CHAPTER II

COMPOSITE REQUISITE

Section A – Reinforcing Agent: Pine Cellulosic Fiber

Section B – Matrices: The resins

- Phenol – Formaldehyde
- Urea – Formaldehyde
- Phenol – Resorcinol – Formaldehyde
- Phenol – Lignin – Formaldehyde
The present chapter discusses on the materials required for the preparation of pine cellulosic-based composites. The chapter is therefore, divided into two sections, i.e. Section A and section B. Section A deals with the discussions on pine needle based cellulosic fibers, used as reinforcing material and section B, on the chemistry, preparation and characterization of the adhesives, used as the matrix, for the manufacture of particle board composite.

SECTION - A

REINFORCING AGENT: PINE CELLULOSIC FIBER

The increasing demand of timber wood has forced the polymer chemists to search for an alternative to wood and their continuous efforts in this direction led to the development of different polymer based (particle boards) composites. The main raw material used for the preparation of these composites, as the reinforcing agent, is the fibrous lignocellulosic material. These materials can be obtained from a variety of naturally occurring raw materials such as wood waste in the form of round wood, saw waste including saw dust, planer shaving, veneering waste, or agro based industrial residues like bagasse, rice husk, rice or wheat straw, jute sticks, etc. In recent years, therefore, polymer composites containing wood fiber/natural fibers have received considerable attention both in the literature and in industry. Studies have been reported on natural fiber based composite products\(^1\). Particularly, agro based natural fibers have attracted the attention of scientist and technologist for energy-intensive applications since cellulosic fibers are strong lightweight, abundant, non-abrasive, non-hazardous, renewable and inexpensive. The flexibility and reduced tear of
processing machinery with no health problem makes these materials as excellent reinforcing agents for plastics.

Over the past decade cellulose based natural fibers have found use as a potential resource for making low cost composite materials, especially in developing tropical countries where these fibers are abundant. Sisal and jute fibers possess moderately high specific strengths and stiffness and can be used as reinforcement in polymeric resin matrices to make useful structural composite materials. Lack of good interfacial adhesion and poor resistance to moisture absorption make the use of natural fiber reinforced composite less attractive. This problem can be overcome by suitable chemical modification of these fibers. Several studies have been reported based on the surface modification of fibers. Kuruvilla Joseph et al. have reported the effect of alkaline treatment and cardanol derivatives of toluene diisocyanate (CTDI) treatment on the physical and mechanical properties of sisal-LDPE composite.

Short fiber elastomer composites containing natural fibers have gained much importance due to their renewable nature, low cost, and amenability to chemical and mechanical modification. A considerable amount of research work has been done in the field of short natural fiber reinforced rubber composites. The processing advantage of short fiber reinforced elastomer composites has been investigated by Foldi. Chakraborty et al. have reported the properties of short jute fiber reinforced carboxylated nitride rubber (XNBR). Short fiber strength reinforced rubber composites have better processing advantages, high green strength, high dimensional stability and show anisotropy in mechanical properties. Murty and De have studied the properties of short jute fiber reinforced SBR composites. Recently,
Thomas and coworkers\textsuperscript{13,14} have reported the mechanical properties of short sisal and coir fiber reinforced natural rubber (NR) composites. Prasanth Kumar et. al\textsuperscript{15} have evaluated the critical fiber length, the influence of fiber orientation processability and the effect of bonding agent on the mechanical properties of sisal fiber reinforced – styrene- butadiene rubber composites. Cost effective utilization of oil palm fibers as reinforcement in composite materials and their mechanical properties were studied by M.S. Sreekala et. al\textsuperscript{16}. Oil palm fibers being hard and tough, become a cost effective replacement for synthetic fibers. Structural properties and applications of these fibers have been reported\textsuperscript{17}. M.S. Sreekala et al\textsuperscript{18.} have analyzed the tensile, flexural and impact performance of the composites from oil palm fibers and phenol-formaldehyde resins. Hardness of composites was also checked.

