesives in order to improve some of starch adhesive's characteristics and properties.

1.3 Scopes

1) Prepare and test the strength of wood joint samples using 6.83g/100ml of PVA, starch solution, and commercial latex as adhesives.

2) Blend 26.8%, 33.9% and 42.2% dry weight of glutaraldehyde by dry weight of adhesives into PVA solution and starch solution prepared in part1, in order to study the effect of the amount of crosslinking agent.

3) Blend starch and PVA together by altering both of their percentages from 0% to 100%, followed by adding up 26.8%, 33.9% and 42.2% dry weight of glutaraldehyde into each samples to find suitable starch to PVA ratios.

4) Compression loading test following ASTM D 905-89 method.

1.4 Expected results

1) Capable of manufacture a good quality plywood from modified starch adhesive.

2) Capable of manufacture a new water-based natural adhesive in which also environmental friendly, with an improved adhesive strength to match those in the market, along with some properties yet comparable cost as an alternative to all applications, particularly, for wood adhesives.

3) Capable of reduce the cost of plywood.

Chapter II
Theory

2.1 Adhesives [5, 10]

An adhesive is a substance that fastens or bonds materials using surface attachment and can also provide a sealing function. The mechanism of adhesion has been investigated and several theories have been purposed in an attempt to provide an explanation for adhesion phenomena. However, no single theory can explain adhesion in general.

Advantages in using adhesives compared to other fastening methods

- Fatigue, there are a few stress concentrations associated with adhesive joints.
- Surface area for a lap joint the stress is distributed over a large area. This provides a strong joint with lower specific stress.
- Adhesive joint provide a sealing function in addition to a fastening function.
- No high temperature requires compared to welding.
- Wide variety of different materials can be attached.
- Compared to bolted joints and riveted joints, there is less need for mechanical holes and additional machined components.
- There is no weight penalty associated with adhesive joints.
- The stresses developed in an adhesive joint are almost entirely imposed by the operating conditions.

Limitations of adhesive

- Certain adhesives are vulnerable to attack by chemicals and water.
- Surface preparation is needed.
- Some adhesives require time to achieve design strength.
- Many adhesives have temperature limitation.
- Many adhesives are toxic and require care when being applied.
- Adhesive joints are often vulnerable to localized high stress due to peeling effect.

2.1.1 Adhesion theories [10, 11]

The bonding of an adhesive to an object or a surface is the sum of a number of mechanical, physical, and chemical forces that overlap and influence one another. As it is not possible to separate these forces.

2.1.1.1 The mechanical interlock theory

The simplest theory and is based on scope of all surfaces are very rough consisting of cracks, crevices, pores or other irregularities. The adhesives penetrate and harden as key-like then mechanically lock to the surface and form bonds. The adhesive must not only wet the substrate, but also have the right rheological properties to penetrate pores. However, the limitation is the adhesive strength.

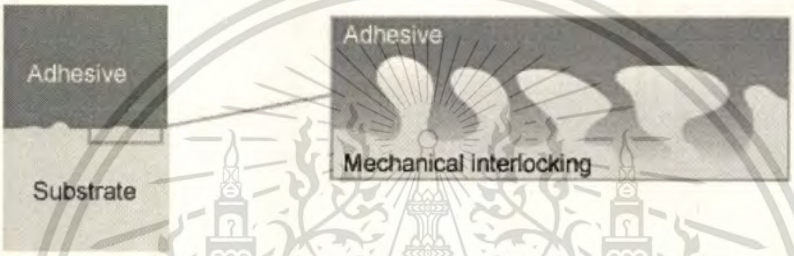


Figure 2.1 Key-like mechanical lock [10]

2.1.1.2 The diffusion theory

This can be viewed as molecular interlock adhesion. When an adhesive contains adherent solvent, the adhesive can diffuse into the adherent surface (substrate) with an interchange of molecules. The theory requires both of adhesive and adherent are polymers which bring about its limitation where the polymer and adherent are not soluble, or the chain movement constrains by its highly crosslinked, crystalline structure and at below glass temperature. Polarity generally increases adhesion.

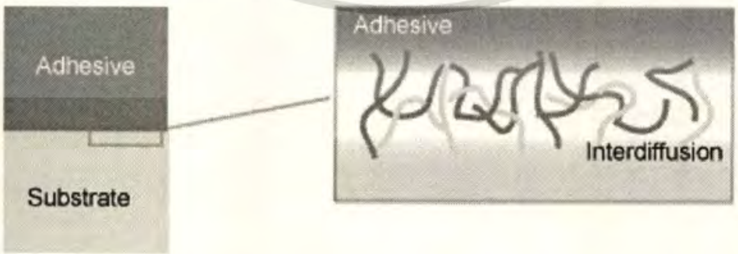


Figure 2.2 Molecular interlock between connecting surfaces [10]

2.1.1.3 The adsorption theory

Based on assumption that adhesive wets (applied to the adherent spreads spontaneously when the join is formed) the surface. Adhesion resulted from intimate intermolecular contact between adhesive and adherent. According to this theory, at intimate contact between the adhesive and adherent, the adhesive strength arises as a result of interfacial secondary intermolecular forces at the interface. These may include Van Der Waals forces –dipole-dipole, dipole-induced dipole interactions and hydrogen bonds. Adhesive materials being developed have lower surface tension than the adherent surface.

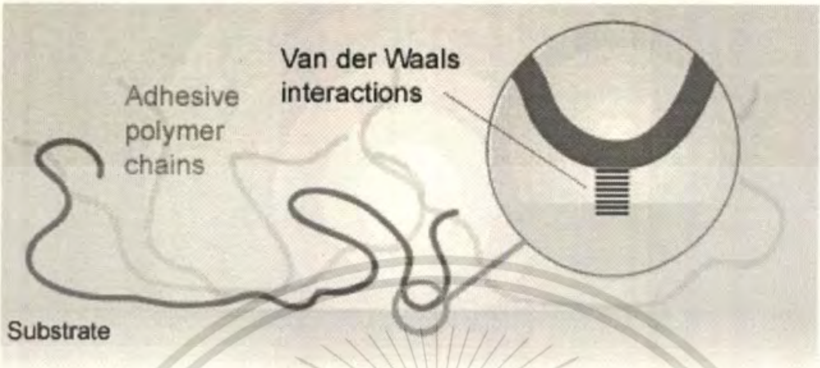


Figure 2.3 Intermolecular contact between adhesive and adherent [10]

2.1.1.4 The chemisorption theory

This is a variation on the adsorption theory in that stronger primary chemical bonds (ionic, covalent, metallic) form across the joint interface. The introduction of molecular bonding between the adhesive and adherent obviously improve the adhesive strength cause by reactions at the surfaces, using proper surface treatments, or using additional coupling agents.

Figure 2.4 Chemisorption at joint surfaces [10]

2.1.1.5 The electrostatic theory

The basis of the electrostatic theory of adhesion is the difference in electronegativities of adhesing materials. Adhesive force is attributed to the transfer of electrons across the interface creating positive and negative charges that attract one another. It has been identified that no change in adhesion performance results with gross variations in electronic character of the adhesives. Also, improved adhesion strengths with lowering the temperature for a large number of adhesive systems (lower temperature should result in poorer electrostatic forces).

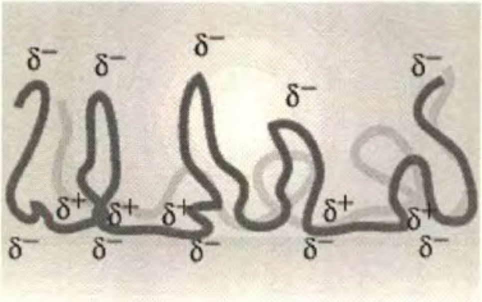


Figure 2.5 Electronegativities differences attract one another [10]

2.1.1.6 The weak boundary layer theory

For most metals, there is a surface layer and for successfully bond this layer is ideally removed by surface treatments before a strong adhesive bond can be achieved.

2.1.2 Types of adhesives [5, 10]

2.1.2.1 Natural adhesives

Generally set by solvent evaporation. They are given low strength and are susceptible to moisture and mold. Their use is restricted to the joining of low strength materials. Natural adhesives include:

- Animal glue
- Starch based vegetable glue
- Soybean glue
- Casein glue
- Inorganic adhesive

2.1.2.2 Elastomer adhesives

Based on natural and synthetic rubbers set by solvent evaporation or heat curing. They have relatively low shear strength and suffer from creep and are therefore used for unstressed joints. They are useful for flexible bonds with plastics and rubbers. Elastomer adhesives include:

- Natural rubber (NR)
- Styrene butadiene styrene (SBS)
- Styrene butadiene rubber (SBR)
- Butyl rubber (IIR)
- Reclaim rubber
- Chlorinated rubber (CR)
- Nitrile rubber (NBR)

- Polyurethane (PU)
- Polychloroprene (neoprene)
- Polysulfide (PSR)
- Silicone (Si)

Note: Polyurethane has been included as rubber like adhesive. It can equally be considered as a thermosetting adhesive.

2.1.2.3 Thermoplastic adhesives

They have low to medium shear strength and may suffer from creep at high loading. They have good resistance to oils but poor resistance to water. Thermoplastic adhesives include:

- Acrylic
- Asphalt
- Polyamide (PA)
- Polyvinyl acetate (PVAc)
- Polyvinyl alcohol (PVA)
- Polyarylate
- Polyester acrylics
- Acrylic solvent cement
- Ethylenevinyl acetate copolymer (EVA)
- PVC plastisols
- Silicone resins
- Acrylic acid diesters

2.1.2.4 Thermoset adhesives

Set as a result of the build up of molecular chains to produce a rigid crosslinked structure. There are included epoxy resins, which are some of the most widely used adhesives. Thermoset adhesives include:

- Epoxy (Ep)
- Superglue or Cyanoacrylate (Cy)
- Phenol resorcinol formaldehyde (PRF)
- Phenol formaldehyde (PF)
- Phenolic neoprene
- Saturated polyester (SP)
- Unsaturated polyester (UP)
- Urea formaldehyde (UF)
- Melamine formaldehyde (MF)
- Polyimides

2.1.2.5 Toughened adhesives

They have small, rubber-like particles dispersed throughout the glassy matrix. The profound effect of these particles is to change the mechanical characteristics of the adhesive making it much more resistant to crack propagation. This technology has only been successfully applied to the acrylic and epoxy-based adhesives.

2.1.3 Factors that influence the adhesion [5]

There are accepted conditions which resulted in higher adhesive bond strengths. First, cleanliness of surfaces, the bond surface is ideally cleaned of loose matter and also surface oxides and adsorbed gases. Second, the choice of adhesive should be that it wets the adherent surface and also solidifies under an acceptable regime of time, temperature and pressure. The differences in coefficient of therma expansion between the adhesive and adherent can have an important effect on the joint design, working over a significant temperature range. Nevertheless, the following factors are predominant in the adhesion process:

2.1.3.1 Wetting of the surface [10]

To enable the adhesives bond between the adhesive and the surface, the adhesive must first be wet the surface (it must be applied in the liquid form; as a solution, dispersion or hot-melt).

A measure of wettability of a surface is the angle of contact between a drop of liquid and a surface. A good wetting, the angle of contact (θ) is inferior to 90. The contact surface formed during wetting depends on the surface tension, the viscosity of the adhesive, and also on the structure (shape and size of the pores) of the surface. The size of the effective surface is generally smaller than the true surface of the substrate, because the pores and uneven parts of the surface are not completely filled by the adhesive. Pressure may also help enhance the adhesion. Generally, bonds that have been set under pressure have higher adhesive strength. Pressure imparts better wetting and consequently a more complete interfacial contact. The viscosity of the adhesive is critical to wetting. It is obvious to say that the rheological properties of the adhesive must adapted to the application conditions (substrate's surface, curing time, pressure, temperature).

