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**PREPARATION AND EVALUATION OF
ENVIRONMENTAL FRIENDLY ADHESIVE FROM
RICE BRAN (RB)**



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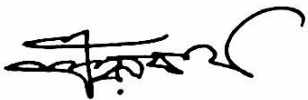
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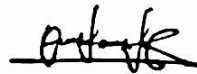
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DECLARATION

I, Md. Omar Faruk, Student ID- 140549, hereby declare that this project thesis is based on my own research work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at other institutions.



Md. Omar Faruk

Date: 06.11.18

*Dedicated
To
My Beloved Parents*

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ABSTRACT

The purpose of this study was to utilize rice bran (RB) to prepare a bio-adhesive with chemical additives. The utilization of rice bran (RB) in the production of RB adhesive will increase its economic value and provide environmental friendly products for wood industry. Though synthetic phenolic resins are not environmental friendly, this can be used as an alternative of those resins. In this study, different types of chemical additives were used at different percent in the modified RB adhesive system. Two types of adhesive were prepared from rice bran with chemical additives, mainly potassium permanganate and poly(vinyl alcohol) modified RB adhesive and urea and formaldehyde modified RB adhesive. Evaluation was carried out on both viscosity and gel time of the adhesives, as well as the strength of the adhesives through block shear specimens test according to ASTM D-905 in comparison with commercial UF resin. The performance of the adhesives was evidenced by differential scanning calorimetry analysis. Where, the produced adhesives showed shear strength ranges from 1.87 to 3.69 MPa. The resulted properties of the adhesives comparatively better in Type B adhesive than Type A adhesive. Chemical change was obvious during RB modification in comparison between the two adhesives. Further research is needed to modify the method to improve the physicochemical properties as well as gel time, viscosity, etc. Thus, the adhesives could be used as an alternative bio-adhesive for different composite industries.

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Chapter One: Introduction

1.1 Background of the study

Natural bio-based raw materials have been utilized as adhesives for centuries such as starch, protein and tannin (Lambuth, 1994). Due to impoverished bonding quality, natural bio adhesives have been discouraged to use (Sulaiman et al., 2018). Over the last few decades, synthetic adhesives (formaldehyde-based resins) have been used instead of natural adhesives concerning the advantages of their superior bonding and greater water resistance properties (Vick, 1999). Despite of carcinogenic nature of formaldehyde based adhesives from their formaldehyde emission, have many advantages over natural bio-based adhesives in their use (Moubarik et al., 2010). Because of its carcinogenic nature, a sharp investigation has been taken under to find alternative non-formaldehyde based adhesives to alleviate the emission problem. As a consequence, researchers has reclaimed the interest of the study of natural adhesives (Nasir et al., 2013; Mayers, 1986) and natural bio-based adhesives or modified adhesives are attractive examples of that (Norström et al., 2014; Wang et al., 2008).

In recent years, due to concerns about protection of environment from hazardous pollutants of synthetic adhesives, natural adhesives are regaining their focused (Wang et al., 2010). That's why, scientists are seeking alternative adhesive systems through replacing a portion or all of the currently used synthetic adhesives. That adhesives must be less expensive and environmental friendly in comparison with synthetic adhesives (Pan et al., 2005). Various attempts have been taken to protect the environment or to diminish toxic pollutants resulting from utilizing formaldehyde resins as wood product or composite adhesives. Enormous studies and works have been dealing with the use of toxicants (formaldehyde) free adhesives, such as, thermosetting or cross-linked type polymers, e.g. isocyanate binders and polyvinyl alcohol. Some other studies dealing with various types of natural bio-based adhesives, e.g. natural tannin and proteinaceous or starch-based adhesives (Navarrete et al., 2013; Guangyan et al., 2012; Pizzi, 2010). Among numerous natural bio-products, high protein containing materials (e.g. soy protein, etc.) or starch based materials (e.g. corn starch, etc.) have played an important role in searching for natural adhesive. Attempts have also been taken to use these bio-based adhesives in particleboard systems (Weiling et al., 1998)

Adhesives from soy-based or protein, tannin and starch have been relatively studied in a good and satisfactory way. However, other natural resources need to be researched to establish as adhesive, such as rice (*Oryza sativa*) bran (RB) (Wang et al., 2008). RB is a by-product of rice milling and produced from brown rice through abrasive milling to produce pure polished rice (Juliano and Bechtel, 1985). RB produced in a amount of 40-50 Mt per year worldwide (Agricultural Information Web, 2006). Which may be considered as a huge amount of agricultural resources to be utilized as raw material. The likely constitutive composition of RB is 12-15 % protein, 15-20 % fat, 36 % starch, and other inorganic material (Dai and Xie, 2000).

In the production of new form of adhesives, defatted RB flour may be useful as a raw material. However, few reports have been published related to the production of glue from this RB. According to Wang et al., (2008) and Pan et al., (2005), RB was treated with thermal and hydraulic sodium. This adhesive was used in particleboard and plywood. Pan et al, (2006) reported that RB adhesive could show a good result when it is used 30 % incorporation with polymeric diphenyl diisocyanate. Another studies reported through Wang et al., (2010), RB adhesive could modified with Poly (vinyl alcohol) PVA at adjusted pH to bond veneers and straw particleboard. However, the RB adhesive has its main limitation of low water resistance capacity and dark in color (Wang et al., 2010, 2008). Altaf et al., (2016) reported that the performance of RB-modified UF (Urea formaldehyde) adhesive system exhibited better properties of particleboard, those obtained with commercial formaldehyde based resins. Research on the modification of RB is in its infancy. Further research is needed with suitable chemical additives and on its modified adhesive systems and properties for the betterment. Thus, this study is intended to manufacture RB adhesive from rice (*Oryza sativa*) bran with chemical additives and evaluate the properties of the adhesive and particleboards produced through the adhesive and assessing the technical feasibility of RB adhesive as an alternative of commercial formaldehyd based adhesives in the composite industry..

1.2 Objectives of the Study

The objective of this study is to develop a natural adhesive from defatted RB by controlling pH , gelatinisation with some chemical additives and feasibility study for particleboard fabrication. This could increase the economic value of this less important by-product and provide environmental friendly products for the wood-based industry. Every year, Bangladesh produced

huge amount of RB from brown rice. RB has mostly been utilized as an animal feed ingredient, fertilizer, oil and fuel. But it can be used in wood or composite industries as an adhesive. Thus, the specific objectives of the study are as follows-

1. To produce and evaluate the adhesive properties of the rice bran-based adhesive.
2. To evaluate the properties of particleboards produced using the RB-based adhesive by analyzing their physical and mechanical properties.

Chapter Two: Review of Literature

2.1 Binder or Adhesive

Wood adhesives are polymeric materials, which are capable of bonding with the surface of wood physically and chemically or both. Today, large amount of adhesive is used in the industrial production of plywood, laminated veneer products, particleboards as well as manufacture of building materials for various purposes, such as constructional purposes, decorative purposes, etc. The bonding of wood with adhesives is known to date back at least to the Pharaohs, and in all likelihood dates even further back in history (Keimel, 1994). Up to World War II the dominant adhesives for bonding wood were made from natural sources (Lambuth, 1989).

Adhesives or binders are the materials used in the fabrication of timber structures and components offers a neat and efficient method of bonding together the separate pieces of wood. The bond attained must meet the strength requirements for the structure as a whole and this bond must remain unaffected by the condition to which it will be exposed throughout its life (Youngquist, 1999). The principle attribute of adhesives is their ability to form strong bonds with surfaces of a wide range of materials and to retain bond strength under expected use conditions (Lehman, 2004). However, ASTM (1997) defines an adhesive as a substance capable of holding materials together by surface attachment.

2.1.1 Classification of wood adhesives

There are mainly two types of adhesive. One originated from natural sources known as natural adhesive and another is synthetic adhesive.

2.1.1.1 Natural adhesive

Natural adhesives that have been used by the forest products industry include adhesives derived from starch, soybeans, animal waste and by-products of the meat processing and tanning industries, and casein from skim milk. Of these, protein-based adhesives (soy, blood, and casein) were most commonly used (Pizzi, 1994). In addition to the proteinaceous adhesives (i.e. animal, soy, casein, and blood adhesives) used in the past, several other natural materials have been and continue to be investigated as sources of wood adhesives. Carbohydrates, tannins, lignins, and 'dissolved' whole wood and bark have been studied as total or partial replacement of the phenolic component in phenolic resin adhesives (Stoeckel et al., 2013).

Though, adhesives derived from natural sources, they have limited application because of their weak bonding strength and performance. However natural adhesives are still being used in some non-structural products, they do not provide the necessary strength and durability required for engineered wood products (Dunky, 1998). Although natural adhesives were at one time the predominant adhesives used in the wood industry, since the mid-twentieth century they have been all but displaced by synthetic adhesives. Nowadays, due to the environment friendly nature, the use of bio- based adhesive as wood adhesives has gained preference over synthetic adhesive in wood adhesive system.

A. Proteinaceous adhesives

Protein-based adhesives can be derived from animals and agricultural sources. These were widely used in the past as wood adhesives. The adhesive is sold in solid form. This is mixed with sufficient water to soften the adhesive, and the mixture is melted at a temperature under 66^o C before application to the wood. Very clean conditions need to be maintained because this adhesive is very susceptible to bacterial attack.

Soybean, casein, and blood adhesives are proteinaceous adhesives. The proteins have a complex three dimensional structure of highly coiled chains. The three dimensional structure is dependent on the types of amino acid in the polypeptide chain and their sequence and the hydrogen bonding and disulfide cross-links between individual amino acid side groups. For the protein to function as an adhesive, the internal cross-links must be broken, and the highly polar side groups on the amino acids made available for interaction with a polar adherend such as wood (Bye, 1989). The disruption of the internal cross-links is accomplished by dissolving (dispersing) the protein, usually in alkaline media.

B. Tannin adhesive

The word tannin has been used loosely to define two different classes of chemical compounds of mainly phenolic nature: hydrolysable tannins and condensed tannins. The former are mixtures of simple phenols, such as pyrogallol and ellagic acid, and of esters of a sugar, mainly glucose, with gallic and digallic acids (Pizzi, 1983). The lack of macromolecular structure in their natural state, the low level of phenol substitution they allow, their low nucleophilicity, limited worldwide production, and higher price somewhat limit chemical and economical interest in these.