Among various natural fibers, pineapple leaf fibers (PALF), exhibit excellent mechanical properties due to its high cellulose content and comparatively low microfibrillar angle. Among matrix resins, unsaturated polyester, have been commonly used for making thermoset composites especially with glass fiber\textsuperscript{19}. But high level of moisture absorption, poor wettability and insufficient adhesion between untreated fibers and the polymer matrix leads to debonding with age\textsuperscript{20-22}. Because mechanical properties of composites depend on interfacial adhesion, it is necessary to have good adhesion between the reinforcement and the polymer matrix\textsuperscript{23,24}. Mishra et.al\textsuperscript{25} have analyzed physico-mechanical properties of PALF-reinforced polyester composites. The high cellulose content and the low microfibrillar angle (11 degree) of banana fiber indicate that it has also the potential as a reinforcing material\textsuperscript{26}. Composites made out of banana/cotton hybrid fabric has
been found to be useful in the preparation of low strength material\textsuperscript{27}. Effect of banana fiber on the mechanical properties of polyester composites with reference to fiber length and fiber content has been analyzed\textsuperscript{28}. The fiber matrix interfacial bond strength is expected to be very poor due to hydrophilic nature of sisal fiber and hydrophobic nature of SBR. The efficiency of sisal as reinforcement in SBR composites can be achieved by modifying the surface topology of sisal fiber by suitable chemical treatment or by selecting a bonding system. Several treatments have been reported to improve the fiber matrix interfacial bonding\textsuperscript{29-35}. Kokta et.al\textsuperscript{34} have reported that compiling agents like silanes and isocyanates improve the mechanical properties and dimensional stability of cellulose fiber–PE composites. It has been observed that mercerization of sisal fiber will enhance the bonding of fiber with rubber matrix. Sapieha et. al\textsuperscript{36} have reported that the addition of small amount of DCP into cellulose fiber composites, during processing, improve their tensile properties significantly. Prasantha and Sabu Thomas\textsuperscript{37} have explained the effect of different chemical treatments of sisal fiber on the mechanical properties of short sisal fiber- reinforced SBR composites.

Various juvenile woods have been used as reinforcing agent in different thermosetting resins thus substituting the timber wood. However, the poor mechanical properties as well as higher water absorption due to the incompatibility of polymer with wood are obstacles in the frequent use of wood polymer composites. Hemp and Agave fibers are employed as filler for the preparation of wood polymer composites with high-density polyethylene (HDPE) in different ratios 55:45, 50:50, 45:55 and 60:40 (wt./wt.) respectively. The Young modulus and tensile strength
decrease with increase in the amount of fiber concentration in wood polymer composites. The Agave fibers showed higher strength among the fiber composites for all ratios. The maleic anhydride treatment shows significant improvement in Young's modulus and tensile strength over the untreated fiber/polymer composites. Improvements in the mechanical properties are due to the compatibility of HDPE with fibers. Recently, cellulosic plots and wastes such as shell flour, wood flour and pulp have been used as filler in thermoplastics, and primarily to achieve cost saving fiber reinforced plastic based composites. In fact, synthetic fibers such as nylon, rayon, aramid, polyesters and carbon are extensively being used as the reinforcement of plastics. But these materials are expensive and are non-renewable resources. There is therefore, growing interest in the use of agro-based fibers as reinforcing components in different composite materials. Because of the uncertainties in the supply and the price of petroleum-based products, it is important to use the naturally occurring alternatives. Natural fibers are renewable resources; they are cheaper, cause no health hazards and finally provide solution to environmental pollution by finding new uses for waste materials. Natural fiber reinforced composites therefore, come prior to synthetic fiber reinforced polymer composite in properties such as biodegradability, combustibility, light weight, non toxicity, decrease environmental pollution, low cost, ease of recyclability etc. These advantages place the natural fiber composites among the high performance applications of natural fiber composites having economical and environmental advantages.