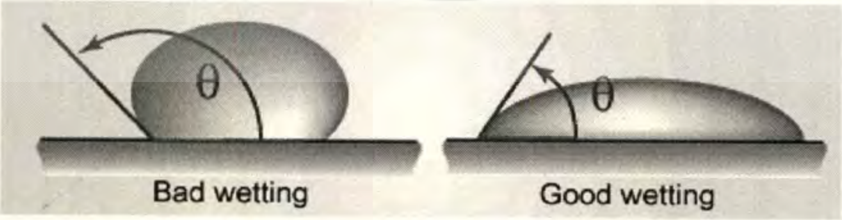


Figure 2.6 Wetting surface [10]

2.1.3.2 Surface treatment / preparation [5]

All surfaces exposed to the normal atmosphere under go gas and water absorption, and can also be changed by oxidation processes. It is necessary to ensure that the substrate surfaces of the components being attached are suitably prepared. For all adhesive joints the minimum surface preparation is to clean the surface such that all loose substrate and grease is removed. The surface to be joined should be flat, some adhesives are more capable of filling spaces, but the flatter the surface the stronger the joint. The important surface preparation routines:

- Degreasing with steam, organic solvents or alkaline cleaners
- Mechanical methods such as blasting, brushing or grinding with emery-paper
- Dipping in boiling water after etching in caustic soda
- Yellow or green chromate treatment
- Anodizing in chromic, phosphoric or sulfuric acid
- Applying a suitable primer

2.1.3.3 Structure of the materials [10]

Besides the surface condition, the structure of the materials to be bonded is also of the decisive important. For example, porous materials absorb low viscosity adhesives. The molecular structure of the adhesive is decisive for the cohesion and interconnection with the surface condition for the adhesion. The principal molecular influencing factors are the molecular weight and the distribution of the molecular weight, number and site of the side-groups, and the polarity

The macromolecules acting as an adhesive are either produced by a preceding polyreaction then applied in the liquid form (solution, dispersion, or hot-melt) to the adherent, or they are produced by polyreaction of reactive low-molecular compounds in the glue line direct. In the case of adhesives produced by preceding polyreaction, the molecular weight must not be infinitely high (viscosity and solubility depend on the molecular weight). With adhesives produced by polyreaction of reactive low-molecular compounds, it is frequently a desired objective to achieve a high molecular weight which is often obtained by crosslinking reactions. The higher the molecular weight the higher tensile strength of polymers, which is measure for the cohesion.

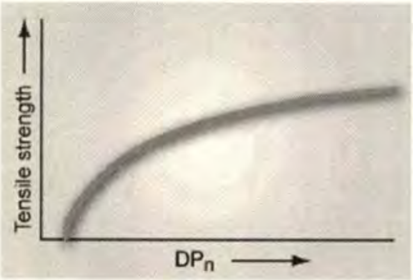


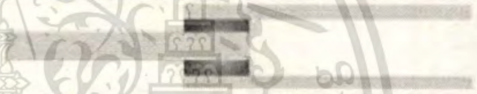
Figure 2.7 Tensile strength (TS) of a polymer as a function of the degree of polymerization DP (n) [10]

2.1.3.4 Structure of the joint [5, 10]

The strength of adhesive joint depends on the strength of attachment of the adhesive to the material surface (substrate) termed "adhesion", and the strength of adhesive termed "cohesion"

Care must be taken to provide a sufficiently large bonded area, such as a large area of overlap of the mating parts. The ideal bonded joint is one under all practical loading conditions. The adhesive is stressed in the direction in which it most resists failure. Favorable stress can be applied to the bond by using proper joint design. Bonded joints are particularly vulnerable to peeling stress and should, therefore always be designed in such a way that the applied force do not give rise to stress of this type.

Table 2.1 Tensile shear stress and stress induced by shear force [10]

Tensile shear stress	
	
Butt joint = unfavorable	Simple butt joint = favorable
	
Beveled joint = very favorable	Double-strap butt joint = favorable
	
Shouldered double-strap butt joint = favorable but labor-intensive	Double overlap = favorable
Stress induced by shear forces	
	
Pure peeling stress = unfavorable	Tensile peeling stress = very unfavorable
	
Transformation into tensile and compressive stress = favorable	Transformation into tensile shear stress = favorable
	
Combined rolling and peeling stress = very	Transformation into tensile and compressive

<table>
<tr><td>unfavorable</td><td>stress = favorable</td></tr>
<tr><td colspan="2"></td></tr>
<tr><td colspan="2">Reinforcement = favorable</td></tr>
</table>

However, some joints design may be impractical, expensive to make or hard to align. The design does often have to weigh these factors against optimum adhesive performance.

2.2 Starch [7]

Starch is carbohydrate, polysaccharides contain many -OH groups, consist mainly of carbon, hydrogen and oxygen in the ratio of 6: 10: 5. The general formula is $(C_6H_{10}O_5)_n$. Carbohydrate is glucose polymer consist of glucose units connect by glucosidic linkage at the first carbon position at the end of polymer chain contains aldehyde group called "reducing end group". Carbohydrate composes of two types of glucose polymers: one is linear polymer, Amilose, another one is branch chain, Amilopectin.

In general, "starch" refers to high purity of carbohydrate while the word "flour" means that carbohydrate contains high percent of contaminants such as protein, fat and mineral. Due to starch has high purity, starch that not yet alter call "raw starch" or "native starch". In contrary, starch that has been treated called "modified starch".

2.2.1 Structure and combination of starch granule

In nature, starch found as granule. When observe with a microscope and scanning electron microscope we found that, starch granules have different size, shape and appearance depend on sources.

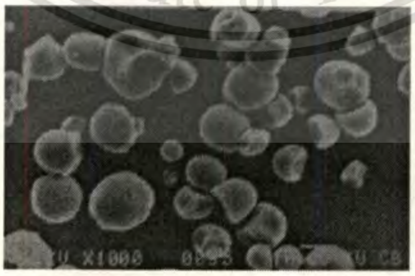


Figure 2.8 SEM image of Tapioca starch [7]

2.2.1.1 <u>Water absorption, inflation and solubility</u> [7, 8]

Water amount absorb depend on temperature and relative humidity. Water stays in 3 different forms; water in crystalline, bound water and free water.

Combining strength between starch granules and water is respectively. Furthermore, 8 to 10% moisture starches hold tighter than ones that contains higher moisture percent.

Raw starch would not dissolve in water lower than gelatinization temperature due to close proximity of hydroxyl group created hydrogen bond that link in carbohydrate molecule. Therefore, whenever temperature reach higher than gelatinization temperature, hydrogen bond will break and water molecule comes closer to bind with unattached hydroxyl group. Then starch granules swell when heat in excess water, and their volume fraction and morphology play important roles in behavior of starch dispersions. The gelatinization process occurs by which the internal structure of the granule is broken down and the whole granule decomposes and releasing the polysaccharide into surrounding medium, accompanied by the variety of changes. Being semi-crystalline, the granule exhibits birefringence when viewed between crossed polar. This birefringence is lost as the starch granules gelatinize and their structure is disrupted.

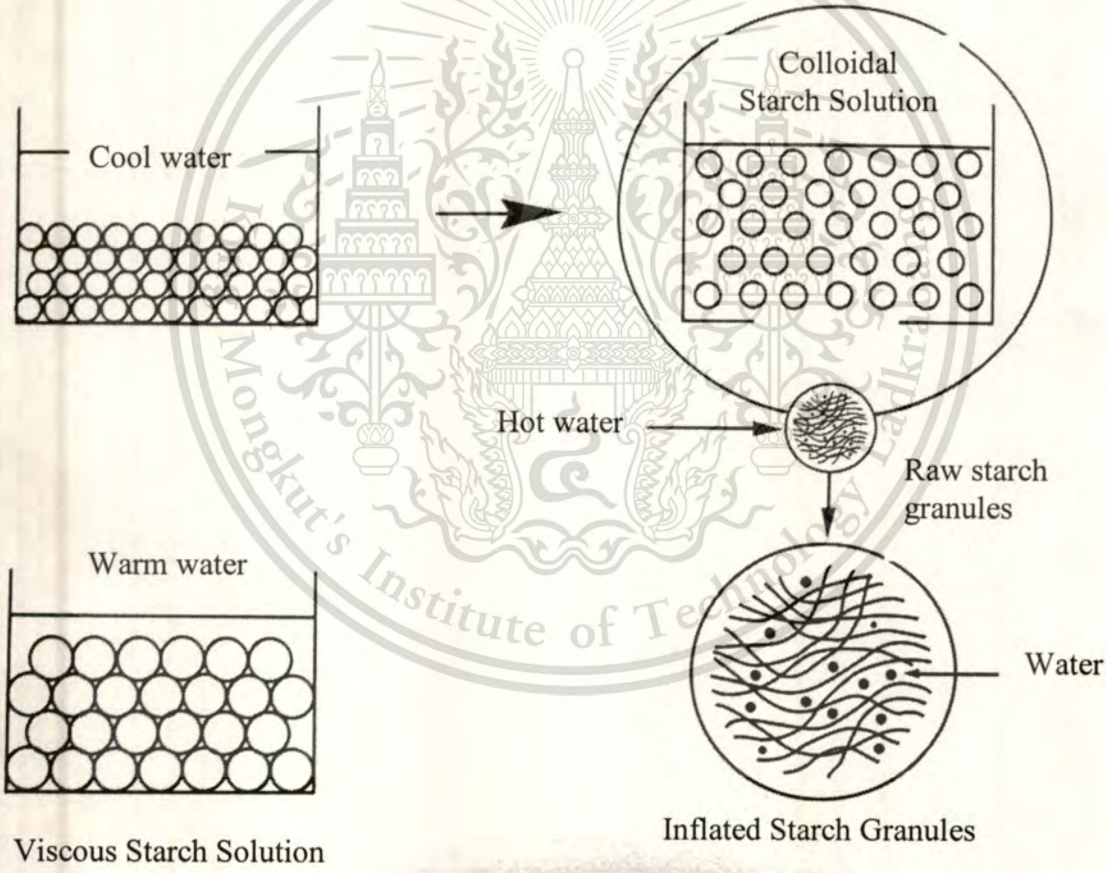


Figure 2.9 Starch granule transformations under applied heat [7]

2.2.1.2 <u>Viscosity</u> [7]

Viscosity is characteristic property for starch that cause by physical changes and depend on starch types and modification. Types, different starch gives different viscosity as shown. Modification, there are many method to modify starch and of course that the different the method, the different viscosity will get.

- Physical modification, for example, pregelatinized starch disperses in cold water or at room temperature can be viscous right away. It is good for those aspects that need no heat apply.

- Dextrinization or modify with acid_is a viscosity at which the temperature is lower than raw starch. Gel obtain from this process would be clearer and harder than raw starch.

- Esterification modification will get starch acetate or starch phosphate monoester in which has higher viscosity and ability to maintain than raw starch. Pasting temperature is lower than raw ones. Gel is clear and stable toward low temperature.

- Cross-linking, starch obtains from this would likely to maintain its viscous toward high temperature.

Besides, all mention factors. Those that will affect viscosity are also starch granule size and amilose percent. So to say, the bigger size of granules will give high inflation and maximum peak viscosity. And for amilose percent affect retrogadation, means high in amilose will consequently show high value of final viscosity. For External factors, there are heat and compression forces. If the granules crush, viscosity will drop.