Condensed tannins, on the other hand, constituting more than 90% of the total world production of commercial tannins (200 000 tons per year), are both chemically and economically more interesting for the preparation of adhesives and resins. Condensed tannins and their flavonoid precursors are known for their wide distribution in nature and particularly for their substantial concentration in the wood and bark of various trees.

C. Lignin adhesive

Much has been written about and many studies have been conducted regarding the use of lignins for wood panel adhesives. It can safely be said that this natural raw material has probably been the most intensely researched one as regards wood adhesives application. Lignins are phenolic materials, they are abundant and of low cost, but they have lower reactivity towards formaldehyde, or other aldehydes, than even phenol.

In general, lignin and liginosulphonates have been mixed in small proportions with synthetic resins, such as PF resins (Newman and Glasser, 1985) and even UF resins, to decrease their cost. Their low reactivity and low level of reactive sites, however, causes that for any percentage of lignin added the cost advantage is lost in the lengthening of the panel press time. The only step forward that has found industrial application in the last 20 years is to pre-react in a reactor the lignin with formaldehyde to form methylolated lignin, i.e., to carry out part of the reaction with formaldehyde first, and then add this methylolated lignin to PF resins at the 20 to 30% weight level (Gardner and Seller, 1986).

D. Carbohydrate adhesives

Carbohydrates in the form of polysaccharides, gums, oligomers and monomeric sugars have been employed in adhesive formulations for many years. Carbohydrates can be used as wood panel adhesives in three main ways: (i) as modifiers of existing PF and UF adhesives, (ii) by forming degradation compounds which then can be used as adhesives building blocks and (iii) directly as wood adhesives.

2.1.1.2 Synthetic adhesive

Adhesives which are made in a synthetic process or manmade process are called synthetic adhesives. These adhesives are more resemble to natural adhesives in physical characteristics but they can be well tailored to meet specific wood working requirements (Dunky and Pizzi, 2002). The typical synthetic adhesives are epoxies, polyurethanes, cyanoacrylates, polyimides,

silicones, acrylics, polyamides, cyanoacrylates, polyacrylates, polyvinyl acetate (PVA), nitrile, and neoprene. Synthetic adhesives allow efficient and economical utilization of diverse and changing wood resources because of their highly durable nature. Synthetic adhesives can be categorized into two groups, namely thermosetting adhesives and thermoplastic adhesives.

A. Thermosetting adhesives

Thermosetting resins form polymers that are cross-linked during cure by strong covalent intermolecular bonds, forming one giant molecule. Cross-linking is irreversible therefore thermosets cannot be reprocessed (re-melt). Cross-linking is achieved in curing process initiated by heat, chemical agents, radiation or evaporation of Solvents. Curing results in sharp increase of strength, elasticity and stability of thermosets (Pizzi, 2015). The bonds formed by thermosetting adhesives are generally moisture resistant and support loads under normal use. Examples of this category of adhesives include amino resins, phenolic resins, epoxy resins, and isocyanates (Sellers, 1998). Amino resins, phenolic resins, and isocyanates are the three most important thermosetting adhesive systems used by the wood products industry.

Phenolic adhesives

A. Phenol formaldehyde adhesives

The PF resins are formed by the reaction of phenol with formaldehyde. By varying the reaction time, reaction temperature, catalyst type and the ratio of formaldehyde to phenol, a number of adhesive systems with different characteristics can be produced (Knop and Scheib, 1979). Novolac resins are produced using an acid catalyst and an excess of phenol. Initially, formaldehyde reacts with phenol to form hydroxymethyl derivatives preferentially at the aromatic ring carbon para to the phenolic hydroxyl. As the reaction proceeds, reactions also take place between the hydroxymethyl groups and the aromatic ring carbons of phenol or another hydroxymethyl group to form methylene linkages. In this manner, the polymeric structure of the resin is produced. Due to the excess of phenol in the reaction; novolac resins do not have active hydroxymethyl groups. As a consequence, novolac resins are fairly stable. Resole resins are produced with a base catalyst and an excess of formaldehyde. For resins used in the wood industry, sodium hydroxide is the most important catalyst, although other base catalysts, such as sodium carbonate, alkaline oxides and hydroxides, and ammonia can also be used. Typical resole

resins contain a molar ratio of phenol to formaldehyde to sodium hydroxide equal to approximately 1:2:0.5, with a resin solids content of about 35–50%.

The PF adhesive resins are used primarily in the production of soft wood plywood, oriented strandboard, and waferboard. Actually, PF resins are the major adhesives used for bonding wood panels for use in exterior applications.

B. Phenol resorcinol formaldehyde

By incorporating resorcinol during the synthesis of PF resins or by replacing phenol with resorcinol altogether, phenolic resins can be made with significant decreases in cure time compared with PF resin adhesives. The chemistry associated with the formation and cure of PRF and RF resins is similar to that for PF resins.

The PRF and RF resin adhesives are used in situations where fast or room temperature curing is required (e.g., finger jointed structures) or where the wooden assembly being bonded is too thick to allow sufficient heat for resin cure to reach the bond lines in the interior of the assembly (e.g., laminated timbers). The main disadvantage of these resins is the much higher cost of resorcinol compared with that of phenol.

Amino adhesives

A. Urea formaldehyde

The synthesis of UF resin takes place in two stages. In the first stage, urea is hydroxymethylated by the addition of formaldehyde to the amino groups. This reaction is in reality a series of reactions that leads to the formation of mono-, di-, and tri- hydroxymethylureas. The addition of formaldehyde to urea takes place across the entire pH range but is faster under acidic and basic conditions than under neutral conditions. The second stage of UF resin synthesis consists of the condensation of the hydroxymethylureas to low molecular weight polymers. The rate at which these condensation reactions occur is very dependent on the pH and, for all practical purposes, occurs only at acidic pH.

More than 70% of this resin is used by the forest products industry (White, 1995). The UF resin is used by the forest products industry in the production of particleboard (61%), medium-density fiberboard (27%), and hardwood plywood (5%), and it is used as a laminating adhesive (7%) for bonding furniture overlays to panels and for interior flush doors, etc.

B. Melamine urea formaldehyde

MUF and MF resins are more resistant to moist environments than are UF resins. However, melamine is much more expensive than urea. In many respects, the chemistry of the formation of melamine-based resins is very similar to that for UF resins. However, the addition of formaldehyde to the amino groups of melamine is faster and more complete than is the addition of formaldehyde to urea. Thus, complete hydroxymethylation of melamine occurs (Pizzi, 1983), which as mentioned above, is not the case with urea. Another important difference is that the condensation reactions of the hydroxymethylated melamines occur not only under acid conditions but under neutral and slightly alkaline conditions as well (Pizzi, 1994; Pizzi and Mittal, 1994). The MF and MUF resins are used for scarf jointing of plywood and end jointing of structural lumber that can be used in protected exterior exposure. In addition, these resins are used for bonding low and high pressure laminates and overlays.

Isocyanate resins

Isocyanates are important industrial chemicals used in injection molding and for the production of poly urethane foams. All isocyanates of industrial importance contain two or more isocyanate groups ($\text{N}=\text{C}=\text{O}$) per molecule. MDI has become an important adhesive in the wood products industry, especially for bonding oriented strandboard. Isocyanates are made by phosgenation of amines. The synthesis of MDI starts with the condensation of aniline with formaldehyde in acid solution. A complex mixture of isomeric di amines and oligomeric poly amines is formed. The 4, 4-diamine predominates. This complex mixture is phosgenated to give PMDI. PMDI, rather than a purified diisocyanate, is the material used by the wood products industry as an adhesive.

2. Thermoplastic adhesives

Synthetic adhesives are further classified as thermoplastic resins by the nature of the polymer after it has set or cured. Thermoplastic resins are polymers that soften when exposed to heat then solidify on cooling to room temperature (Sellers, 1998). The bonding process basically involves softening or melting the polymer while in contact with their adherents, and allowing the joint structure to cool. The structure can be easily disassembled or repositioned by reheating while applying force. These polymers are generally soluble as well. Although not used in the same quantities as the thermosetting resins, thermoplastic adhesives, nevertheless, are extremely

important for bonding wood. The prime examples of this class of adhesives used in wood bonding are Polyvinyl Acetate (PVAc) and Ethylene Vinyl Acetate (EVA) (Pizzi, 2015).

Polyvinyl acetate

PVAc is most widely used as an emulsion of PVAc polymers in water. The emulsion is formed by polymerization in water of vinyl monomers, predominantly vinyl acetate, a process known as emulsion polymerization. The emulsion is white to off-white in color and is the familiar 'white glue' used in many household projects. Because of its resistance to attack by microorganisms and its low cost, this adhesive has replaced natural adhesives made from hide and casein.

PVAc softens as its temperature is raised above room temperature, and it is less resistant to moisture and humidity than thermosetting resins. For this reason, PVAc adhesives are used in interior applications. In addition, PVAc tends to creep ('cold flow') under a sustained load. Several modifications are used to enhance the resistance to moisture and to decrease creep of PVAc adhesive bonds. One such method is the addition of other types of vinyl monomer during polymerization to improve the properties. A second method is to add cross-linking agents that increase the rigidity of the polymer.

Ethylene vinyl acetate

In the wood working industry, EVA copolymers and their blends with other resins and fillers are used as hot-melt adhesives. Petroleum based waxes are used to reduce the melt viscosity. Rosin derivatives are used to increase tack. Hot-melts based on polyamide, polyester, and polyurethane are also used. For the hot-melt adhesives to wet the wood surface, they are applied in the molten state. The adhesive then rapidly sets upon cooling. Thus, hot-melts are suited for high-speed, continuous bonding operations. Typical applications include veneer splicing and edge veneering and banding.