Thus, natural fibers, being the source of lignocellulosic materials along with various properties best needed for the preparation of polymeric composites, offer a renewable
resource material as a reinforcing agent. From the literature survey it is observed that different natural fibers from agriculture waste such as flax, bagasse, cotton, hemp and jute stalks have been used industrially in the preparation of different lignocellulosic polymeric composites using suitable synthetic adhesives. A review of literature lists meager studies on utilization of pine needles, the major waste of coniferous forests and rich source of lignocellulosic content, as a reinforcing agent in these polymeric composites. In the present work, therefore, utilization of pine needles, as a reinforcing agent, has been made towards the preparation of wood based polymer composites.

Himachal Pradesh, the land of forests, is mainly covered with thick coniferous forests with different varieties of Pinus. Pinus roxburghii is one of the common species of Pinus genera and is widely spread over the low-lying mountain ranges. It is a tall tree with a spreading crown. The leaves of the trees are in clusters of three, which are needle like. There is a huge fall of pine needles (leaves) in the month of April to June, estimated to about one ton per hectare per season. About 4.0 to 5.0 kg. leaves are shed by one tree of matured growth. The needles are the fire hazards to the forest and an irritant to villagers, as these do not allow the grass to grow underneath for the cattle. Utilization of these wastes in the preparation of composites would give relieve from these problems.
EXPERIMENTAL

MATERIALS AND METHOD

i) Collections of Pine needles: Pine needles of Pinus roxburghii (chil) were collected from the forest near H.P. University, Summer Hill, Shimla, H.P. India, between the periods April to June.

ii) Chopping of Pine needles: The dried pine needles were chopped to a size between 0.5" to 1" in length with chopping machine. These needles were used for further experiments.

iii) Digestions of Pine needles: The dried and weighed pine needles (5 kg.) of 0.5" to 1.0" size were put in the digester. To it was added 50 liters of 5% aqueous solution of NaHSO₃. The digester was closed air tightly and the needles were allowed to digest for 8 hour under pressure. After the specific time, the pressure was released and the needles were removed from the digester. The digested needles were thoroughly washed with water and allowed to dry in the open. In between, while the needles were still wet, a mild thrashing was given with a wooden hammer, to separate the cellulosic fibers. They were further allowed to dry in air and then in the oven at 60-70°C. The moisture content of these pine cellulosic fibers is maintained between 6-8%. These fibers were used as a reinforcing agent in the preparation of particleboards.

CHARACTERIZATION—The physico-chemical properties of pine needles are presented in Table 1. The pine cellulosic fibers obtained after the digestion of the pine needles have been characterized as follow:
IR SPECTROSCOPY

FTIR of pine cellulosic fibers was taken on KBr disc on FTIR spectrophotometer. Pine cellulosic fibers showed a broad band in the region between 3300-3600 cm\(^{-1}\) due to H-bonded hydroxyl groups of the cellulose.

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis of pine cellulosic fibers was recorded on simultaneous Schimadzu TGA-DTG apparatus in air at a heating rate of 10\(^{\circ}\)C/min. The primary thermogram is presented in Figure 1. The initial decomposition temperature (IDT), final decomposition temperature (FDT) and the decomposition temperature (DT) at every 10% weight loss are presented in Table 2. The initial decomposition begins at 250\(^{\circ}\)C and continues up to 296\(^{\circ}\)C for next 10% weight loss. Further loss in the weight from 10% to 40% shows a fast decomposition with temperature difference lying between 10\(^{\circ}\)C to 25\(^{\circ}\)C. Beyond 40% weight loss, the decomposition slows down and the temperature difference between each 10% weight loss i.e. from 40% to 50%, is 25\(^{\circ}\)C, from 50% to 60% weight loss, it is 55\(^{\circ}\)C and finally from 60% to 70% weight loss, the temperature difference again reduces to 29\(^{\circ}\)C. Final decomposition begins at 458\(^{\circ}\)C where about 70% weight loss has been observed and continues up to 72% weight loss with 16% residue. Initial degradation of pine cellulosic fibers may be due to thermo-oxidation and formation of flammable volatile glycosan. Similar thermal behavior of different cellulosic fibers has been observed by Kosik et al\(^{39,40}\).
Fig. 1. Primary thermogram of Pn-Cellulosic fibers.
WATER ABSORPTION BEHAVIOR

Table 3 represents the water absorption behavior of pine cellulosic fibers from atmosphere and after immersion in water for different time periods.