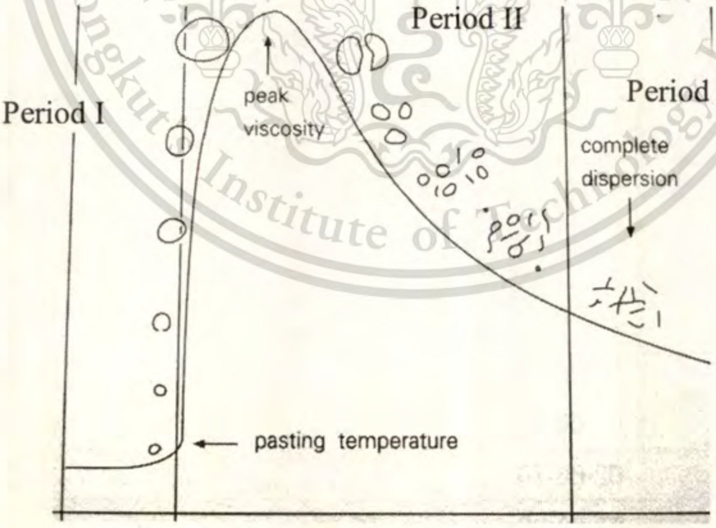


Figure 2.10 Starch gelatinization, x-axis represents starch adhesive's viscosity with y-axis is temperature in degree Celsius. [7]

2.2.2 Starch adhesives properties

Major properties of starch adhesive are viscosity, texture, transmittance, and shear rate. Also factors affected to viscosity are starch types, heating procedure and amount of starch adhesives combinations. For mixing starch adhesives, shear stress that take place will cut off some of inflated starch granules, resulted in lower in viscosity. Therefore, crosslinking starch will tolerate more to shear when heat and stirring are in process. Qualification of adhesive depends on starch types, amount added, heat process, temperature, acid-base, heat duration time, mixing method and equipment.

2.2.3 Starch derivatives

Derived starch called "starch derivatives". It can divide into 3 different chemical reactions.

2.2.3.1 **<u>Etherification</u>**, replace of ether linkage at monosaccharide chain.

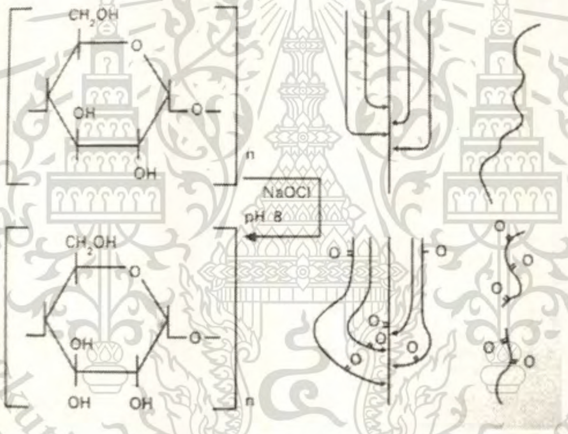


Figure 2.11 Etherification by Hoseney and Lineback, 1996 [7]

2.2.3.2 **<u>Esterification</u>**, replace of ester linkage at monosaccharide chain.

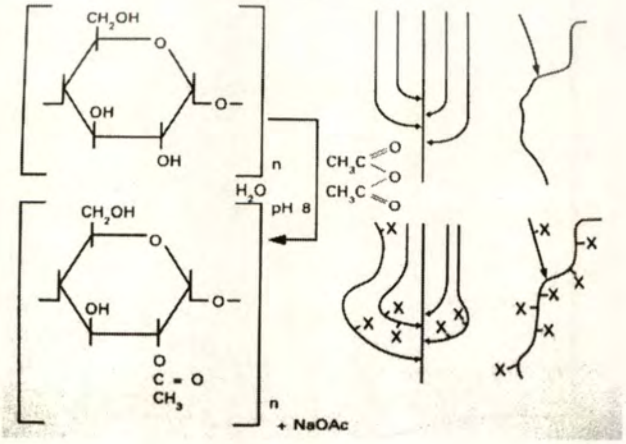


Figure 2.12 Esterification by Hoseney and Lineback, 1996 [7]

2.2.3.3 Crosslinking, a replacement in the molecule contains more than one functional group.

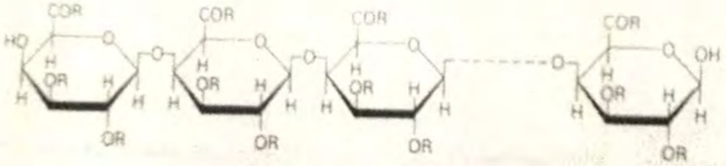


Figure 2.13 Replacement groups on starch chain

Starch ether and starch ester are both stabilized starch obtain from a reaction between starch granules and etherifying or esterifying agent, in base condition. The replacement of ether or ester would affect on starch structural changes. This will consequently make starch solution more stabilized and has constant viscosity.

2.3 Polyvinylalcohol (PVA) [12,13]

$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ - & C & - & C & - \\ & | & & | & \\ & H & & OH & \end{array}$$

Figure 2.14 Structural formula of PVA [13]

2.3.1 Physical and Chemical Properties

Synonyms: Polyvinyl alcohol (PVOH, PVA, or PVAL)
Chemical Formula: $[\text{-}CH_2CHOH\text{-}]_n$
Molecular Weight: Not applicable to mixtures.
Incompatibilities: Strong oxidizers.
Appearance: White free-flowing granules.
Odor: Mild odor.
Solubility: Moderately soluble.
Specific Gravity: 1.19 - 1.31
pH: Aqueous solution is neutral or slightly acid.
Melting Point: ca. 200°C (ca. 392F)
Flash point: 79°C (174F) As with most organic solids, fire is possible at elevated temperatures or by contact with an ignition source. Minimum dust cloud ignition temperature: 450°C (842F).
Stability: Stable under ordinary conditions of use and storage.
Hazardous Decomposition: Complete combustion will emit carbon dioxide and water when heated to decomposition. Incomplete combustion gives in addition carbon monoxide and oxidation products, including organic acids, aldehydes and alcohol.

Explosion: Fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source is a potential dust explosion hazard. Maximum explosion pressure: 78 lb./sq. in.
Strength: Very good
Set time: 5-10 min.
Cure time: 1 hour
Flexibility: Medium
Water resistance: Fair

It has excellent film forming, emulsifying, and adhesive properties. It is also resistance to oil, grease and solvent. It is frequently used as an adhesive and thickener, and to form a barrier to carbon dioxide in polyethylene terephthalate bottles.

PVOH is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it. It has high tensile strength, flexibility, as well as high oxygen and aroma barrier. However these properties are dependent on humidity, i.e. the higher the humidity the more the water absorbed. The water which acts as a plasticiser will then reduce its tensile strength, but increase its elongation and tear strength. PVOH has a melting point of 230°C and 180-190°C for the fully hydrolysed and partially hydrolysed grades.

PVOH also decompose rapidly above 200°C. The hydrophilics property of PVOH makes it permeable for both water and hydrated salt. Biodegradation of PVOH depends on the microbe population of the aqueous or soil environment. Decreasing the molecular mass of PVOH also increase the biodegradation. Temperature is another important criterion for biodegradation of PVOH. 90% elimination of Total Organic Carbon (TOC) was achieved at room temperature in 42 days. Biodegradation of PVOH also improved by adding natural components like starch, cane sugar or protein.

2.4 Glutaraldehyde

Figure 2.15 Skeleton formula of glutaraldehyde [15]

2.4.1 Physical and Chemical Properties [15,16]

IUPAC name: 1,5-Pentanedial; 1,5-pentanedione; glutaric dialdehyde; Aldesen; Cidex; Sonacide
Chemical formula: $C_5H_8O_2$
Structural formula: $CHO\text{-}(CH_2)_3\text{-}CHO$
MW: 100.12 g/mol
Appearance and Odour:. Colorless liquid/oil. Commonly available as a clear colourless aqueous solution. Pungent, aldehyde odour.
Boiling point: 188°C (decomposes)
Melting point: −6°C

Solubility: Soluble in water, alcohol, benzene
Conversion factor: 4.1 µg/m3 per ppb at 25°C
Composition/Purity: Most commonly available as 1%, 2%, 25% or 50% solutions of glutaraldehyde liquid in water, but other formulations are also available. Commercial solutions may contain other chemicals which may affect the overall toxicity and characteristics of the solution. This record discusses the hazards and control measures for glutaraldehyde solutions of 25% or greater.

2.4.2 Major Uses and Sources [14, 16]

Glutaraldehyde is a chemical frequently used as a disinfectant and sterilizing agent against bacteria and viruses (2% solution), an embalming fluid and tissue fixative, a component of leather tanning solutions, and an intermediate in the production of certain sealants, resins, dyes, and electrical products.

It has fairly small molecules, each with two aldehyde groups, separated by a flexible chain of 3 methylene bridges. It is $HCO\text{-}(CH_2)_3\text{-}CHO$. The potential for cross-linking is obviously much greater because this can occur through both the -CHO groups and over variable distances. In aqueous solutions, glutaraldehyde is present largely as polymers of variable size. There is a free aldehyde group sticking out of the side of each unit of the polymer molecule, as well as one at each end. All these -CHO groups will combine with which they come into contact, so there is enormous potential for cross-linking. There are also lots of left-over aldehyde groups (not bound to anything) that cannot be washed out of. For commercial purposes, solutions of 99%, 50%, and 20% are available.

There are 4 important bottom lines for glutaraldehyde.

1) If it's to be any good as a fixative, the glutaraldehyde solution must contain the monomer and low polymers (oligomers) with molecules small enough to penetrate the tissue fairly quickly. This means glutaraldehyde (25% or 50% solution), not a cheaper "technical" grade, must be used. The cheaper stuff is for tanning leather.

2) The chemical reaction of glutartaldehyde is fast (minutes to hours), but the larger molecules, especially the oligomers, penetrate tissue slowly. Glutaraldehyde is also an atmospheric reaction product of cyclohexene. Objects fixed for a few hours in glutaraldehyde are no longer osmotically responsive.

3) The free aldehyde groups introduced by glutaraldehyde fixation cause various problems (non-specific binding).

4) The combination of formaldehyde with glutaraldehyde as a fixative for electron microscopy takes advantage of the rapid penetration of HCHO and the thorough cross-linking by glutaraldehyde.

2.5 Commercial latex [17]

The earliest commercial synthetic resin is based on a Phenol formaldehyde resin with the commercial name Bakelite, and is formed from a elimination reaction of phenol with formaldehyde. Phenol is reactive towards formaldehyde at the *ortho* and *para* sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. This forms a hydroxymethyl phenol, which is not usually isolated in novolacs but is found in "resoles". The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction forms a methylene bridge, and the second forms an ether bridge. Phenol formaldehyde resins, as a group, are formed by a step-growth polymerization reaction which may be either acid or base catalyst. The pathway the reaction follows varies depending on the catalyst type used.

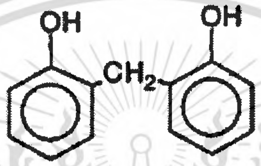


Figure 2.16 Phenol-formaldehyde molecular structure

Urea-formaldehyde is a transparent thermosetting resin or plastic, made from urea and formaldehyde heated in the presence of a mild base such as ammonia or pyridine. These resins are used in adhesives, finishes, and molded objects. Urea-formaldehyde resin has a high tensile strength, flexural modulus and HDT, low water absorption and mould shrinkage and higher surface hardness, elongation at break and volume resistance. Urea-formaldehyde foam insulation, or UFFI, was used as cavity-wall insulation beginning in the 1950s. In the 1980s concerns began to develop about the toxic formaldehyde vapor emitted in the curing process and from the breakdown of old foam, and its use was discontinued.

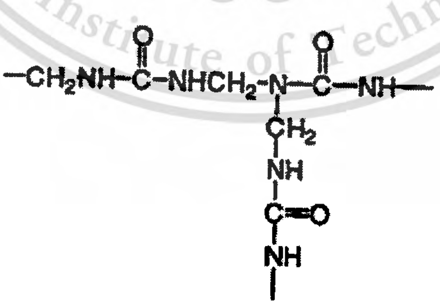


Figure 2.17 Urea-formaldehyde molecular structure

2.6 Plywood [17-19]

Plywood was the first type of engineered wood to be invented. It is an assembly of layers of an odd number of thin sheets of wood (veneer) joined together by means of an adhesive (glue) under pressure with grains of the successive layers at right angles. Plywood is noted for its strength, durability, lightness, rigidity, and resistance to splitting and warping. It is a multi-use material characterized by its ability to be designed and engineered for construction and decorative purposes, flat shapes, curves, and bent shapes.