2.2 Rice Bran (RB) adhesive as a natural adhesive

2.2.1 General information about Rice (*Oryza sativa*) bran

Rice (*Oryza sativa*) is a cereal plant and the outer layer of the rice grain is called as rice bran. It is also called as cereal fiber, dietary fiber, etc. RB is a by-product of rice milling process (the conversion of brown rice to white rice). One hundred kilogram (100 kg) of paddy rice will produce approximately 6-10 kg of bran. In modern rice mills, several different kinds of bran are produced, such as coarse bran, fine bran and polish bran (Barron, 2010). RB is a mixture of

substances, and the major substances are proteins, fats, starch and ash contents which are largely depend on the milling process of rice. It also contains a high level of dietary fibres (beta glucan, pectin and gum). However, RB has mostly been utilized as an animal food ingredient, fertilizer and fuel. Although it can be a human food ingredient, through undergo some processing that increases its cost compared to other foods (Wang et al., 2010). Rice bran has a high nutritive value with an excellent source of vitamins B and E. It also contains small amounts of antioxidants, which are considered to low cholesterol in humans (Saunders, 1985).

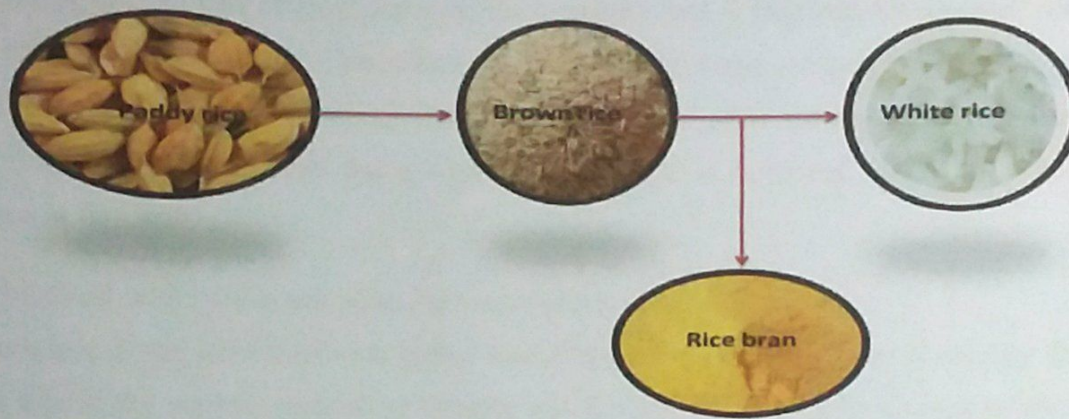


Fig. 1. Manufacturing process of Rice Bran (RB)

2.2.2 Component of Rice bran (RB)

Rice bran (RB) is a mixture of some substances. Following are the component of RB-

Table 1. Typical chemical composition of RB

Name of the component	Composition (%)
Protein	12-15
Fat	15-20
Starch	36
Ash content	17

(Sources: Wang et al., 2010; Saunders, 1985)

2.2.3 Sources of Rice Bran (RB)

Paddy rice (*Oryza sativa*) is the one and only source of rice bran (RB). RB is the outer layer of paddy rice grain, and it is collected from the rice mill in which the paddy rice is processed for the conversion of brown rice to white rice. It can be collected from all over the world because the paddy rice is cultivated in all over the world.

2.2.3.1 Paddy rice (*Oryza sativa*)

Paddy rice is the individual rice kernels that are in their natural, unprocessed state. Sometimes referred to as rough rice, it is harvested directly from rice fields or paddies and transported to a processing site. As part of the processing, the protective hull is removed, leaving only the actual rice kernel for consumption. The hull on rice is not edible. Some producers parboil the rice with the hull on before milling it, which increases its nutritional value and makes it more durable. In the milling process of paddy rice a huge amount of hull is removing, which is commercially known as rice bran.

2.2.3.2 Paddy rice (*Oryza sativa*) as the source of Rice Bran (RB)

Rice is one of the most important global food crops and a primary source of calories for more than half of the world's population (Dogara and Jumare, 2014). Day by day the production of rice increases worldwide. However, the consumer of milled rice is also increases. According to Muthayya et al., (2014), rice is currently grown in more than hundred countries and approximate 700 million tons of paddy rice is produced annually. Whereas, the amount of RB is produced more than 200 million tons (approximate) per year. These can be a vast resource for the production of RB adhesive. Therefore, multisectoral approaches are needed for the production, promotion and implementation of RB adhesive from RB in countries all around the world.

2.2.3.3 Geographical distribution of paddy rice (*Oryza sativa*)

Rice is the world's leading food crop, cultivated over an area of about 180 million hectares with a production of about more than 700 million tons (approximate). Among the rice growing countries, India has the largest area (44.8 million hectares) followed by China and Indonesia. In respect of production, India ranks second with 131 million tons of paddy next to China (200 million tons of paddy). In regard to average yield per hectare, Egypt ranks first followed by USA. The leading countries producing rice crop are Japan, Brazil, China, India, Indonesia,

Bangladesh, Vietnam, Thailand, Myanmar and Philippines (Dogara and Jumare, 2014; Jeong et al., 2017).

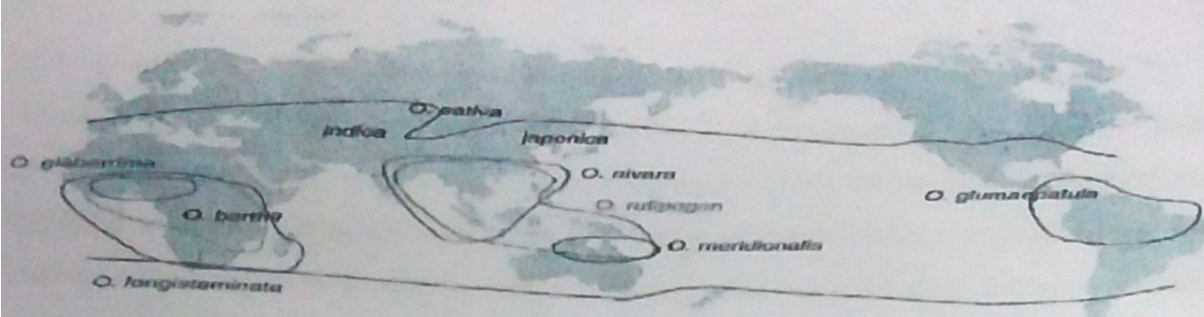


Fig. 2. Geographical distributions of rice with genus (Source: Agnoun et al., 2012)

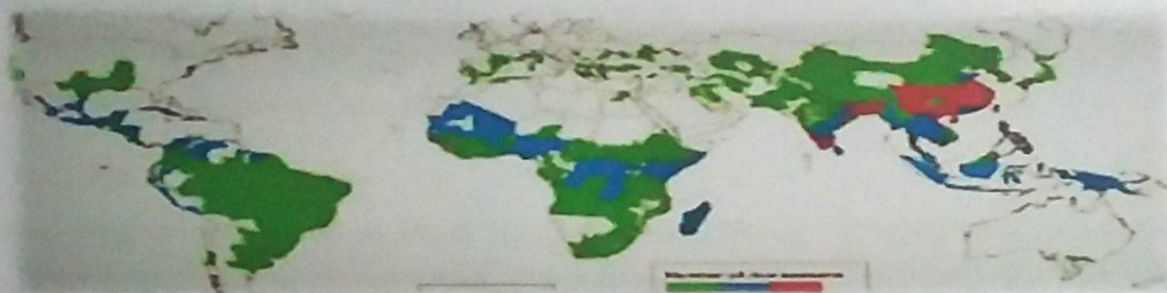


Fig. 3. Geographical distributions of rice with seasons (Source: Laborte et al., 2017)

2.2.4 Current use of Rice Bran as an adhesive

Natural adhesives were extensively used before the 1930s. Since then they have been gradually replaced almost completely by synthetic adhesive (Pizzi, 2006). Nowadays, the synthetic adhesive is widely used for industrial production, such as for plywood, particleboard as well as engineered building materials or decorative purposes. But the problem of synthetic adhesive is that they are not environment-friendly. However, significant efforts have been taken to develop glue from natural materials to reduce or replace phenol and formaldehyde content (Sowunmi et al., 1996).

The adhesive properties of protein and starch have long been recognized and relatively well studied from various natural sources, such as soy bean, wheat, corn, etc. (Myers, 1993). However, a new natural resources, such as rice bran which has the potential to become an adhesive because of its properties. Actually, these RB adhesive is in its infancy but this vast

resource of RB is useful to develop a new form of natural adhesive. This could increase the economic value of the important by-product of rice milling and provide the best substitute for formaldehyde in adhesive production (Wang et al., 2010).

2.2.5 Advantages of RB adhesive

The natural RB adhesives are used to replace the formaldehyde-based adhesive system in order to reduce formaldehyde and volatile organic compound (VOC) emissions from the synthetic formaldehyde based adhesives. Formaldehyde is produced worldwide on a large scale. It is used mainly in the production of adhesives that are used as adhesives and binders for wood products, engineered building materials, etc. International Agency for Research on Cancer (IARC), part of the World Health Organization, concluded that formaldehyde is carcinogenic to humans (IARC, 2004). So, people are trying to replace it with a natural environmentally friendly one. Amongst the possible alternatives, RB is an excellent renewable resource which can be used for replacing petroleum-derived phenolic compounds (Wang et al., 2008).

2.2.6 Chemical additives

Based on previous studies, an initial formulation for preparing RB adhesive is designed. To produce a new form of natural adhesive, Potassium permanganate (KMnO_4) and Poly (vinyl alcohol) (PVA) are considered to use in the mixture of RB powder to increase its strength and properties.

2.2.6.1 Potassium Permanganate

Potassium permanganate is a purplish colored crystalline solid, also known as Chameleon mineral, Condy's crystal, Permanganate of potash, etc. J.R. Glauber was the first person who mentioned the chemical name (Weeks and Liecester, 1968). Molecular formula of potassium permanganate is KMnO_4 consisting of K^+ and MnO_4^- ions. Potassium permanganate is produced industrially from manganese dioxide. In this process manganese dioxide is fused with potassium hydroxide and heated in air to produce the chemical (Reidies, 2000).