0.200 g samples of pine cellulosic fibers were kept in the open for different time periods. The moisture absorption by the samples was determined from the increase in the initial weight of the samples. Similarly, water absorption by the samples was determined by immersing the samples in water for different time periods. After a definite time period, the samples were taken out of water and the adhering water was removed by gently pressing against dry filter paper and weighed. Percent water absorption is determined from the increase in weight of the original fiber. Results are presented in Table 3.
SECTION- B

MATRICES : THE RESINS

Phenol–Formaldehyde

Urea–Formaldehyde

Phenol–Resorcinol–Formaldehyde

Phenol–Lignin–Formaldehyde

This section deals with second and the most important component of composites i.e. the matrix. It constitutes the binding material, which holds of the reinforcing agent. With wood or similar material forming the basis and the bulk of the particle board, adhesive binds the fragments of the reinforcing agent together into a homogenous mass and thus is no less important.

Adhesive are derived either from

1. The natural resources such as animals, vegetable, casein, soyabean and blood albumin, glue or

2. They are synthetic products of chemical industries drained from petroleum, natural gas, coal, air and water.

Glue from animals and plant cells have been known for a long time and are still widely employed for bonding porous materials such as paper. These materials however, have limited resistance to moisture and mould growth. These limitations of adhesives of natural origin provided the stimulus, and are responsible for the great expansion of new adhesives, which are based upon synthetic resins and other materials.
Synthetic resin adhesives were introduced in the wood processing industry in the early 1930’s. The chief advantage of some of the synthetic adhesives is their excellent durability, making glued wood products serviceable under more severe exposure than was possible with natural glues. Some synthetic resin adhesives are capable of maintaining their strength under practically any conditions of service where wood is the suitable material. Others have only moderate resistance to heat or moisture or both and are not suitable for use under critical severe conditions. Between two extremes in durability, wide ranges of synthetic resins are available.

Development of synthetic resin adhesives has facilitated manufacture of many important glued wood products, which have extensive use in various fields like engineering, construction, architecture, furniture, housing, agriculture, boat building and other exterior uses. Synthetic resin adhesives for wood may be thermosetting or thermoplastic. A thermosetting resin is one that undergoes cross-linking upon hardening and become substantially infusible. The cross-linking or hardening reaction is catalyzed by heat or chemicals and is irreversible. The most important thermosetting adhesives are phenol-formaldehyde (PF), urea-formaldehyde (UF), etc. Thermosetting plastics have a large number of uses including uses as adhesives, coating encapsulates and molding compounds. Paints often contain a thermosetting binder. Thermosetting polyesters can be used to mould parts for automobiles. The traditional term “thermosetting resin” is now generally used for all reactive system that forms a cross-linked network. Thermosetting resins are sold in their unpolymerized form and must be reacted during processing. The reactions consist of a complex combination of both polymerization and cross-linking that involves
conversion of low molecular weight molecules into a tight three-dimensional network. The reaction can be separated into heat activated and catalysts activated systems. Typical temperature activated systems include PF, epoxides, polyimides etc. The most common catalyst activated resins are liquid unsaturated esters. In general, the properties of both types of thermosetting resins are often improved by the addition of additives. A thermosetting plastic consists of a thermosetting polymer resin along with various additives. Each thermosetting polymer resin possesses a unique combination of properties such as strength, stiffness, dimensional stability, thermal stability, processability, dielectric strength, refractive index etc. However, many thermosetting resins would be commercial failures if they do not contain additives.