There are two types of plywood: hardwood and softwood. Hardwood plywood is generally used for decorative purposes and has a face ply of wood from broad leaf trees (birch, mahogany, walnut, or white ash). Softwood plywood is generally used for construction and structural purposes, and the veneers are of wood from needle bearing trees (fir). Most plywood plants make their own veneers at plant sites. The layers in inexpensive plywood are glued together with starch pastes, animal glues, or casein, but those of the strongest plywood are glued with waterproof synthetic resins. Other material, such as metal or fabric, may be substituted for the usual wood core. A common reason for using plywood instead of plain wood is because plywood is more stable and because it is less prone to change (shrink, twist or warp).

2.6.1 Advantages of Hardwood Plywood [20]

Hardwood plywood has several key advantages:

2.6.1.1 **Environmental Investment** - It is a natural product made from a renewable resource. Therefore, it is one of the most environmentally friendly decorative products available to the consumer.

2.6.1.2 **Strength** - Pound for pound, plywood is stronger than steel in static bending strength. What makes plywood so strong is its unique cross-layered structure. The adhesives used to bond the veneers in plywood are actually stronger than the wood itself.

2.6.1.3 **Efficiency** - The plywood manufacturing process achieves more complete utilization of the log than does lumber manufacturing. No sawdust results from either rotary cutting or slicing (the two most popular methods of cutting veneer). Greater square foot coverage, in comparison to solid wood products, is achieved by using veneer. Thus, plywood manufacturing makes better use of the high value woods prized by consumers today.

2.6.1.4 **Beauty** - Architects and designers prefer the beauty of wood over any other material. The natural characteristics of wood make it attractive to the eye. Wood defies imitation. No material can match the infinite variety of natural markings and figure patterns offered through fine hardwood.

2.6.1.5 **Versatility** - A great variety of products in various sizes and shapes can be manufactured from hardwood plywood. Chair backs and seats, domes, bowling alley channels, and pianos are just a few of the many curved plywood products.

2.6.1.6 **Durability** - In museums all over the world are ancient examples of plywood furniture and decorative veneers that have lasted hundreds of years.

2.6.2 Test methods

2.6.2.1 Mechanical testing

Variety of mechanical tests method including tensile, compression, bend, shear, torsion and toughness. Testing can be conducted over a wide range of rates and temperature. For example, rates can be up to 4m/s and temperature could range from -196°C to 40°C. [10]

2.6.2.2 ASTM

According to adhesives ASTM D905-89 of the year 1990, this experiment is taken strength properties of adhesive bonds in shear by compression loading.

2.7 Literature reviews

One of adhesives paper by Syed H. Imam and co-workers, found that to treat corn starch and PVA in order to chemically crosslink with Cymel 323 (hexamethoxymethylmelamine) using citric acid as catalyst and latex on qualities improvement purpose. Where PVA and cornstarch combined at 63°C, solid content ranged from 27% to 37%, before addition of crosslinking agent corresponded to an immediate application. Then, undergo 125 to 175°C curing temperature for 15 to 30 minutes. Resulted in, better adhesion especially for wood application with also no sign of microorganism growth within two months period time along with high relative humidity ambient exposure. [6]

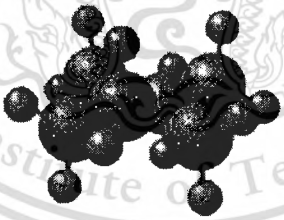


Figure 2.18 Three-dimension view of hexamethoxymethylmelamine

An approach by Korean researchers, using glutaraldehyde (GA) as crosslinking agent by 3 mol% and HCl as catalyst by 1 wt% of reactant monomer, in order to create the interpenetrating polymer network (IPN) with 5wt% PVA solution operated at 80°C was mixed with monomer to form hydrogels. [21] The degree of crosslinking is severely limited by the mechanical properties of the gels that deteriorate beyond a glutaraldehyde concentration which decreases with increasing polyvinyl alcohol chain length. [22] In Addition, variety of glutaraldehyde percent was used, according to other paper suggested gelatin glutaraldehyde (GA) cross-linking methods were used to coat a hydrophilic membrane on silicone rubber proceeded a newly formed 5% gelatin membrane was cross-linked with a 2.5% GA solution. [23]

For a similar experiment, mechanism study of crosslinked reaction of glutaraldehyde. It was found that by react with different types of collagen, exhibit similarity to starch chains, exposed to various concentration of crosslinking agent. The degree of intramolecular and intermolecular crosslink formation was evaluated by measuring solubility, chain formation and resistance towards cleavage. With low concentrations of glutaraldehyde, intramolecular crosslinks were observed as the predominant crosslinks. When the glutaraldehyde concentration was increased, the collagen became more insoluble, indicating the formation of intermolecular crosslinks. When the glutaraldehyde concentration was increased, the materials became more soluble resistant. This reflects an increase in the molecular length of the glutaraldehyde polymers extending from the initial glutaraldehyde and reaction sites rather than an increase in the actual number of crosslinking sites. [24]

The crosslinking of PVA with glutaraldehyde at 80°C was also characterized by viscosity and pulse field gradient (PFG) nuclear magnetic resonance (NMR) techniques. NMR signified an initial dormant period of approximately 6 hr, in which the self-diffusion coefficient of PVA was found to be constant and independent of time. During the next 7 hr, the "primary" gel period, this induction period was succeeded by a fast decay of the self-diffusion coefficient of rate followed by a slower decay rate in the "secondary" gel period. The viscosity of the solution showed the same time behavior, i.e. an initial dormant period (~ 6 hrs), followed by a fast increase of the viscosity for the next 7 -8 hr. During the "secondary" gel regime, the viscosity became too large to be reliably determined. However, within the time regime where both techniques produced reliable data, they gave identical information regarding the kinetics of the gel process. [25]

Chapter III
Experimental Details

3.1 Materials

1) Tapioca starch; commercial grade with 13% moisture from Thai Wah Products Public Company Limited.
2) Polyvinylalcohol solution; 6.83 g/100ml, MW = 100,000
3) Glutaraldehyde solution; 50% by weight in water from Merck.
4) Commercial Latex, formaldehyde-resin based adhesives; 23.59% of dry solid weight from TOA (Thailand) Inc.
5) Siamese Sal wooden block; 44.4mm × 50.8mm × 19mm in dimension

3.2 Equipments

1) Laboratory glass wares
2) Fischer Scientific Hotplate
3) Universal tensile and shear instrument; Lloyd Instruments model LR30K

3.3 Experimental procedures

3.3.1 Adhesives preparation

3.3.1.1 Preparation of latex adhesives

Commercial latex

Commercial latex was used as purchased.

Latex solution

Latex solution was prepared from commercial latex. First, % dry weight of commercial latex was determined by evaporating the water off in the oven at 100°C until solid weight did not change. It was found that there was 23.59% of dry solid latex in commercial latex adhesive. In order to prepare 6.83g/100ml. of latex solution, 28.952g at approximately 60°C of commercial latex in 100ml. distilled water was used. This solution was stirred until it became homogeneous. The solution was left to cool down for a few minute before use.

9.1% starch in commercial latex

2g of starch and 20g of commercial latex were weight and mixed together in a 250 ml beaker under room conditions. Stirring was kept until the mixing was thorough.

3.3.1.2 Preparation of non-crosslinked adhesives

PVA solution

PVA solution with a concentration of 6.83g/100ml. was used as received.

Pure starch solution

6.83g of starch was gently poured into a 250 ml beaker containing 100 ml of preheated distilled water at approximately 60°C. Stirring was kept for 3 minutes or until the solution was homogeneous. The solution was then allowed to cool down for a few minute before use. Be cautious not to add the starch in too fast since it might cause disperse clusters of starch throughout the solution.

3.3.1.3 Preparation of one-component crosslinked adhesives

Starch solution with varied percentage of glutaraldehyde

1) 5g (26.8% dry weight of adhesives) of 50% by weight of glutaraldehyde solution was weight and poured directly into the starch solution prepared from 3.3.1.2.

2) The solution was then stirred until it became homogeneous.

3) The procedure was repeated two more times by using 7g (33.9% dry weight) and 10g (42.2% dry weight) of 50% by weight of glutaraldehyde solution, respectively.

PVA solution with varied percentage of glutaraldehyde

1) PVA solution was heated until the temperature reached approximately at 60°C.

2) 5g (26.8% dry weight) of 50% by weight of glutaraldehyde solution was then weight and poured directly into the PVA solution.

3) Stirring was kept for 3 minutes until the solution became homogeneous.

4) The procedure was then repeated twice using 7g (33.9% dry weight) and 10g (42.2% dry weight) of 50% by weight of glutaraldehyde solution, respectively.

3.3.1.4 Preparation of two-component crosslinked adhesives

1) Prepared 3.415g of starch, 50 ml. of PVA solution, and 50 ml. of distilled water. (50:50 ratio of starch to PVA solution)

2) 5g (26.8% dry weight), 7g (33.9% dry weight) and 10g (42.2% dry weight) of 50% by weight of glutaraldehyde solution were also weight.

3) 50 ml of distilled water prepared from 1) was then preheated at approximately 60°C on a hotplate stirrer.

4) Starch and PVA solutions from 1) were added into the preheated water.

5) Stirring was continued until the mixture became homologous. Then, glutaraldehyde prepared from 2) was added into the mixture.

6) The procedures was repeated twice by varying the ratios between starch and PVA solution to 20:80 (starch 1.366g, PVA 80 ml., 20 ml. distilled water), and 80:20 (starch 5.464g, PVA 20ml., 80 ml. distilled water)

3.3.2 Preparation of wood specimens

1) Hard wood blocks were cut into 50.8 mm lengths, 44.4 mm widths, and 19 mm thicknesses. In this experiment, Siamese Sal was used.

2) A width line called "glue line" was drawn by 6.3 mm from blocks edge, in order to patch up with another side. The area calculated was to be 19.177 cm^2. These blocks were prepared to be free from defects within shearing area, and were cut so that at least ten specimens could be used in one test of the samples.

Figure 3.1 Glue line

3) Adhesives were applied only on one side of the wood blocks with approximately 1g of the samples used for cover the joining-surface and not beyond glue line.

Figure 3.2 Glue samples; average weight of 1g.

4) Test specimens were prepared to have smooth surfaces and parallel to each other, and perpendicular to height.

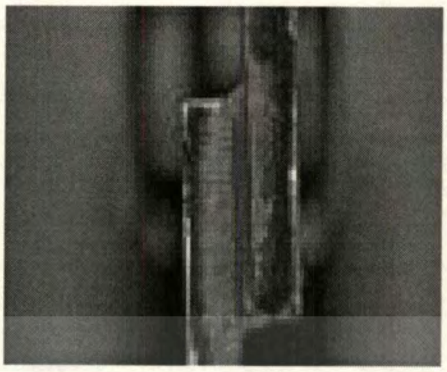


Figure 3.3 Parallel joint

5) Specimens were kept in the oven at 80°C for 24 hours.

Figure 3.4 Oven wooden specimens

3.3.3 Test Method

Using 1990, ASTM D905-89. “Standard test method for strength properties of adhesive bonds in shear by compression loading”

Testing procedures:

1) The testing machine should be located under normal atmosphere so that wood specimens factors would not be altered during the test.

2) Place wood specimens in shearing tool containing self-aligning seat so that load may uniformly be applied vertically to joint as illustrated. Apply continuous motion loading with not less than 6810 kg (15000 lb) and maximum to 30 kN in compression.

3) As strong adhesives were used, wood joint failure is likely to be found. However, the strength measure is lower than true adhesive bond strength.