The physical state of potassium permanganate is an odorless solid and water soluble. It is also a well-known and strong oxidizing agent because of its permanganate ion (MnO_4^-). However, potassium permanganate has various uses in various fields such as water treatment, organic chemistry, analytical chemistry, etc. It disinfects water from attacking microorganisms such as

bacteria, fungi, virus, etc. (Wagenet et al., 1995). In organic and analytical chemistry, potassium permanganate is a very valuable reagent.

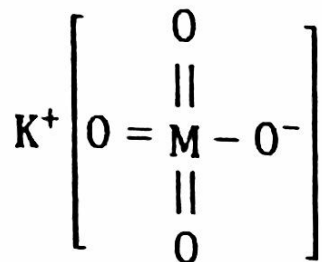


Fig. 4. Ionic structure of $KMnO_4$

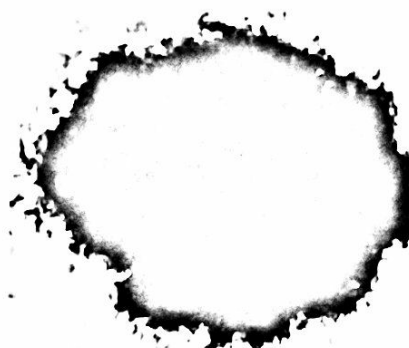


Fig. 5. Solid form of $KMnO_4$

2.2.6.2 Poly(vinyl alcohol) (PVA)

Poly(vinyl alcohol) (PVA) is an odorless and tasteless, biodegradable, translucent, white or cream colored granular powder also known as Vinyl alcohol, Hydroxyethene, Hydroxyethylene, etc. (Halima, 2016). Molecular formula of PVA is $(C_2H_3OR)_n$, where $R = H$ or $COCH_3$ or $(CH_2CHOH)_n$ or CH_2CHOH or C_2H_4O . It is soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents. It has a melting point of 180 to 190°C. It is also unique among polymers (chemical compounds made up of large, multiple-unit molecules) in that it is not built up in polymerization reactions from single-unit precursor molecules known as monomers. Instead, PVA is made by dissolving another polymer, polyvinyl acetate (PVAc), in an alcohol such as methanol and treating it with an alkaline catalyst such as sodium hydroxide (Priyadarshini and Priyadharsini, 2018).

Polyvinyl alcohol has various applications in the industries as a binding and coating agent. It is a film coating agent especially in applications where moisture barrier or protection properties are required (Moulay, 2015). However, PVA can be a de-characterizing agent of thermosetting resin mainly used as a binding agent such as carbamide, formaldehyde resin and melamine, for plywood, artificial board and timber processing. When mixed with melamine-formaldehyde resin, the PVA size paste helps increase the viscosity and shortens both curing and cooling time with stronger initial cohesion (IARC, 1979). Although PVA is used as an additive to cement and mortar for efficient increase of their cohesion and fluidity, and reduce the drying time for the concrete surface, thus increasing coating adaptability and preventing concrete cloth from chapping (Nair, 1998). It can be also used as an adhesive agent for profiles, e.g. prefabricated

plasterboard and sound absorption board that are made of organic fibers (cane, residue and wood-shavings) or non-organic materials.



Fig. 6. Powder form of PVA

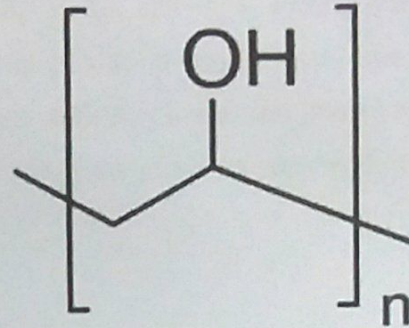


Fig. 7. Molecular structure of PVA
(Source: Seol et al., 2013)

2.3 General information about particleboard

Particleboard is a wood-based composite and it has a wide range of applications such as, for furniture, in flooring and as panels. Particleboards consist of various kinds of wood particles that are glued together with the help of one or more agents. The wood particles can consist of sawdust, saw shavings, recycled wood, agricultural residue, etc. and the agents are heat (high temperature), pressure, humidity, catalyst, etc. (Shrivastava, 1997). The particles are varied based on size, after they have been dried. The sizes of the particles are of great importance and will influence the properties of the final product. However, some other properties related to the production of particleboards may influence the final products, such as particle geometry, resin levels, board density and manufacturing processes, etc. In the manufacturing process, additives should be incorporated in a good and satisfactory way to increase the specific performance including greater dimensional stability, increased fire retardancy and moisture resistance (CPA, 1996).

2.3.1 Particleboard

A particleboard is defined by various scientists in a various scientific way. A particleboard is a structural material made of wood fragments, such as chips or shavings which are mechanically pressed into sheet form and bonded together with resin. However, particleboard is defined as a panel product manufactured from lingo-cellulosic materials, primarily in the form of discrete

particles, combined with a synthetic resin or other suitable binder and bonded together under heat and pressure (Maloney, 1977).

According to Shrivastava, (1997), a particleboard is a board (or sheet) constituted from fragments of wood and/or other lingo-cellulosic materials (chips, shavings, flakes, splinters, sawdust, etc.), bonded with organic binders with the help of one or more agents like heat, pressure, humidity, catalyst, etc. Thus, from the above definitions we can mention that particleboard is produced from lingo-cellulosic materials which are glued together with a resin under heat and pressure.

2.3.2 History and development of particleboard

For hundreds of years, people have used glue to join wood parts. Theoretically, the first particleboard was manufactured, when two pieces of wood were first glued together (BRI, 1956). It was first introduced in the 19th century. The first publication about making concept of particleboard was 'utilization of wood waste' published by Earnest Hubbard in 1902 (Eastman et al., 1997). Before particleboard, modern plywood, as an alternative to natural wood, was invented in the 19th century, but by the end of the 1940s there was not enough lumber around to manufacture plywood affordably. By that time particleboard was intended to be a replacement (Sheng et al, 2004). For making plywood more raw materials is needed and it has some negative effect on forest. As this reason, first efforts were made in the early 1920's for manufacturing of particleboard. But it was unsuccessful as for the lack of suitable adhesives. After an unsuccessful application of manufacturing of particle board a new technique was applied in the early 1930's. Resin is applied for the growing demand paved the way for the industrial production of particleboard in the early 1940's (Moslemi, 1985)

The first important developments in particleboard manufacture occurred, just prior to World War II, with the discovery and large scale production of urea glues at a factory in Bremen, Germany (Maloney and Mottet, 1970). It used waste material such as planer shavings, off-cuts or sawdust, hammer-milled into chips, and bound together with urea resin. When particle board first came onto the market, it was only made available to the wealthy because the price was higher than some real timbers. Over time, the manufacturing process matured, the supply became steadier, and the material became cheaper. Today's particleboard manufacturer provides high-quality products that consumers require due to up gradation of manufacturing techniques (Moslemi, 1985; Sheng et al, 2004).

2.3.3 Types of particle board

There are different types of particleboards depending on particle size, types of particles, thickness and density of the board, types of resin used in the production, production process, etc. Thus the types are:

2.3.3.1 According to the particles used

Flakeboard: A particleboard in which the wood is largely in the form of flakes, giving the surface a characteristic appearance (Shrivastava, 1997). A small wood particle of predetermined dimensions specifically produced as a primary function of specialized equipment of various types, with the cutting action across the direction of the grain (either radially, tangentially, or at an angle between), the action being such as to produce a particle of uniform thickness, essentially flat, and having the fiber direction essentially in the plane of the flakes, in overall character resembling a small piece of veneer (Shrivastava, 1997).



Fig. 8. Various types of flakeboard (Source: Flakeboard Design Center, 2013)

Chipboard: A particleboard made from chips. It is made in varying thickness and may be surfaced with paper, veneers, plastic materials, etc. (Shrivastava, 1997). Gluing together wood particles with an adhesive, under heat and pressure makes chipboard. This creates a rigid board with a relatively smooth surface. Chipboard is available in a number of densities: -normal, medium and high-density. It is often used for kitchen tops (which are laminated with melamine) and fire doors. Medium density is somewhere between normal and high density. There are exterior grades of chipboard available but most are only suitable for internal use. Chipboard with a veneered surface is widely used for flat-pack furniture and work surfaces. High-density

chipboard is often used as the carcass for kitchen units and worktops and flooring. This type of chipboard is hardwearing, rigid and heavy (Salehuddin, 1992).



Fig. 9. Chipboards (Source: Dreamstime, 2009)

Shavingsboard: A particleboard in which wood shavings are the chief constituents. (Shrivastava, 1997). Shavings are produced from various kinds and sizes of trees being converted to lumber of different dimensions. Often instigated by the need for reducing costs of disposal of materials that clog production, or by the desire to get some return from material that in the log form has represented a considerable outlay of money. Shavings ordinarily come from air-dried or kiln-dried wood. Shaving produced from machining dry wood of a single species affords their producer the best prospects for marketing waste material. Uniform particle sizes (achieved by screening) are needed for some uses. For most uses only fresh material is acceptable. Shavings, when exposed to the weather, deteriorate very rapidly and lose much of their value (Salehuddin, 1992).



Fig. 10. Shavingsboard (Source: Shutterstock)

Waferboard: It is a structural material made from rectangular wood flakes of controlled length and thickness bonded together with waterproof phenolic resin under extreme heat and pressure (Salehuddin, 1992). Waferboard is a widely used, versatile structural wood panel. Manufactured

from waterproof heat-cured adhesives and rectangular shaped wood strands that are arranged in cross-oriented layers, Waferboard is an engineered wood panel that shares many of the strength and performance characteristics of plywood. Waferboard's combination of wood and adhesives creates a strong, dimensionally stable panel that resists deflection, delamination, and warping; likewise, panels resist racking and shape distortion when subjected to demanding wind and seismic conditions. Relative to their strength, waferboard panels are light in weight and easy to handle and install (Shrivastava, 1997).