Thermoplastic resins do not normally undergo any cross-linking during curing or hardening but remain in a reversible state and can soften on subsequent heating. The most important thermoplastic resin for wood adhesive is poly vinyl acetate resin. Thermoplastic resin is usually produced by addition polymerization. The backbone polymer provides the strength for the adhesive joint. It makes up usually the major properties of the adhesive and also confers its name for the formulation e.g. phenol-formaldehyde adhesive, urea-formaldehyde adhesive etc. Although the backbone polymer provides the framework, they are to be modified by incorporating other constituents so that it can simultaneously meet several performance criteria favorably. However, it is a problem to make an adhesive mix, which is adequate to meet the desired requirements. The underlying factor here is that the adhesive mix is then not a one-component system, rather it may now frequently
contain as many as six or seven components. Since so many variables are involved, the making of an adhesive mixture is usually a trial and error processes often ending up as a patented formulation. The various constituents and the role they play in improving the characteristics of a polymer, so that it can function efficiently as an adhesive are as follows:

1. **Solvents**
   
   These are needed in most adhesives to disperse the binder to a spreadable consistency. In most wood bonding adhesives, the solvent is water. For reconstituting PF resin powder, some alcohol is used together with water. Demineralized water is to be preferred, although only potable water may be used.

2. **Catalysts**
   
   These are the substances, which speed up the rate of curing reaction of an adhesive when added in small proportions. A good example of a catalyst is ammonium chloride, commonly used to speed up the curing of UF adhesives. The proportions of catalyst to resin are adjusted to provide a practical working life for the adhesive while ensuring complete cure of the resin. The catalytic action may be further controlled by the addition of modifiers. For example, buffers or retarders such as hexamine, ammonia, tricalcium phosphate, zinc oxide, urea and melamine may be added to control the acidity of catalyst added to UF resin.

3. **Hardeners**
   
   These are substances added to an adhesive to promote or control the curing reaction e.g. paraformaldehyde is used with resorcinol-formaldehyde and phenol-resorcinol-
formaldehyde resin, and ammonium chloride is the hardener for urea-formaldehyde resins.

4. Fortifiers

These are the materials, which are added to an adhesive to improve the strength, moisture resistance and durability of resultant bonds. They usually have some distinct adhesive values. An example is melamine or melamine-formaldehyde resin added to urea-formaldehyde glue to improve water resistance and durability. A fortifier may also sometime function as an accelerator.

5. Fillers

Fillers are relatively inert substances with little or no paste forming properties and are added in the fine powder form to the adhesive. These materials improve the spreading characteristics of synthetic resin adhesive on conventional roller spreader and control excessive adhesive penetration into porous wood.

6. Extenders

These are the substances having some adhesive property when added to the backbone resin adhesive. It improves the performance quality of the backbone resin and reduces the quantity of primary binder required per unit area of the panel products, thus reducing the cost of the adhesive.

7. Preservatives

These are added to certain adhesives to prevent or retard decomposition by microorganisms either while the adhesive is being stored and applied or during service of the complete bond.
8. Plasticizers
These are high boiling liquids or low melting solids incorporated in the adhesives to increase their flexibility and workability.

9. Viscosity builders
These are the materials, which when added even in a small quantities during the production of synthetic urea-formaldehyde and phenol-formaldehyde resin adhesives or during their application increase their viscosity enormously and this property is exploited to decrease the extender cost of the adhesive to a large extent as well as to improve the consistency of the resin glue.

10. Wax
Wax in the form of wax emulsion, is an additive used with phenol or urea-formaldehyde resin adhesive during the production of particle board and fiber board. Wax sizing is designed to confer a degree of water repellency upon the board products.

11. Fire retardants
Fire retardants are the chemicals, which can be used to reduce the flammability of cellulosic materials and can generally be applied with the resin. If they are insoluble powders they can often be added in quite large amounts. But since the wood rather than the resin needs fire proofing, the most efficient way is to treat the chips with fire retardant before applying the resin.

12. Insecticides and fungicides
Any fire retardant chemical also have insecticidal and fungicidal properties, especially boron and halogen compounds. Since the cellulose and not the resin is the
object of attack, the most effective way to control the attack is again by applying the substance to the wood chips separately instead of mixing it with the resin.