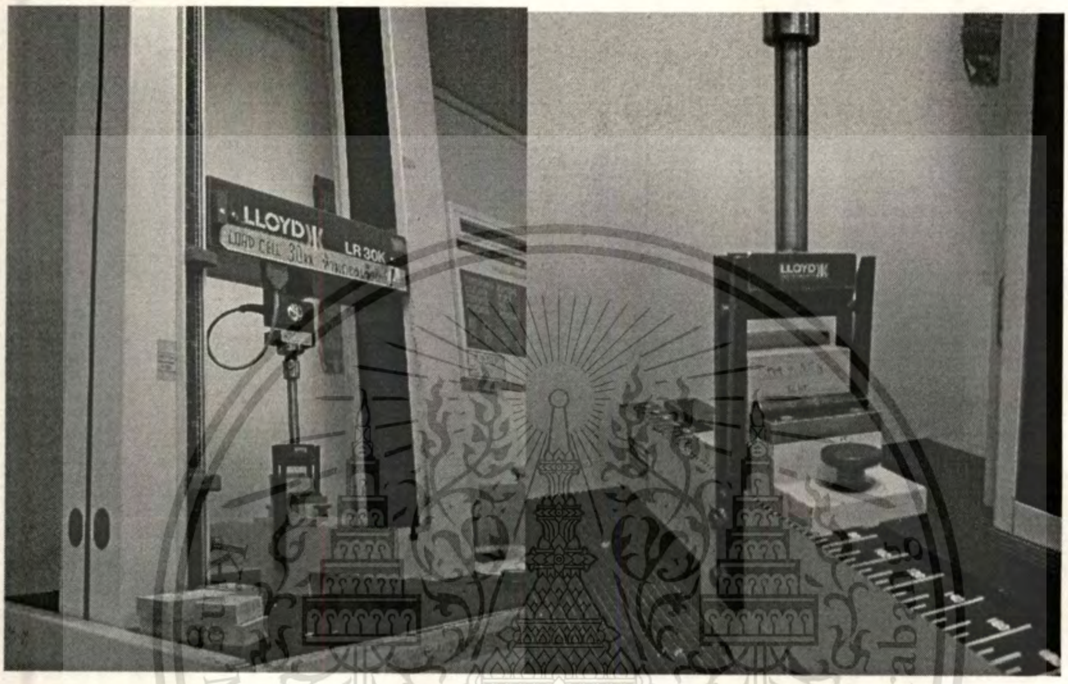


Figure 3.5 Universal tensile and shear instrument

Chapter IV
Results and Discussion

4.1 Strength of plywood joint using PVA, starch and latex solutions

The specimens prepared under section 3.3.1.1 and 3.3.1.2 with approximately 1 g. of adhesives on adhering surface, were subjected to compression loading using universal tensile and shear instrument according to the test method in section 3.3.3. The results are shown in Table 4.1 and render as Figure 4.1.

Table 4.1 Average compression loading of plywood specimens using adhesives prepared in section 3.3.1.1 and 3.3.1.2

Samples	Average shear strength (N)
PVA solution	2383.5
Pure starch solution	0.0
Commercial Latex	> 28000.0
Latex solution	1312.7
9.01% starch in commercial latex	2695.3

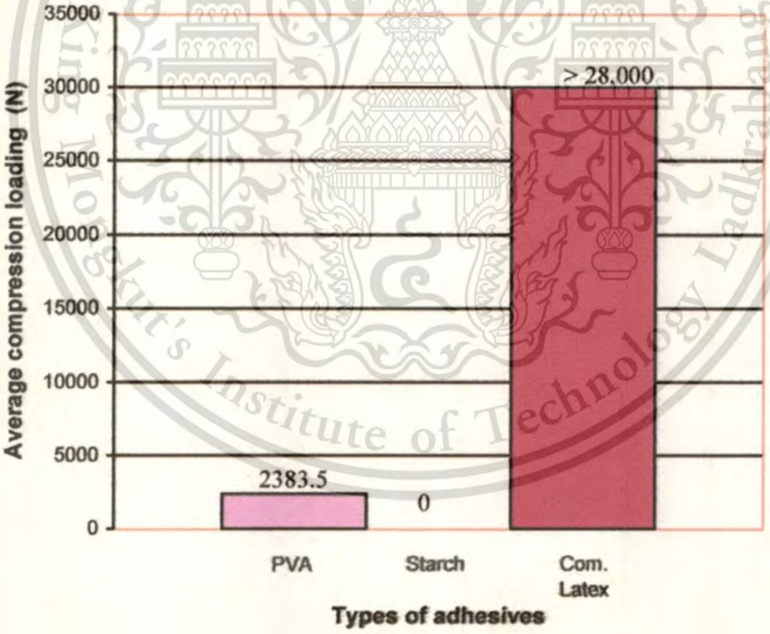


Figure 4.1 Average compressions loading of plywood specimens using pure component adhesives

Figure 4.1 shows the adhesive strength of plywood specimens using PVA and starch solutions at fixed concentration of 6.83g/100ml as adhesives comparing with those using commercial latex. According to the illustration, PVA does not exhibit as much, however, it still shows adhesion trend while starch shows no adhesion sign. Consider PVA molecules are straight chain with no bulky size groups, therefore, crystalline regions can formed upon solidify. On the contrary, starch, long and bulky macromolecules stay in amorphous form when dried. This causes PVA solution to result in better strength than starch solution. Commercial latex exhibits the highest strength of over 28,000 N when subjected to compression loading. This is because the higher percentage of solid content in commercial latex, 23.59% compared with 6.83% of PVA and starch solutions. When diluted to the same concentration of 6.83g/100ml, its strength drops even lower than that of PVA solution as shown in Figure 4.1. Combination of 9.01% starch in commercial latex, 2g starch in 20g commercial latex, also give a significant decline in strength from the commercial one but still give the higher strength than that using latex solution at this fixed concentration.

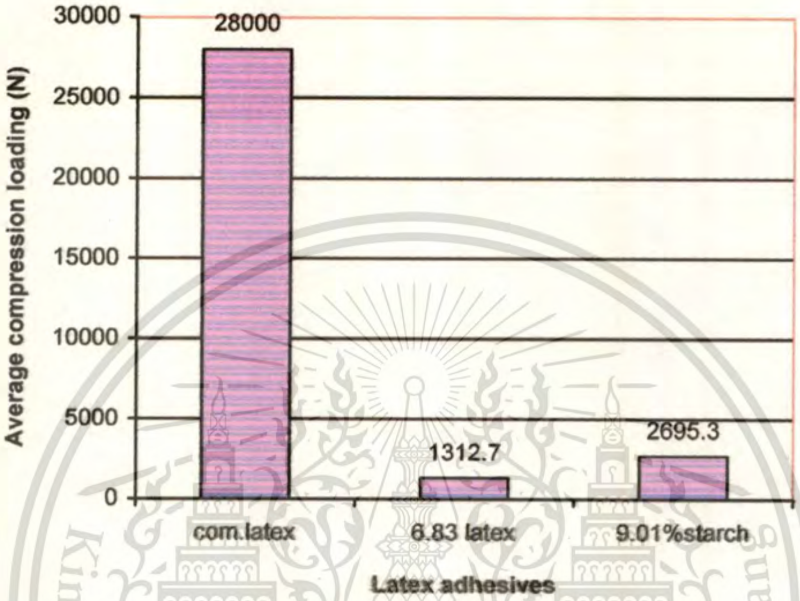


Figure 4.2 Average compressions loading of plywood specimens using latex Adhesives

4.2 Strength of plywood joint using one-component adhesives with varied percentages of crosslinking agent

The specimens prepared under section 3.3.1.3 with approximately 1 g. of starch adhesives on adhering surface, were subjected to compression loading using universal tensile and shear instrument according to the test method in section 3.3.3. The results are shown in Table 4.2 and render as Figure 4.3.

Table 4.2 Average shear strength of wood joint specimens using starch solutions with varied percentages of glutaraldehyde as adhesives

Starch solution : dry wt% glutaraldehyde	Average shear strength (N)
0%	0.0
26.8%	8.0
33.9%	282.0
42.2%	240.4

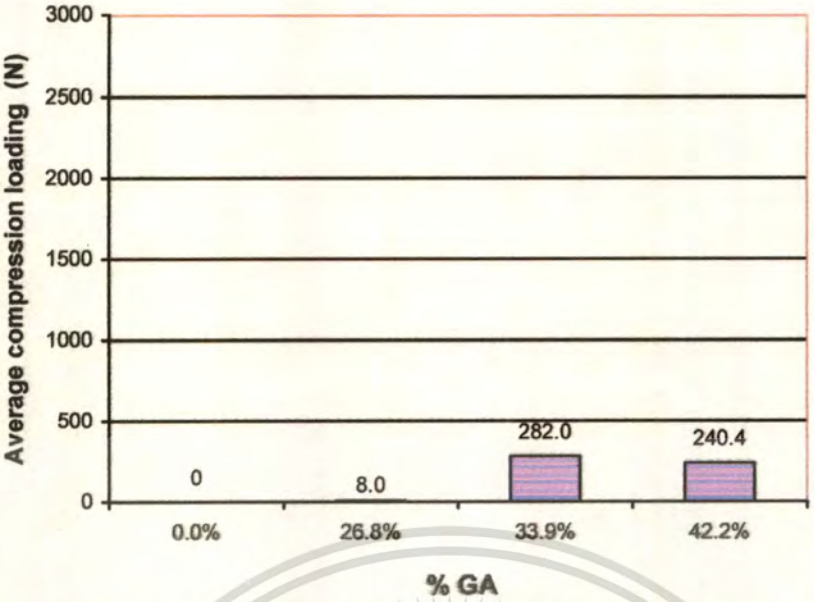


Figure 4.3 Average compression loading of plywood specimens using starch solutions with varied percentages of glutaraldehyde as adhesives

Figure 4.3 shows that the strength of wood joint specimens can be raised by the presence of a crosslinking agent, glutaraldehyde, in starch solution. An addition of 33.9% is also shown to be an optimum amount of glutaraldehyde in starch solutions since further use would not increase joint strength. Increasing in the movement resistant capability of adhesing molecules due to crosslinking increase adhesive's adhesion strength further than that from H-bond and Van Der Waals intermolecular force. And since the number of OH-groups in starch is high, therefore, more percentages of glutaraldehyde can be added before trend starts to decline.

The specimens prepared under section 3.3.1.3 with approximately 1 g. of PVA adhesives on adhering surface, were subjected to compression loading using universal tensile and shear instrument according to the test method in section 3.3.3. The results are shown in Table 4.3 and render as Figure 4.4.