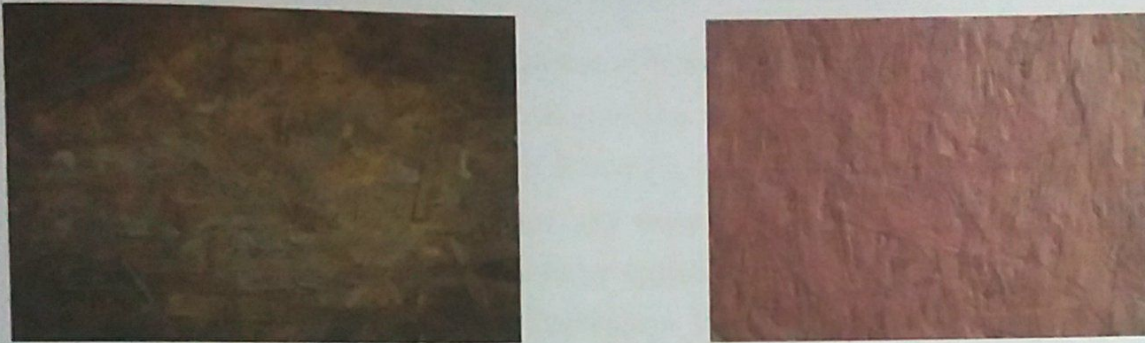


Fig. 11. Waferboards (Source: Dreamstime.com)

Oriented strand board: Oriented strand board, or OSB, or Sterling board (UK) or Smart Ply (UK and Ireland) is an engineered wood product formed by layering strands (flakes) of wood in specific orientations (Salehuddin, 1992). Oriented strand board is manufactured in wide mats from cross-oriented layers of thin, rectangular wooden strips compressed and bonded together with wax and synthetic resin adhesives. The resin types typically used include phenol formaldehyde (PF), melamine fortified urea-formaldehyde (MUF) or isocyanate, all of which are moisture resistant binders. In Europe, it is common to use a combination of binders, typically PMDI would be used in the core and MUF in the face layers and this has the advantage of reducing press cycles whilst imparting a bright appearance to the surface of the panel (Shrivastava, 1997).



Fig. 12. Oriented strand boards (Source: Wikimedia, 2008)

2.3.3.2 Particle size distribution in the thickness of board

Single layer or homogeneous board: Single-layer particleboards are made from pressing together wood particles of similar sizes to form a flat, dense board. This type of particleboard is suitable as a base for plastic lamination and veneering, but not for painting. Single-layer particleboards are used commonly for interior applications. They have some water-resistance capabilities, but are not fully waterproof (Shrivastava, 1997).

Three layer board: A three-layer particleboard is made from sandwiching a layer of larger wood particles between two layers of high-density, finer wood particles. The outer layers have a higher amount of resin adhesive than the inner layer. Three-layer particleboards have smooth outer layers that are suitable for painting. These boards are not as dense as single-layer boards and tend to split easily (Shrivastava, 1997).

Graded-density boards: Graded-density particleboards are similar to three-layer particleboards. They have an inner core of coarse wood particles sandwiched between two outer layers of finer particles. However, unlike a three-layer particleboard, the transition between the coarse surfaces to the finer ones is gradual. Graded-density particleboards are used in cabinet construction and for furniture components (Salehuddin, 1992).

2.3.3.3 Cost effectiveness and market availability of board

Laminated Particleboard: Laminated particle board is manufactured by attaching a thin layer of laminates on the surface of plain particle board. The lamination enhances beauty and increases durability of particle board (Buyuksari, 2012).



Fig. 13. Laminated particleboards (Source: Homeverity, 2018)

Veneered Particleboard: Veneered particle board is manufactured by attaching veneer on the top surface of the plain particle board. Veneered particle boards have more resistance to warping, as they are properly sealed. They provide the aesthetics of a natural wood in low budget cost (Hse et al., 2012).



Fig. 14. Veneer particleboard (Source: Wu, 2013)

Cement Bonded Particleboard: A cement bonded particle board is manufactured using cement, wood waste particulate like wood chips, sawdust, wooden shavings and water. Due to cement content, these boards are more durable, fire-resistant and termite resistant (Irel, 1993). The cement bonded particle board has high expansion and shrinkage properties in presence of moisture. They are generally used in the production of fire resistant furniture, false ceiling, internal and external walls and permanent shuttering for concrete floors and walls.

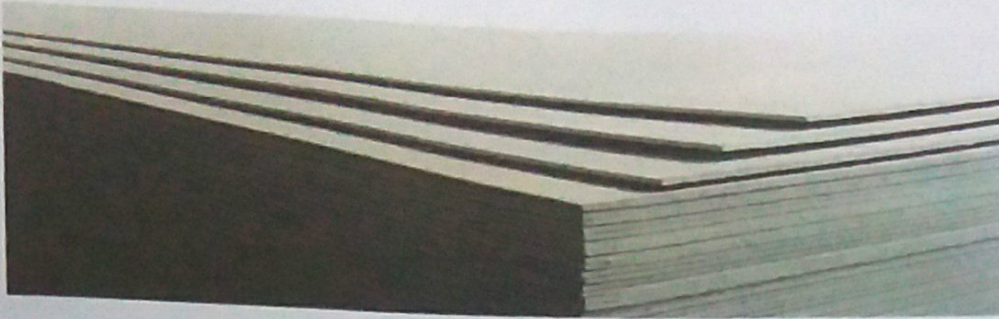


Fig. 15. Cement bonded particleboards (Source: India mart, 2013)

Melamine Particleboard: A sheet of melamine-impregnated decor paper is attached on the top surface of the plain particle board under heat and pressure. Also, melamine-urea formaldehyde resin is used along with wax emulsion to bond the particle board and make it water resistant (Maylor, 1995). Melamine particle boards are very durable and have resistant to scratches. They are available in various colors and textures to impart decorative look to the interior of your house.



Fig. 16. Melamine particleboards (Source: Weiku.com, 2011)

2.3.4 Raw materials for particleboard manufacturing

2.3.4.1 Ligno-cellulosic materials

Woody materials, planer savings, sawmill residues, such as slabs, edging, trimmings, etc. Residues from timber cutting in furniture and cabinet manufacturing plants, residues from match factories, veneer and plywood plant residues, saw dusts, Logging residues, such as short logs, broken logs, crooked logs, small tree tops and branches, forest thinning , etc. and bark (Salehuddin, 1992).

2.3.4.2 Non-woody materials

Jute sticks, bagasse, bamboo, flax shaves, cotton stalks, cereal straw, almost any agricultural residue (such as husks, coconut coir etc.) after suitable treatment (Youngquist, 1999).

2.3.5 Manufacturing process of particle board

Particle board manufacturing processes are as follows-

A. Raw material preparation:

Debarking to remove bark which can reduce the properties of particleboard and sorting classification of waste wood for further processing.

B. Conversion to particles:

Aim to manufacture a homogeneous product and need therefore to produce chips of a suitable size & shape to form the furnish for the board

C. Particle drying:

Ensure that the “furnish” has a homogeneous MC because this will cause problems with board blows, too little will lead to poor heat transfer in the press and incomplete resin cure, resulting in poor mechanical properties. Generally, driers work on the principle of passing the particles through a stream of hot air (180-200⁰ C).

D. Particle classification:

Particle classification depends on control particle size distribution and the classification systems are Sieving, Air classification, etc.

E. Blending with a resin and additives:

Addition of adhesive and other chemicals such as wax, hardeners etc. to the dry particles furnish is called blending. Basically, three systems are used- a) the contact and friction system, i.e., simple mixing, b) the spreader roll system and c) spray nozzle system.

F. Mat formation and conveying:

After the particles have been prepared, they must be laid into an even and consistent mat to be pressed into a panel. Generally, Mat is formed into 3-4 times and even 20 times thicker than the target board thickness. This is typically accomplished in a batch mode or by continuous formation.

G. Pre-pressing & hot pressed:

Pre-pressing to the furnish to reduce the bulk and give some mechanical strength to the mattress and hot-pressing to finally consolidate the board and cure the adhesive. Density profile generated during hot-pressing. Presses can be divided into platen and continuous types. Further development in the industry has made possible the construction of presses for producing increasingly larger panel sizes in both single- and multi-opening presses.

H. Conditioning and Finishing:

The hot boards conditioned to equilibrate moisture content and to stabilize and fully cure the resin. This conditioning usually follows cooling in star coolers for boards with urea formaldehyde resins. Phenolic bonded particle board is usually hot stacked for some days to ensure final cure of the resin. Then, the board is trimmed to obtain the desire length and width. Trim losses usually amount to 0.5% to 8% and sanded or planed prior to packing and shipping.

2.3.6 Considerations for the production of quality particleboard

Everyone try to produce particleboard but the quality production of particleboard largely depends on some factors or considerations, such as density, layering, types of adhesives, geometry of the particles (length, width, thickness, diameter, etc.), raw materials, surface quality and internal bonding strength of the particles i.e. surface quality and internal bonding strength are higher with small particles (Salehuddin, 1992).

2.3.7 Uses of particleboard

Particleboard is a common building material used in almost all types of construction projects. It is a standard in the industry and is utilized as a substitution for plywood to save money. Particleboard is available in different grades depending on the size of the particles used in the material. Various types of particleboards are used in various forms, such as store Fixtures, kitchen cabinets, office and residential furniture, manufactured home decking, furniture, ceilings, shelving, dore cores, etc.

Chapter Three: Materials and Methods

3.1 Materials

Raw materials for manufacturing of RB adhesive were rice bran (RB), potassium permanganate (KMnO_4), poly (vinyl alcohol) (PVA) ($\text{C}_2\text{H}_5\text{O-R}$), hexane (C_6H_{14}), commercially formulated urea formaldehyde, sodium hydroxide (NaOH), urea, formaldehyde and methanol. Hexane is another chemical which is used for treating the collected RB to remove the fat content. All the chemicals were used in the manufacturing process of RB adhesive as chemical additives to increase its strength and bonding properties. Water is also used for making solution of the RB powder.

3.2 Methodology

3.2.1 Collection of raw materials

RB is locally available in Bangladesh, and it is collected from local rice mill around Khulna city. The Urea-formaldehyde (UF) resin used for the study was commercial grade UF and was collected from Akij Particle Board Mills Ltd. (APBML), Manikgonj, Bangladesh. All the chemicals were as laboratory grade chemicals and were collected from the commercial market.