The common resins, used as adhesives are, phenol-formaldehyde (PF), urea-formaldehyde (UF) and melamine-formaldehyde (MF). Sometimes combinations of these resins are also used. Recently isocyanine based resins have been used for particle board preparations.

The chemistry and adhesive properties of some of the resins, used in the present studies, such as phenol-formaldehyde, urea-formaldehyde, phenol-resorcinol-formaldehyde, phenol-lignin-formaldehyde is discussed here. A comprehensive literature of the utilization of these resins in the manufacture of the particle boards is also reviewed.

CHEMISTRY AND ADHESIVE PROPERTIES OF SOME RESINS.

PHENOL-FORMALDEHYDE RESINS

Although phenol-formaldehyde, a synthetic resin adhesive, was invented by Bakeland about 80 years ago, its large-scale application to the plywood industry was a development of the thirties. Phenolic resin is the reaction products of phenol and/or substituted phenol with formaldehyde. An unlimited variety of resins are possible depending on (i) the choice of the phenol, (ii) the formaldehyde to phenol molar ratio, (iii) the type and amount of catalyst used (iv) time and (v) temperature of the reaction. The formaldehyde to phenol molar ratio, compiled with the type of catalyst used, determines whether the polymer will be phenol-terminated or methylol (—CH₂OH) terminated. On the basis of this, two types of phenolics have been described
(i) phenol terminated resin, referred to as novolac and (ii) methylol terminated resin referred to as resol.

Novolacs are two-step resins, in which the formaldehyde necessary for cross-linking is added in two successive steps. An acid catalyst is used and phenol-formaldehyde ratio is usually about 1:0.8. This produces a novolac resin, which is permanently thermoplastic and soluble, because of the absence of free methylol groups. Moulding powders are then prepared by mixing the powdered resin with filler and pigments, together with a source of sufficient methylene bridges to yield a resite upon subsequent thermal curing. As a methylene source, paraformaldehyde or more commonly, hexamethylene tetramine (hexamine) is added, since it liberates no water, a desirable feature, when resins of high electrical quality are being prepared.

Methylol terminated resins i.e. resole, is a one step resin in which all the formaldehyde is added at one time. An alkaline catalyst is used and the phenol-formaldehyde ratio is usually about 1:1.5. Condensation is interrupted while the resin is still thermoplastic and soluble. These spirit soluble resins are used for laminating, although molding materials for special purposes can also be prepared from them by adding fillers and catalyst to the carefully dried resol. Subsequent application of heat completes the conversion of resite.

Phenolic resins are more durable and impact resistance to cold and hot water than urea resins. Phenolic resins are not attacked by weak acids or alkalis and are resistant to common organic solvents. These adhesives also show good resistance to high temperature. These adhesives are boil proof, can be soaked indefinitely, and in weather exposure will outlast the wood. The boil proof quality permits steaming of
phenolic bonded plywood to soften it for bending and foaming operations. Extreme resistance to the action of moulds and fungi is another important property.

However, phenolic adhesives are at a disadvantage compared to urea resin adhesives in a number of respects including solid contents, storage life, cure speed, tacki characteristics, compatibility with additives including wax emulsion and cost. Furthermore, they impart color to the resulting boards. PF resin undergoes a more gradual transition and therefore higher temperature and longer time for cure is required. Phenol adhesives that require temperature above 100°C to effect their cure in a reasonable length of time are considered to be high temperature setting. These are usually set by alkali hardener. Intermediate temperature setting adhesives (between 25° to 100°C) are cured by either alkaline or acidic hardeners. However, the nearly neutral or mildly alkaline adhesives are more common and are usually preferred because of the possibility of wood weakening by strongly acid adhesives. Apart from the slower curing rate, PF resin tends to penetrate the wood to a greater extent than UF resins, and in order to achieve required strength characteristics, a higher resin to wood ratio has to be employed. PF resin increases its viscosity during storage and hence it may be necessary to adjust it to maintain the required spraying consistency by the addition of water.