Table 4.3 Average shear strength of wood joint specimens using PVA solutions with varied percentages of glutaraldehyde as adhesives

PVA solution: dry wt % glutaraldehyde	Average shear strength (N)
0%	2382.3
26.8%	2788.3
33.9%	1485.0
42.2%	1319.0

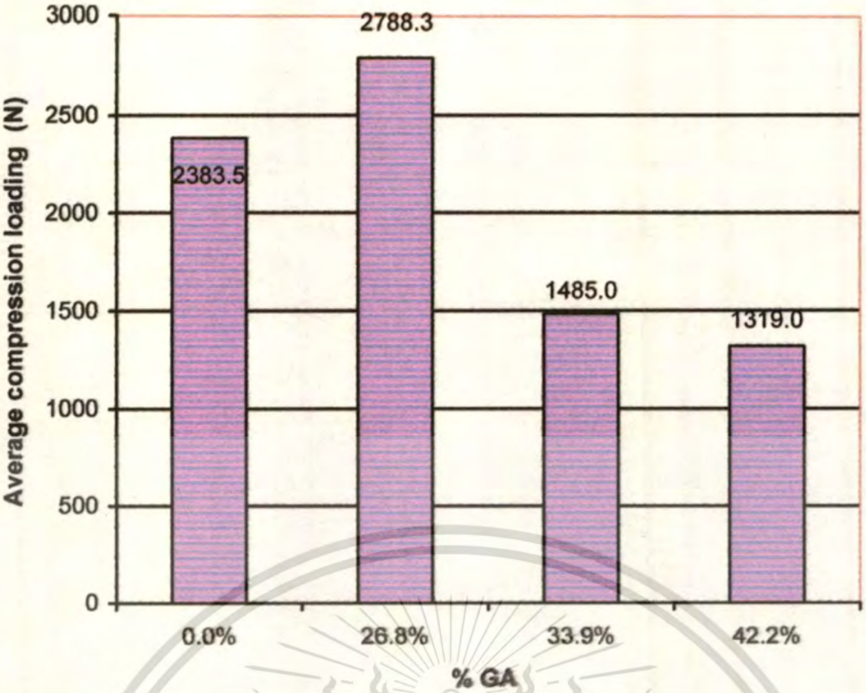


Figure 4.4 Average compression loading of plywood specimens using PVA solutions with varied percentages of glutaraldehyde as adhesives

The results shown in Figure 4.4 indicate that glutaraldehyde is capable of increasing the strength of PVA adhesives when 26.8% of crosslinking agent was added. According to Figure 4.5 below, it is clearly shown that crosslink occurs between adhesives and wooden surface, therefore cohesion within adhesives is the one broken when subjected to compression. However when percentages of glutaraldehyde increase to 33.9% and 42.2%, the trend drops.

Figure 4.5 Crosslinked surface

Consider the nature of PVA in which lower in OH-groups than those of starch. Only 26.8% of glutaraldehyde was enough for the crosslink generation. However, trend of adhesion falls beyond 33.9% of crosslinking agent. It is mainly because of excess percentage of crosslinking agent causes brittleness in adhesive, according to the Figures 4.6 to Figure 4.9.

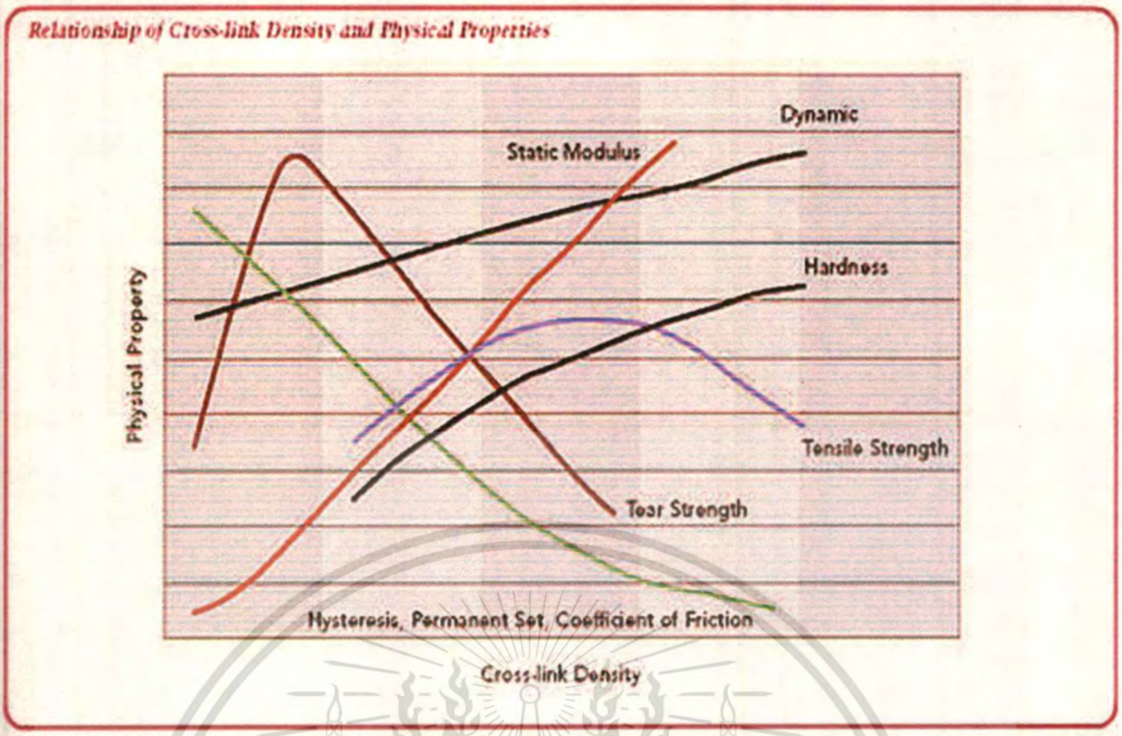


Figure 4.6 Relationship of crosslink density and physical properties [26]

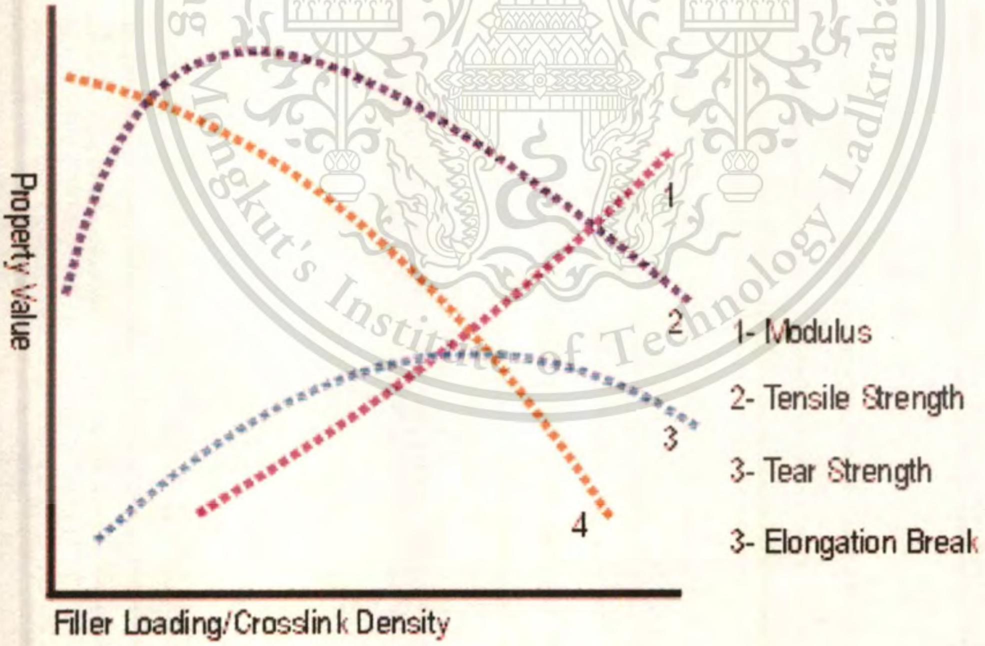


Figure 4.7 Elastomer's properties vary with cross-linking density [27]

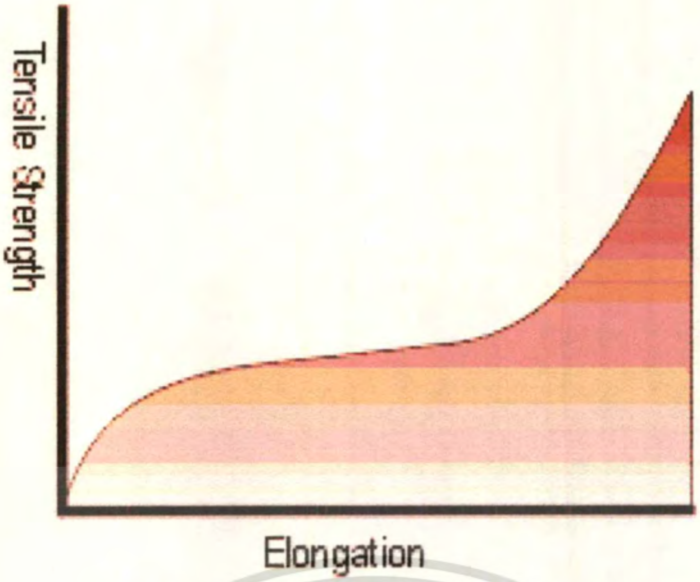


Figure 4.8 Typical tensile behaviour of an Elastomer [27]

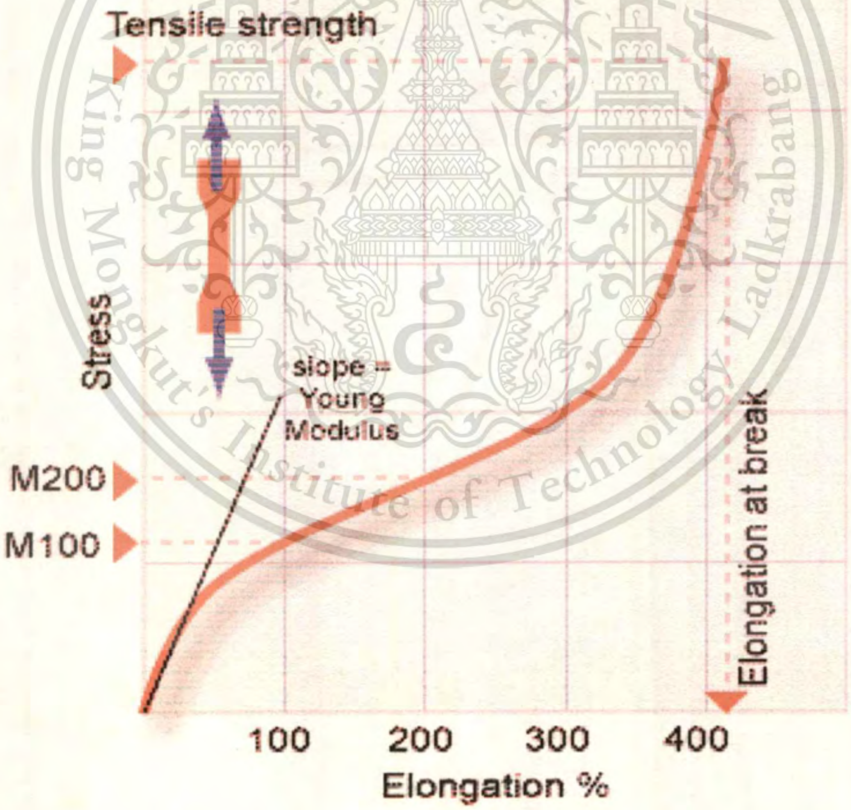


Figure 4.9 Typical curve Stress VS Elongation for Rubbers [27]

Since water was a sole solvent using on this experiment, it played an important role on viscosity. In this experiment, it was difficult to control the amount of water because it stayed in many forms, for example, free water and bound water in adhesives matrix, additional water from different percent of GA and ambient humidity returning into adhesives when samples must be kept over a period of time before test. A decreasing of strength on an increasing percent of GA is also corresponded to water dilution. Although, the trend of strength should be rising with an increasing GA percent, but when account water as one factor, it was found that higher percent of added GA comes greater proportion of water into solution - since 50 wt% of GA was used. That additional water eventually makes samples became less viscous, and affected when applying on specimen surfaces. Also because of adhesives weight between two surfaces must remain the same throughout all trials, the more water would certainly cause slippery in which excess amount of sample will run down a side of test specimens then crystallized inside oven during curing time as shown in Figure 4.10. Furthermore, this will effect on crosslinking distribution on surfaces. Since water will run samples down a side, therefore crosslinked joint could assemble in one area and do not spread out to cover all areas.

Figure 4.10 Excess samples on the side of specimens

4.3 Strength of plywood joint using two-component adhesives with varied percentages of crosslinking agent

The specimens prepared under section 3.3.1.4 with approximately 1 g. of adhesives on adhering surface, were subjected to compression loading using universal tensile and shear instrument according to the test method in section 3.3.3. The results are shown in Table 4.4 and render as Figure 4.7 and 4.8.