3.2.2 Preparation of raw materials

The RB was collected in the fine form (fine bran). The collected fine RB was sieved by 44 mesh size (0.35 mm) for the removal of oversized husk, grits and other major impurities. Afterwards, RB was defatted according to Wang et al. (1999), with hexane having the ratio of 1:3 (w/v) for bran to hexane. The mixture was then stirred with a high speed laboratory stirrer (Glassco: 700.AG.01, India) for 1 hour and later centrifuged (Thermo Scientific Fibertile Carbon Rotors; F14- 6*250Y, USA) at 4000 rpm for 10 min at room temperature. One more extraction process was performed using the same conditions previously described. Therefore, the hexane with fat was removed. Later, the defatted RB was washed with water and placed in a container to dry. The defatted wet RB was air dried at room temperature for a variation of times to evaporate the excess water. A high speed blender (Vitamix: VM0105E) was used to make the defatted RB into powder.

3.2.3 Formulation of RB adhesives

Type A

The RB powder was mixed with distilled water having the ratio of 1:4 (w/v) for bran to water. Then potassium permanganate (1 %) was gradually added to the RB mixture and stirred with a stirrer (Heat and Stir; Glassco: 700.AG.01, India) in a stirring condition. When the addition of potassium permanganate was finished, the mixture was heated in a shaking water bath (Reciprocal Shaking Water Bath; JSSB- 30T, Korea) at 70° 0Cc for 1.5 hours. Thereafter, PVA powder was added to the slurry (RB mixture) with the ratio of 1:6 (w/w) for PVA to RB powder. Half of the PVA powder (2 %) was slowly added at heated stirring condition having the temperature of 70° C for 30 minutes. The other half of the PVA (2 %) was added to the slurry over five minutes after removing the heat sources. After adding PVA to the slurry, it was stirred for an hour by a maximum speed of the laboratory stirrer (Heat and Stir; Glassco: 700.AG.01, India) for better mixing. The mixture was then stored in the laboratory refrigerator for further use as glue.

Type B

The RB powder was mixed with distilled water having the ratio of 1:3 (w/v) for bran to water and adding methanol (2 g) as an antifreezing material. Then the mixture was heated at 90° C for an hour. Exactly 6.5 % formaldehyde was added in the mixture drop wise over five minutes with high rpm (120) of the stirrer and the mixture was heated (Heat and Stir; Glassco: 700.AG.01, India) again with the same temperature for an additional 55 minutes. Another 5.7 % of solid urea was added over a period of 10 minutes into the solution at room temperature having the rotation speed of stirrer was 80 rpm. Additional 10.8 % formaldehyde was added to the mixture at 75° C for 15 minutes on the stirrer. Immediately after adding the formaldehyde, 3g NaOH was added to the solution and heated for another 90 minutes. It was then ready to use as adhesive and was stored in laboratory refrigerator at room temperature until further use.

The following percentages of materials were followed for the formulation of the two types of adhesives (Table 2):

Table 2. Chemical additives used to produce adhesive from RB

Type of adhesive	Water (%)	RB (%)	KMnO ₄ (%)	PVA (%)	Formaldehyde (%)	Urea (%)
Type A	76	19	1	4	0	0
Type B	58	19	0	0	17.3	5.7

3.3 Evaluation of RB adhesive

Three types of adhesives were prepared according to their specific pH treatment varying with their chemical additives. Thereafter, these adhesives were tested in a good and satisfactory way with equipped manner under certain condition.

3.3.1 Pre-treatment yield

The dried RB was milled for 3 min and sieved through a US #100 mesh screen. The sieved portion containing particles smaller than the 0.15mm nominal sieve opening was further referred to as the rice bran adhesive. Pre-treated RB yield was determined with the following equation (1):

$$Yield = \frac{A_t - A_r}{A_t} \times 100\% \quad \dots \dots \dots (1)$$

(Pan et al., 2005)

Where A_t is the total amount of oven-dried RB and A_r is the amount retained by the 100 mesh sieve.

3.3.2 Gel time of adhesive

RB adhesive of 25.0 g and ammonium chloride (NH₄Cl) of 1.0 g were respectively added into a beaker and were fully mixed. The mixtures of 5.0 g in the beaker was transferred to a test tube. A stirring rod was inserted in the test tube for checking the condition. The test tube together with the stirring rod was placed in a short neck flask with boiling water, and a stopwatch was immediately started to count the gel time of the adhesive. Each value was obtained from the average of three tests.

The adhesive samples of 5.0 g were placed on a piece of aluminum foil which had been dried to constant weight. The aluminum foils with pre-loaded adhesive were put in a vacuum drying oven (name of instrument). The temperature of the oven was increased to 102±3°C and maintained

under vacuum for 1.0 hr. Then, the aluminum foils together with the dry adhesive samples were removed to a dryer and cooled about 20 min. The solid content (R) of the adhesive can be determined from the following formula (2):

$$R = \frac{m_2 - m_0}{m_1 - m_0} \times 100\% \dots\dots\dots (2)$$

(Zhao et al., 2018)

In which R, m₀, m₁, m₂ are solid content, quality of aluminum foil, aluminum foil with wet adhesive sample, aluminum foil with dry adhesive sample.

3.3.3 Viscosity of adhesive

The viscosity of the prepared adhesive was determined by using a viscometer According to the standard... (Sheen VM1-R) with L #4 spindle. Viscosity was measured at 100 and 200 rpm immediately after vigorous stirring and each value was obtained from the average of three tests.

3.3.4 Shear strength

The strength of RBA was determined according to ASTM D 905 block shear specimens (shear area = 50*40 mm²) and EN 250 single lap joint (shear area = 20*20 mm²) method as the test of adhesives for bonding wood products. Shear strength was measured by the Universal Testing Machine (UTM) (SHIMADJU, 50 KN, Japan).

3.3.5 Glass Transition Temperature (T_g)

The Glass Transition Temperature (T_g) is the temperature region which provides the nature of the adhesive at its service temperature whether it is rigid and glassy or flexible and rubbery. T_g is measured by using Differential Scanning Calorimetry (DSC) (Model: lab Sys evo) according to ASTM E1356 in a nitrogen atmospheres and at a temperature range from room temperature (25 °C) to 600 °C, with a heating rate of 10 °C/min.

3.3.6 FTIR analysis

FTIR spectra of the prepared adhesive samples were performed in a FTIR Spectrometer (PerkinElmer, Spectrum Two; USA). Each spectrum was recorded in a frequency range of 600–4000 cm⁻¹ using attenuated total reflection method using diamond as crystal.

3.4 Analysis of data

All the data, obtained during the laboratory tests for proprietary characterization of each type of adhesive were analyzed by using SPSS software and Microsoft office excels. ANOVA (Analysis of Variance) was done to see the variation among the prepared adhesive.

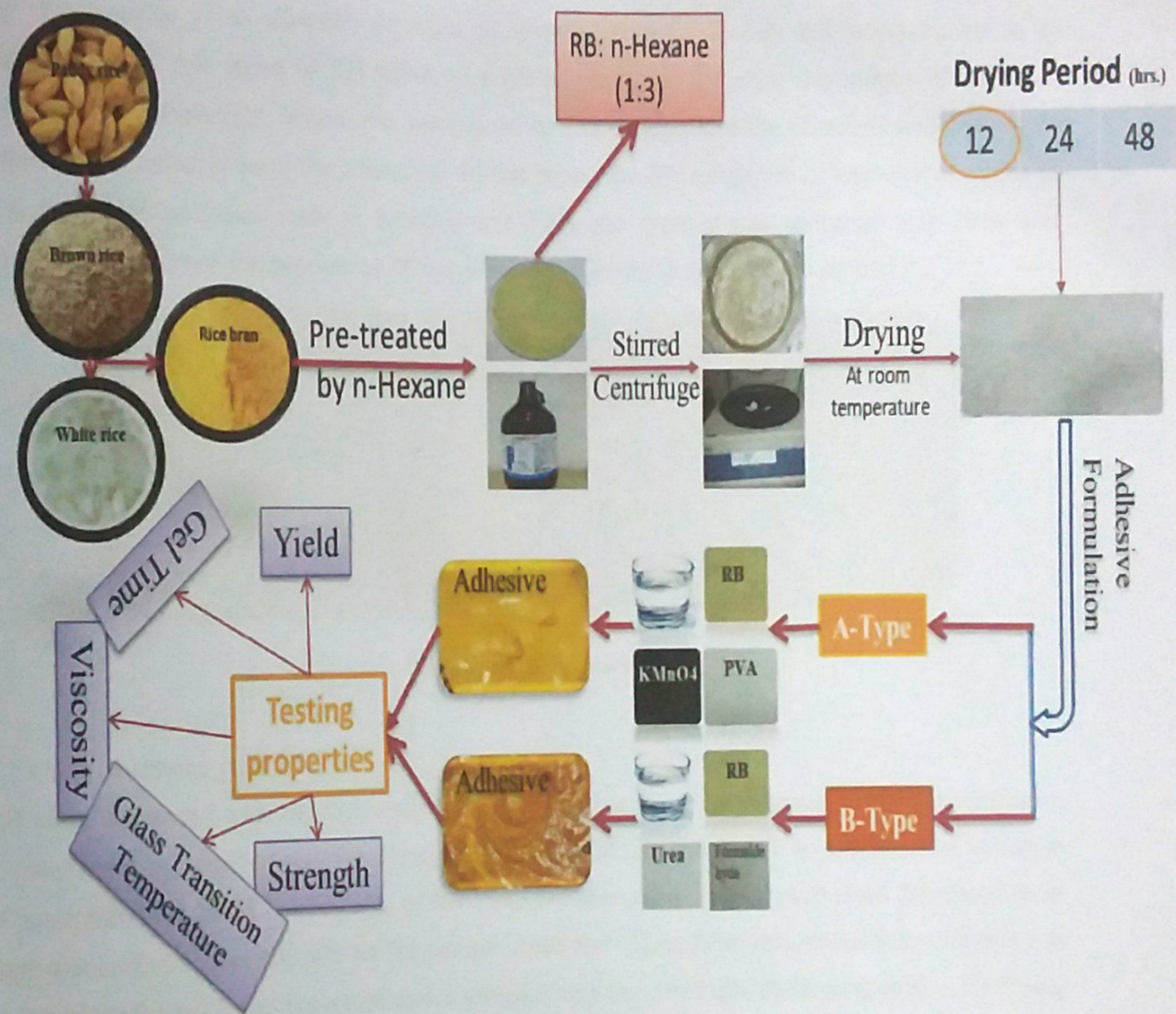


Fig. 17. Flow diagram of Methodology of two type of Rice Bran (RB) based adhesive production and its properties.