Table 4.4 Average shear strength of wood joint specimens using mixed starch-PVA solutions with varied percentages of glutaraldehyde as adhesives

	Average shear strength (N)		
Starch : PVA	**26.8 dry wt % glutaraldehyde**	**33.9 dry wt % glutaraldehyde**	**42.2 dry wt % glutaraldehyde**
0 : 100	2788.3	1485.0	1319.0
20 : 80	8876.3	5141.2	4995.8
50 : 50	6911.8	5308.6	4690.7
80 : 20	81.3	351.7	341.0
100 : 0	8.0	282.0	240.4

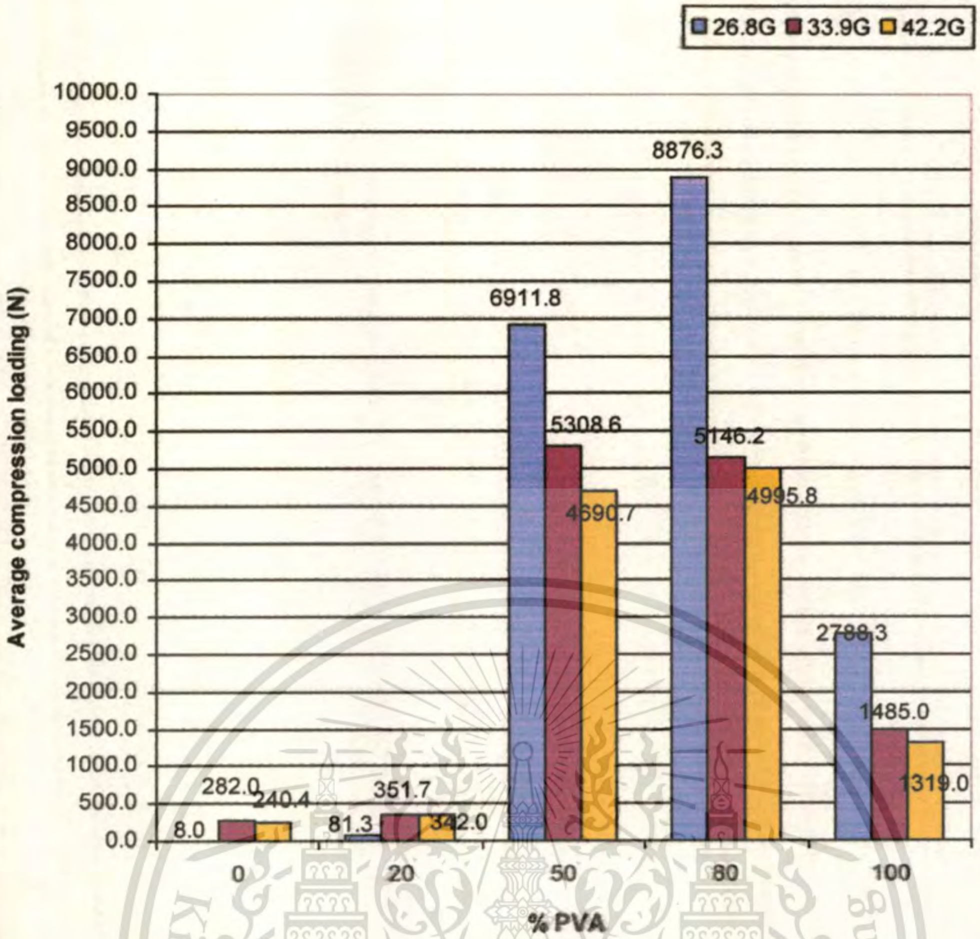


Figure4.11 Average compression loading of plywood specimens using mixed starch-PVA solutions with varied starch/PVA ratios as adhesives

According to Figure 4.11, PVA addition gives rise to the adhesion strength showing the same trend for all percentages of GA. On the other hand, it could be said that the more starch blended in the solutions, strength trends drop. Since more starch blended in the solutions means that the solutions will have more of starch disperses throughout the solutions as granules instead of inflated polymer chains. These results in less cohesion and reduction in crosslinking which further cause weak spots between two surfaces when apply adhesives on wooden surfaces. This leads to easier specimen's breaking.

As to the lower inclination of 100% PVA over 80% and 50%, this is due to the different nature of the blends compared to PVA and starch. Mark that starch-PVA solutions are miscible and homogeneous blends, when higher percent of PVA were used - consider their strong intermolecular attraction occurred through hydrogen bonding between –OH groups. PVA is a long straight polymer chain with one –OH group when starch is long polymer chain that contains cyclic rings with two groups of -OH. As the results, the miscible starch-PVA blends, both at 50% and 80% PVA, somehow present the better strength over that of pure components.

Increasing in percent of glutaraldehyde results in decreasing in strength of starch-PVA solutions at low and moderate starch/PVA ratios of (0:100, 20:80 and 50:50). By calculating the number of OH- groups of the components (starch, PVA), it is found that there are more OH- groups in starch by the same weight. It is the fact that addition of crosslinking agent causes the polymers to become more brittle and easier to break when lower force is applied. As a consequence, by calculating the number of –CHO groups within crosslinking agent (glutaraldehyde), brittleness caused from over –crosslinking is likely to have higher influence over the strength of PVA compared to starch.

On the contrary, starch-PVA solutions at higher starch/PVA ratios (80:20 and 100:0) show less change in strength when using higher percentages of glutaraldehyde. Because starch has more OH-groups and greater ability to attract OH-groups from glutaraldehyde than PVA, therefore, the effect caused by brittleness is less significant.

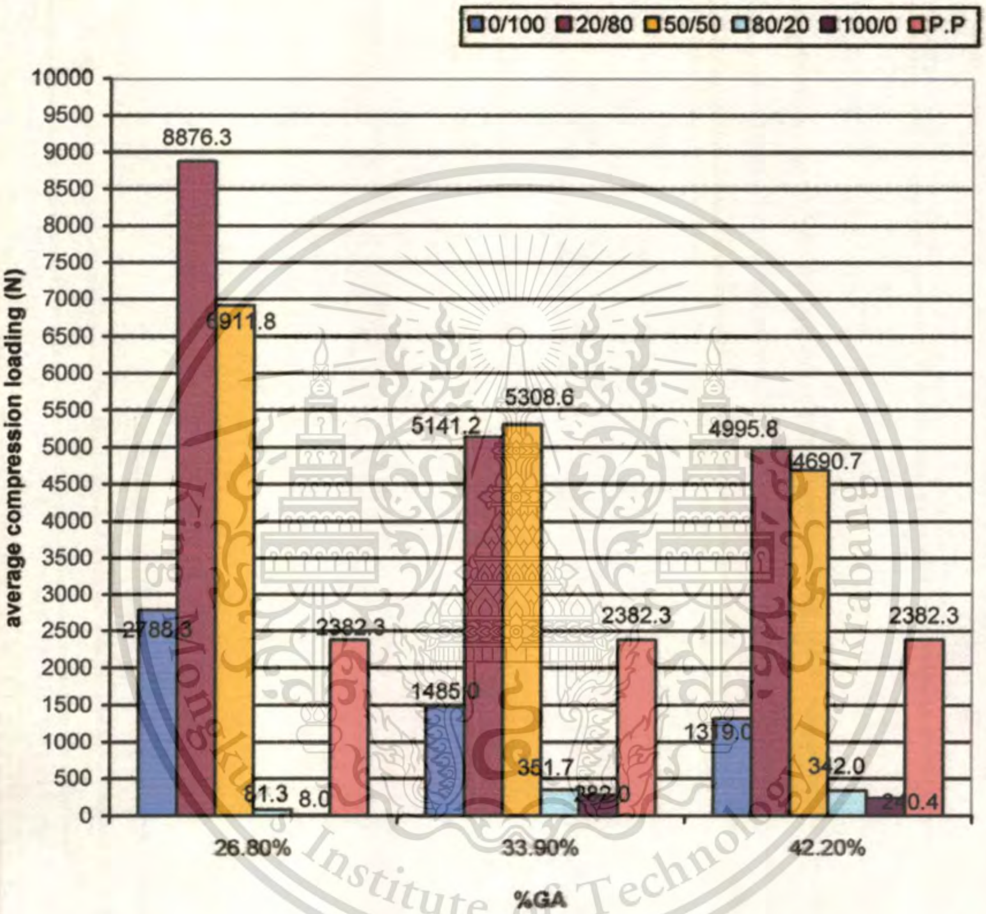


Figure4.12 Average compression loading of plywood specimens using crosslinked starch-PVA blended solutions with varied both starch/PVA ratios and percentages of glutaraldehyde as adhesives

Declination of adhesion strength plywood joint when using more concentrated glutaraldehyde is obviously seen in Figure 4.12 where solutions contain high amount of PVA. It can be noticed that where the solution contains enough crosslink and OH-groups, addition of glutaraldehyde makes the trend drop. This could be explained as with the crosslinked PVA adhesives mentioned earlier. It could be because of the structure rigidity of the adhesives which causes brittleness between two surfaces and hence, the loss of adhesion and cohesion.

Chapter V
Conclusion and Suggestions

5.1 Conclusion

According to the experiments, it can be concluded that, using pure PVA, starch and latex solutions as adhesives at the concentration of 6.83g/100ml, the strength of plywood using PVA solutions is higher than that of latex solution and starch solution, respectively. Due to the straight chain molecular structure of PVA which is smaller than starch's bulky molecule - a straight chain with cyclohexane ring, it gives better adsorption to the active sites of wood surfaces. And since commercial latex that holds the concentration of 23.59g/100ml was reduced to the lower concentration of 6.83g/100ml, naturally, it also resulted in the reduction of adhesion strength plywood joint.

PVA addition increased adhesion's strength while starch addition resulted in the opposite. This was due to the fact that starch was making the blends become more starch – like in nature with an increasing amount of starch granules in the blends. This also led to the formation of weak spots on specimen's surfaces causing by lower crosslink on wood specimens. As a result, it was found that two component adhesive optimized ratio was 20% starch to 80% PVA.

Using glutaraldehyde as crosslinking agent, the strength of plywood joints was better when low concentration was used within adhesives. Increasing in its concentration gave lower strength of plywood joint. This situation resulted from adding too much of crosslinking agent in the adhesives which caused fragility of the adhesive's structure. In this work, it was found that 26.8% weight of glutaraldehyde by weight of solid content gave the highest strength.

5.2 Suggestions for future works

5.2.1 The curing time and temperature should also be studied because it is one of the factors that affect the wood joint strength.

5.2.1 Reduction of glutaraldehyde content in adhesives should be attempted.

5.2.3 The viscosity of adhesives should be controlled within more narrow range because it affects the quantity of adhesives applied on specimens.

5.2.4 Optimization of starch proportion in PVA-Starch blends should be studied within more narrow range to determine the best blended ratio.

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Appendices

Appendix A: overall charts

Figure A.1 overall compression loading strength of adhesives using in the experiment by types of adhesives

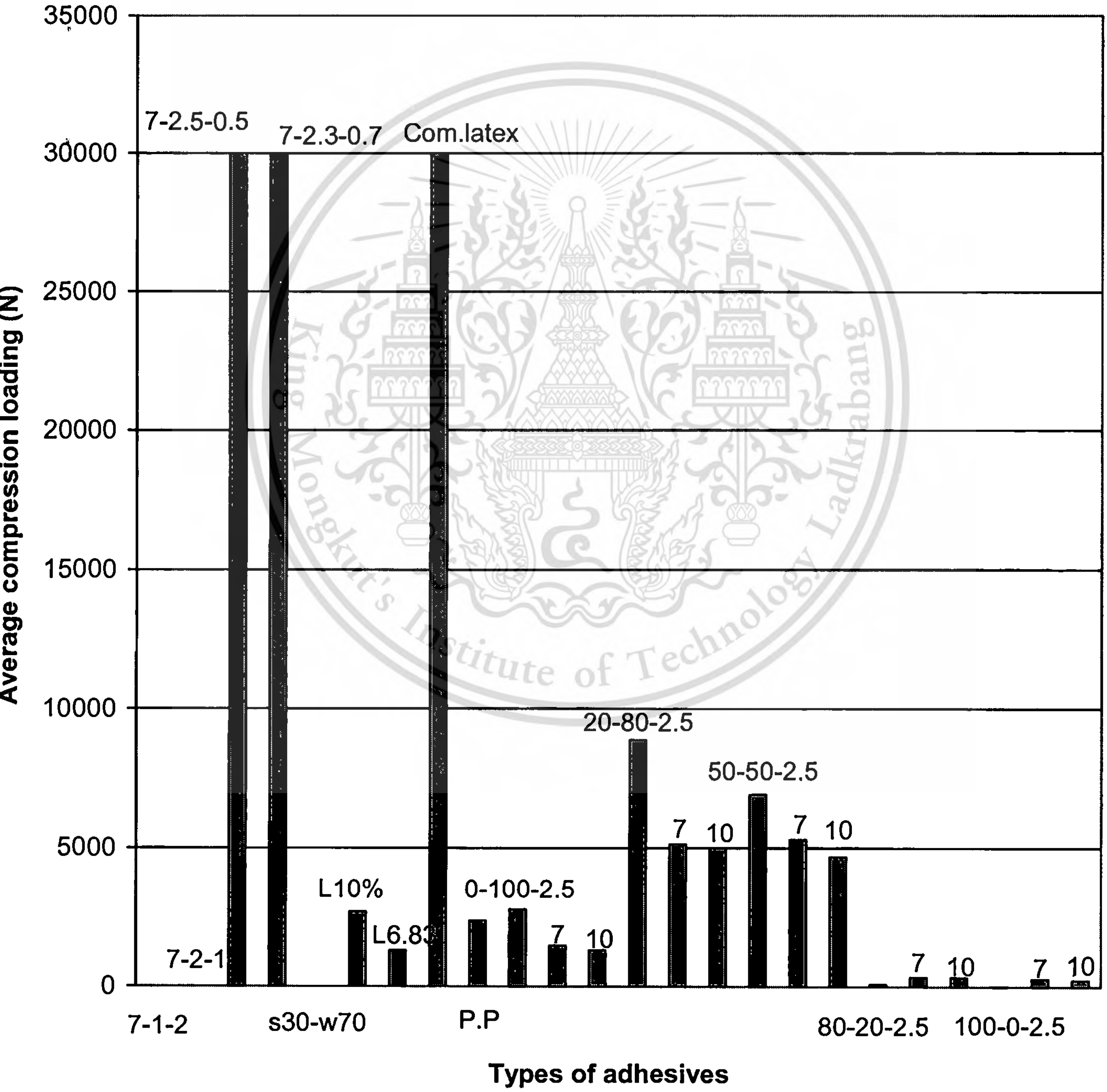
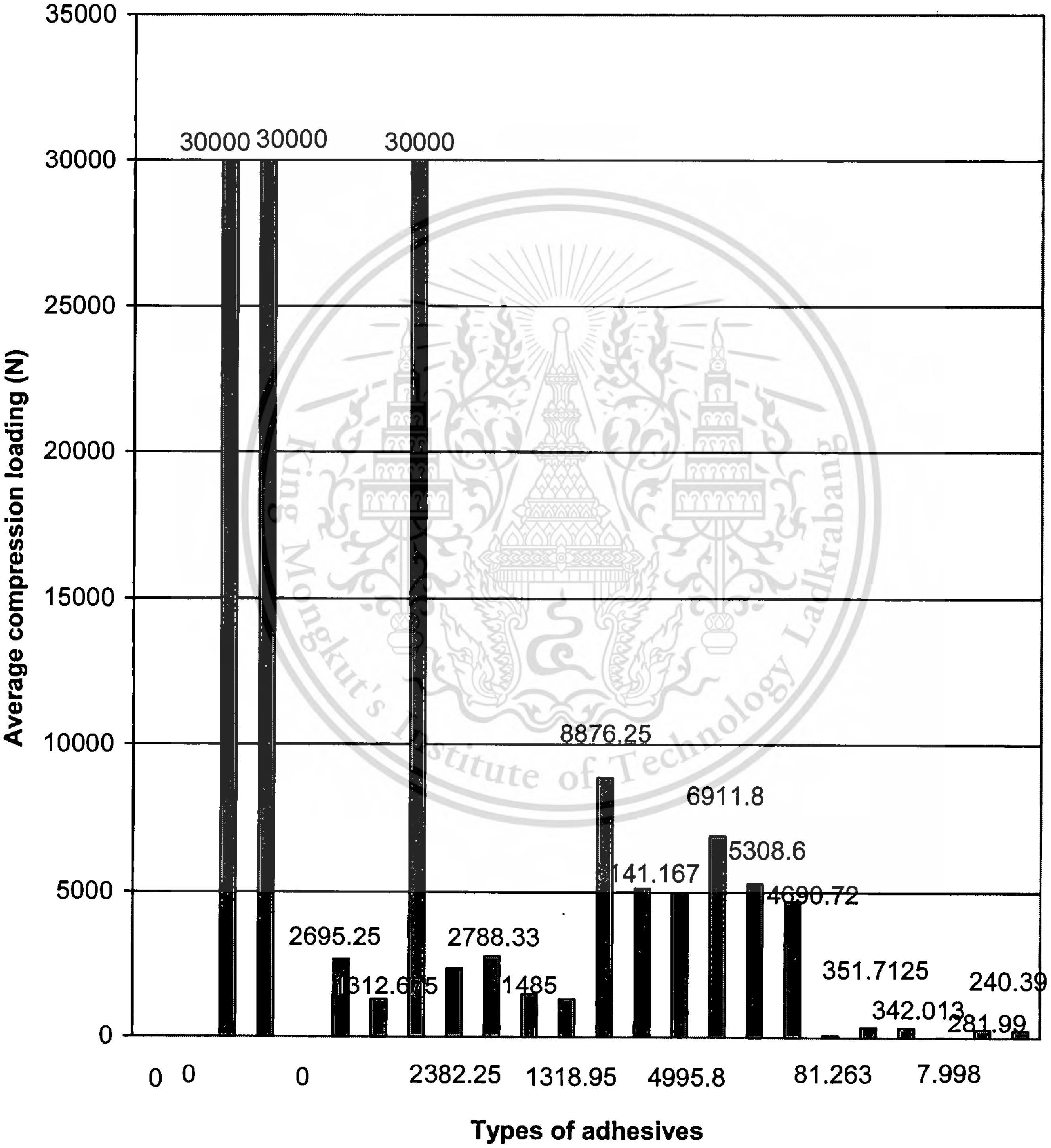


Figure A.2 overall compression loading strength of adhesives using in the experiment by average strength value



Where;

7-1-2	7g starch / 1g PVA / 2g glutaraldehyde
7-2-1	7g starch / 2g PVA / 1g glutaraldehyde
7-2.5-0.5	7g starch / 2.5g PVA / 0.5g glutaraldehyde
7-2.3-0.7	7g starch / 2.3g PVA / 0.7g glutaraldehyde
S30-w70	starch 30g / water 70g
L10%	9.01%starch in commercial latex using 2g starch in 20g commercial latex
L6.83	6.83g solid latex /100 ml. water
Com.latex	commercial latex
P.P	pure PVA
0-100-5	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
0-100-7	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
0-100-10	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
20-80-5	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
20-80-7	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
20-80-10	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
50-50-5	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
50-50-7	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
50-50-10	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
80-20-5	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
80-20-7	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
80-20-10	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
100-0-5	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
100-0-7	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration
100-0-10	ratio of starch/PVA/glutaraldehyde under 6.83g/100ml. fixed concentration

Appendix B: raw data of compression loading in Newton

Table B.1 Latex solutions

Trials	Commercial latex	Latex solution	10% starch in commercial latex
1	>28,000	1466.0	3126.0
2	>28,000	2283.0	3186.0
3	-	497.7	2131.0
4	-	1004.0	2338.0
5	-	-	-
6	-	-	-
7	-	-	-
8	-	-	-
9	-	-	-
10	-	-	-
Ave.	**overload**	**1312.7**	**2695.3**

Table B.2 Non-crosslinked adhesives

Trials	PVA solutions	Starch solutions
1	3160.0	0
2	2910.0	0
3	2667.0	0
4	2372.0	0
5	3925.0	0
6	1439.0	0
7	1531.0	0
8	1064.0	0
9	-	0
10	-	0
Ave.	**2383.5**	**0**

Table B.3 One-component crosslinked adhesives with varied percentages of glutaraldehyde (starch solutions)

Trials	26.8% glutaraldehyde	33.9% glutaraldehyde	42.2% glutaraldehyde
1	25.7	108.7	0
2	30.3	556.2	0
3	0	1309.0	0
4	0	0	0
5	0	108.7	0
6	0	556.2	1669.0
7	0	1309.0	13.7
8	-	-	-
9	-	-	-
10	-	-	-
Ave.	**8.0**	**282.0**	**240.4**

Table B.4 One-component crosslinked adhesives with varied percentages of glutaraldehyde (PVA solutions)

Trials	26.8% glutaraldehyde	33.9% glutaraldehyde	42.2% glutaraldehyde
1	3604.0	1560.0	921.0
2	1927.0	1051.0	2060.0
3	1459.0	1786.0	1380.0
4	2768.0	1213.0	1519.0
5	4763.0	1815.0	1696.0
6	2209.0	6603.0	1789.0
7	-	-	608.7
8	-	-	-
9	-	-	-
10	-	-	-
Ave.	**2788.3**	**1485.0**	**1319.0**

Table B.5 Two-component crosslinked adhesives with 26.8% glutaraldehyde

Trials	**0/100**	**20/80**	**50/50**	**80/20**	**100/0**
1	3604.0	230.6	5683.0	0	25.7
2	1927.0	629.2	44.9	0	30.3
3	1459.0	1026.0	259.0	0	0
4	2768.0	6975.0	7131.0	0	0
5	4763.0	10800.0	7201.0	0	0
6	2209.0	10560.0	8572.0	143.7	0
7	-	7170.0	5972.0	132.1	0
8	-	-	-	0	-
9	-	-	-	74.2	-
10	-	-	-	462.6	-
Ave.	**2788.3**	**8876.3**	**6911.8**	**81.3**	**8.0**

Table B.6 Two-component crosslinked adhesives with 33.9 % glutaraldehyde

Trials	**0/100**	**20/80**	**50/50**	**80/20**	**100/0**
1	1560.0	4339.0	1797.0	247.0	108.7
2	1051.0	3772.0	3722.0	229.0	556.2
3	1786.0	1528.0	1528.0	489.8	1309.0
4	1213.0	10390.0	4466.0	485.6	0
5	1815.0	5617.0	6313.0	937.3	108.7
6	6603.0	4762.0	7765.0	89.3	556.2
7	-	6885.0	4277.0	43.4	1309.0
8	-	5522.0	-	454.3	-
9	-	-	-	101.2	-
10	-	-	-	373.1	-
Ave.	**1485.0**	**5141.2**	**5308.6**	**351.7**	**282.0**

Table B.7 Two-component crosslinked adhesives with 42.2% glutaraldehyde

Trials	0/100	20/80	50/50	80/20	100/0
1	921.0	1340.0	9016.0	0	0
2	2060.0	1021.0	7170.0	0	0
3	1380.0	5050.0	6749.0	0	0
4	1519.0	4384.0	5147.0	845.5	0
5	1696.0	4561.0	5654.0	275.8	0
6	1789.0	4868.0	2398.0	854.7	1669.0
7	608.7	-	1263.3	681.0	13.7
8	-	-	133.5	529.9	-
9	-	-	-	167.1	-
10	-	-	-	96.1	-
Ave.	**1319.0**	**4995.8**	**4690.7**	**342.0**	**240.4**

(-) represents wood failure causing by cohesion and adhesion failure.