Chapter Four: Results and Discussion

4.1 Adhesive properties on chemical treatment

The effectiveness of an adhesive depends on several treatment factors and incorporation of its materials. Here, two types of RB adhesive were prepared, on different treatment with different percent of raw materials. Where the percentage of RB powder and the chemical additives were differently mingled to form the adhesives. In this study, the RB adhesives of type A was prepared with chemical additives such as KMnO_4 and PVA and type B was prepared with Urea and formaldehyde, to test the properties of the adhesives whether it is workable or not.



Fig.18. Final adhesives

4.1.1 Pre-treatment yield

RB yield decreased with the increase of drying period at room temperature. After pre-treatment, the wet RB was dried at room temperature for 12 hrs. 24 hrs. and 48 hrs. to calculate the variation of pre-treated RB yield. The results of RB yield are showed in Table 1. RB yield decreased from approximately 71.2% to 59.9% for the sample dried for 48 hrs. Low pre-treated RB yield that was obtained for the harder and more cohesive samples may indicate high binding capability. As drying Page | 6 periods increased from 12 hrs. to 48 hrs. improved sample cohesion was evident during dried for longer period. While the sample dried for 12 hrs. it appeared more brittle inside the drying tray than the other drying periods. The sample dried for 48 hrs. was much harder and smoother surfaces than 24 hrs.-dried sample. In many cases, the resulted dried products with an uneven moisture distribution where the moistened particles at the center of the sample tended to attach one another and reducing the yield. However, the results showed (Table 1) that the yield decreased as the drying period increased from 12 hrs. to 48 hrs. This study indicates that better adhesive capabilities were obtained as the drying period increased.

However, Pan et al., (2005), showed that the yield decreased from approximately 60% to 35%. But in this study the RB yield decreased from 71.2% to 59.9% and this study have quite good result compare to stated study.

Table 3. Adhesive yields on different drying periods at room temperature

Adhesive yield (%)	Drying periods (hrs.)
71.8	12
66.7	24
59.9	48

4.1.2 Gel time and Solid content

The extensive performance of a material is very important for its implement, practice and material research. The performance of these adhesives in gel time and solid content (%) are showed in Table (2). The gel times reported for the natural resins are always higher than for the synthetic urea formaldehyde adhesives, which registered a value of 2.15 minutes to 3 minutes. Usually, low gel time result is preferable for any kind of adhesive. Because it determines how long the resin can be worked in making polymer composites. In the stated study the gel time is quite a bit higher in comparison with commercial grade UF. The gel time result for Type A adhesive decreased from 5.47 for pH 6 to 5.26 for the sample treated with pH 10. Similarly, gel time for type B decreased from 5.48 for pH 6 to 4.57 for pH 10. The pH treatment had a significant effects on both type of adhesives for gel time. The gel time was almost similar for the samples treated at pH 6 and 8. However, gel time significantly different at pH 10 in both type of adhesive and Type B showed a fairly better result than A type adhesive.

Table 4. The performance of these adhesives in gel time and solid content (%).

Adhesive properties	Adhesives						
	Type A			Type B			UF
	pH 6	pH 8	pH 10	pH 6	pH 8	pH 10	pH 8
Gel time (minutes)	5.47	5.41	5.26	5.48	5.39	4.57	2.30
Solid content (%)	39.4	39.8	40.3	37.1	39.9	40.5	48

The solid content is an important parameter for the products and production for any kind of adhesive. Gel time of an adhesive is strongly affected by the solid content. The gel time decreased with increasing of solid content. By decreasing solid content decreased the reactants concentration. Therefore, the cure rate decreased and resulted in a longer gel time. In the stated study, the solid content percentage was quite impressive and the gel time is decreased by increasing the solid content.

4.1.3 Adhesive viscosity

The effect of pH and chemical treatments on the viscosity of RB adhesive measured at 100 and 200 rpm is shown in Fig. 1. From the analysis of one way ANOVA it was found that there was a significant difference (one way ANOVA, $F= 68.38$, $P<0.05$) among the viscosity of the pH variation between the two type of adhesives in 100 rpm. In case of viscosity in 200 rpm there was a significant difference (one way ANOVA, $F= 25.47$, $P<0.05$) among the viscosity of the pH variation between the two type of adhesives.

The viscosity measured at 100 rpm for Type A increased from 1.05 Pa.s for the pH 6 to 1.21 Pa.s for the sample treated at pH 10 and for the Type B the viscosity ranged from .87 to 1.02 Pa.s. Similarly, viscosity at 200 rpm for Type A increased from .9 to 1.05 Pa.s and for Type B increased from .71 to .89 Pa.s. The increased viscosity of treated RB adhesive compared with the pH treatment variation is likely a result of the combined effects of starch gelatinization and protein denaturation due to pH and chemical treatments.

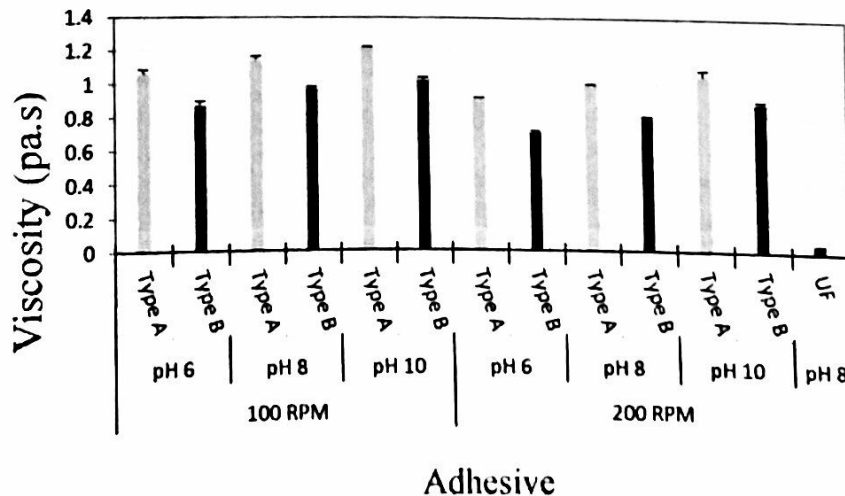


Fig.19. Effect of pH and chemical treatments on RB adhesive viscosity measured at 100 and 200 rpm.

The pH, chemical treatment and pH-chemical treatment interaction had significant effects on RB adhesive viscosity at both 100 and 200 rpm. Viscosity was not similar for the samples due to pH variation and the effects of chemical treatment. However, viscosity significantly increased when pH treatments were increased from 6 to 10. The increase in viscosity at high pH values compared with low pH values may be largely depends on starch gelatinization and protein denaturation (Pan et al., 2005; Angleimer and Montgomery, 1976) along with the chemical treatments.

Generally, low viscosity adhesive is desired for its easy handling and applying in industrial production process. But in this study, the resulted viscosity is quite higher in contrast with commercial grade UF resin. However, in the stated study Type B adhesive showed a comparative better viscosity result than Type A adhesive. Some other related studies showed that the RB adhesive has a higher viscosity result such as .19 to .54 Pa.s (Pan et al., 2005) and Basta et al. (2016), showed a higher viscosity result RB (UF modified) adhesive than the stated study.

4.1.4 Shear strength

The effect of pH and chemical treatments on the average shear strength values of RB adhesive measured at ASTM D 905 and EN 205 methods are shown in Fig. 2. From the analysis of one way ANOVA it was found that there was a significant difference (one way ANOVA, $F= 68.38, P<0.05$) among the strength of the pH variation between the two type of adhesives in ASTM D 905 method. In case of strength in EN 205 method there was a significant difference (one way ANOVA, $F= 25.47, P<0.05$) among the strength of the pH variation between the two type of adhesives.

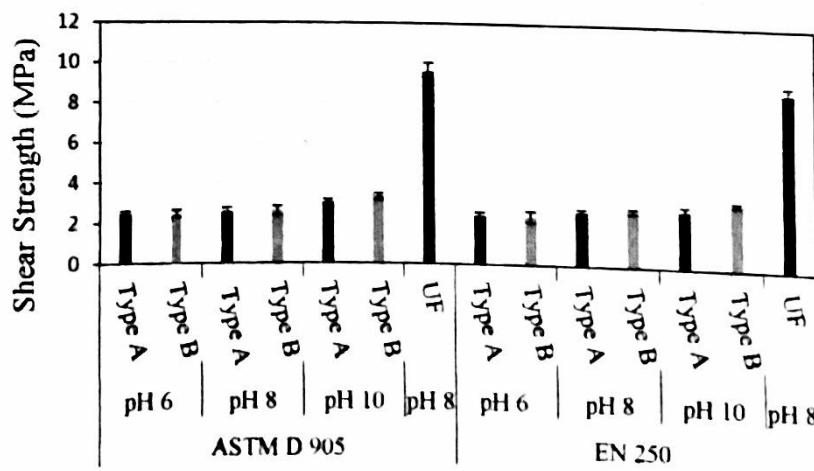


Fig. 20. Average shear strength of adhesives tested in the study.

The pH and chemical treatments appreciably boosted up the performance of RB adhesive. Adhesive strength measured by ASTM D 905 method for Type A increased from 2.42 for pH 6 to 2.99 MPa for the sample treated at pH 10 and for Type B shear strength ranged from 2.45 to 3.29 MPa with the increased of pH values. Similarly, shear strength by EN 205 method for Type A increased from 2.38 to 2.82 MPa and Type B increased from 2.37 to 3.21 MPa. At a given chemical treatment and as pH increased from 6 to 10, the adhesive strength increased with more significantly. However, the adhesive strength is not so much varied in between the two methods with the chemical additives and increased pH treatments. In the stated study Type B adhesive showed quite a bit of better result than Type A.

In the presence of water and an absolute temperature starch gelatinized to develop its adhesive properties and above the temperature protein also increased its strength properties (Ju et al., 2001; Juliano, 1985). The pH-chemical treatments interaction had also great influenced on increasing the RB adhesive strength (figure-2). Though, the resulted shear strength is much lower than the commercial grade UF resin. But the result in the stated study is fairly better in contrast to the previous studies of RB adhesive such as 1.9 to 2.3 (Wang et al., 2010) and 0.9 to 1.16 (Wang et al., 2008).

Variability in shear strength values

Coefficient of variance (CoV) is an important factor to compare the variability or stability of different testing procedures. The CoV is a simple standard which determines the repeatability of an assay. The data set has high stability and less variability when the CoV value is lower. The CoV values from the stated study is shown in figure 3.

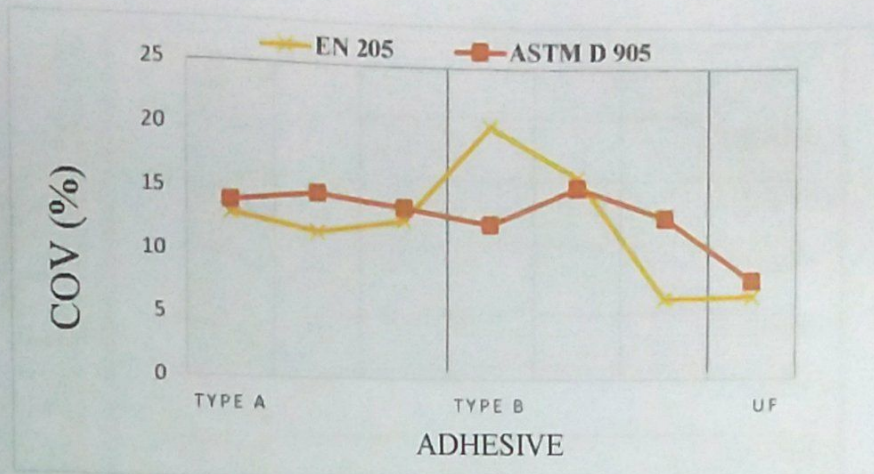


Fig.21. Coefficient of variance (CoV) of shear strength results according to type of adhesive and testing method.

From the Figure () the ASTM D 905 method (average CoV= 13.08 %) turned out to exhibit the highest variability, whereas the EN 205 method (average CoV= 12.49 %) were characterized by the lowest variability. There was a meaningful difference between the CoV values of the two methods. The shear area of the ASTM D 905 method was (2000 mm), which is 5 times greater than that in the EN 205 methods (400 mm). It is well known that the shear stress distribution in an adhesively bonded joint tends to be more uniform as the size of the bond area decreases (Serrano, 2004), hence, variability in the results obtained by the ASTM D 905 method could be related to its larger area of bondline.

4.1.5 Glass Transition Temperature (T_g)

At glass transition, specific heat changes suddenly due to some structural flexibility in the glassy state of adhesive samples. In that time, an endothermic peak or a shift in base line is observed in DSC at glass transition. This is not a particular temperature but a range of temperature at which such changes take place. Sometimes, the baseline peak temperature is taken as glass transition temperature and sometimes, endothermic peak temperature in DSC curve is taken as glass transition temperature; if the heat flow maintains a uniform flow. The Glass Transition Temperature (T_g) of chemically modified RB adhesive (Type A and B) with pH variation and commercial grade UF were shown in Fig. (4).

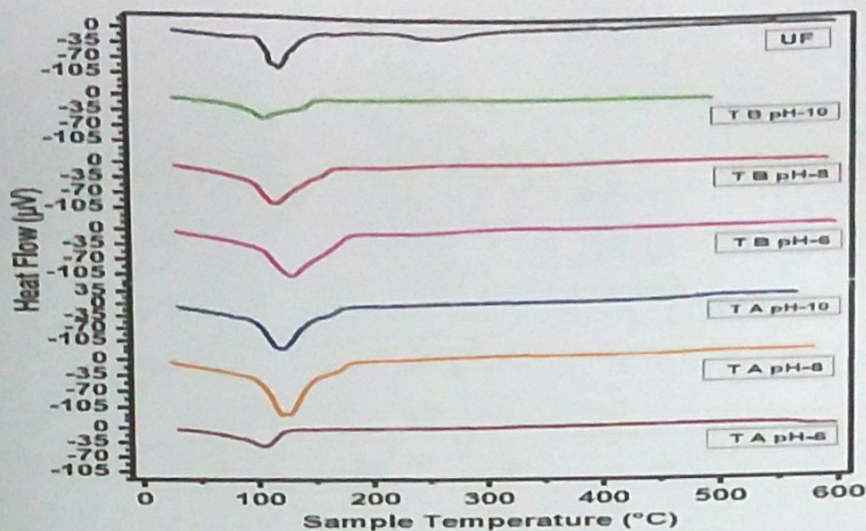


Fig. 22. Glass Transition Temperature (T_g) of chemically modified RB adhesive (Type A and B) with pH variation and commercial grade UF.

From fig (4) it can be seen that the structural flexibility of the adhesives changed drastically as they passed through the glass transition region. In that region the adhesive properties of viscoelastic, dilatometric, enthalpic, etc. were significantly changed (Venditti and Gillham, 1997). In this study, the estimated midpoint of T_g for Type A according to their pH treatment (6, 8 and 10) were 117 °C, 138 °C and 138 °C and for Type B the observed T_g were 155 °C, 121 °C and 136 °C and the commercial UF resin showed a result of 152°C. The pH- chemical treatment interaction had great influence on RB adhesives T_g . Because the T_g range was varied according to their pH treatment. However, the T_g range may be increased when polymer molecular weight, inflexible side group, bond rotation increases and length of side group and chain mobility by cross linking decreases (Jadhav et al., 2014). Thus, we concluded that, the resulted T_g range varied because of alteration of the adhesive properties according to their pH – chemical treatment variation.

4.1.6 FTIR analysis

The FTIR spectrum of native Rice bran (RB), chemically modified RB adhesive (Type A and B) with pH variation were shown in Fig. (5). From Fig.(5) we can be seen that the characteristic bands of these adhesive appeared at 3300 ~ 3400 cm^{-1} for stretching vibration bands of O–H group, 1600 ~ 1650 cm^{-1} for stretching vibration band of carbonyl group, and 1000 ~ 1100 cm^{-1} for bending vibration bands of C–OH group and C–O–C group (Lin, Pan & Liu, 2013).

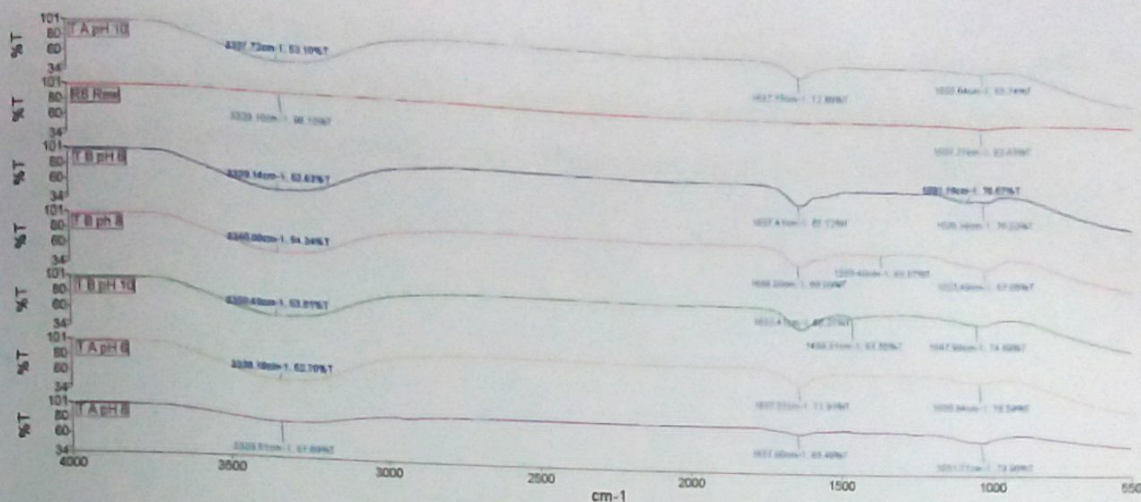


Fig. 23. FT-IR spectrum of native Rice bran (RB), chemically modified RB adhesive (Type A and B) with pH variation.

After oxidation, the bands of $3300 \sim 3400 \text{ cm}^{-1}$ and $1000 \sim 1100 \text{ cm}^{-1}$ were emphasized, which showed that more free hydroxyl groups were generated because of chain rupture in the oxidative process. The band of $1600 \sim 1650 \text{ cm}^{-1}$ was obviously strengthened, which indicated that more aldehyde groups were generated in the oxidative process. In the UFRB-pH 10 adhesive, new stretching vibration band of 1459 cm^{-1} for N-H group and in the UFRB-pH 8, 1399 cm^{-1} for stretching vibration band of $-\text{CH}_2-$ group showed that oxidized carbohydrate and UF were transformed to UF modified RB adhesive by polycondensation reaction (Jiang et al., 2010). The debilitating of the stretching vibration bands of $3300 \sim 3400 \text{ cm}^{-1}$ for O-H group indicated that the polycondensation and somewhat intermolecular hydrogen bonds were originated. The presence of these peaks verified that the basic structural units of carbohydrate starch were not markedly changed by the formation of chemically modified RB adhesive. Thus, we deduced that apparently, a good adhesively bonding reaction took place between the starch and the chemical additives.

5. Conclusion

In the study, a renewable and environmental - friendly chemically modified RB adhesive was obtained by the polycondensation reaction of RB and chemicals. High pH treatment with chemical additives proved to be effective in developing the adhesive properties of RB with improved adhesive strength compared to low pH treatment. The properties of the two types of adhesive increased by increasing the pH treatment. Therefore, the optimal treatment condition was pH 10 along with chemical additives for obtaining higher adhesive strength of RB. In between the two

types of adhesive, Type B showed a fairly better performance in comparison with Type A. However, the properties of the two types of adhesive were impressive but quite a bit lower in contrast with commercial grade UF resin. These issues merit further research.

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