In recent years, continuous research and development to improve the properties of phenolic resins have almost paralleled to that of urea resins. Phenolic resins require longer press time and the color generated by phenolics is considered as a drawback. However, phenolic resin bonded particle boards are still being made on larger scale. Modifications of phenolic resins have also been carried out. Polyvinyl alcohol has
been added to PF resins to increase the viscosity and to provide pressure sensitive character.

**UREA- FORMALDEHYDE RESINS**

Urea-formaldehyde resin adhesives came on the market in middle of 1930s. UF resin commonly used as adhesive is a product of chemical condensation of urea and formaldehyde. The resinous material is prepared in a soluble form, which may be converted to the permanently infusible form by proper treatment during bonding. These adhesives are usually obtained as highly viscous liquids of high resin content (50-60 %), which has a limited period of stability. The resins are also available as dry powder, which when mixed with small quantities of water, form liquid adhesives. The resins in the form of powder have, of course, a larger shelf life. The liquid adhesive is generally prepared by condensing urea and formaldehyde under slightly acidic conditions to a predetermined degree, followed by the addition of alkali to maintain the shelf life. The resins are hardened by a sufficient reduction of the pH value. A catalyst is also used. The function of catalyst or hardener is to reinitiate the interrupted action of condensation and to convert the low molecular weight UF resins into high molecular weight network polymer. The rate of reaction during the hardening process is increased considerably by acid or by a substance capable of liberating acid when mixed with the resin. The amount and types of catalysts added determine whether the adhesive bond is cured at room temperature or at higher temperature range. Cure time varies from a few minutes at high temperature to a few hours at room temperature.
Since the pH value falls too rapidly, pot life becomes too short and the strength of the UF resin glued joints deteriorates with time, the direct addition of UF resin in most cases is unsuitable. Liquid UF resin, is therefore, mixed with the hardner, such as ammonium salt of strong acids before using with the substrate. They are cheap, convenient to handle and has a high ratio of pot life to setting time. A frequently used ammonium salt is ammonium chloride, which reacts with the free formaldehyde, slowly with methylol groups available in the resin solution and forming hexamethylene tetramine, hydrochloride and water.

\[ 4 \text{NH}_4\text{Cl} + 6\text{HCHO} \longrightarrow (\text{CH}_2)_6(\text{NH}_2)_4 + \text{HCl} + 6\text{H}_2\text{O} \]

The liberation of acid results in an immediate decrease of pH value of the adhesives. Additionally, the liberation of formaldehyde from methylol group causes further drop in the pH value, these are further facilitated by the application of heat.

Urea resin, mostly used at elevated temperatures, should have pot life as long as possible at room temperature and they should set very rapidly at high temperature. From this aspect, the free formaldehyde in the urea resin solution, which governs the amount of liberated acid and with it the reaction rate, should be bound in such a way that it is freed again when the temperature rises. To extend the working life of UF adhesives, a pH buffer such as ammonium hydroxide is added along with hardener to slow down the rate of polymerization at room temperature. For cold hardeners, designed for room temperature, cures the resin with in 1–1½ hours. Free acids are preferred to ammonium salts. The most suitable cold hardeners are organic acids such as tartaric acid or citric acid. The hardening or curing of UF resins consists of
chemical curing and migration of the water, which is partly contained in the liquid adhesives and partly chemically, liberated form the resin during the condensation process. Both phenomena must occur simultaneously. If water is removed too quickly or if the wood is too dry, the reaction of hardening cannot be completed due to lack of solvent. If the decrease of water is too slow, induced by too high moisture content of the wood or by too much water in the glue mixture, the hardening will be terminated earlier and instead of adherent glue; a crumbling mass without cohesion will be formed. To further improve the performance and the overall cost of the UF resins, some additives are added during the synthesis of the resin or at the time of applying to the mix for gluing. These may impart better water resistance, strength, flexibility and other properties desirable and useful for the finished products. UF resin is modified mainly by melamine. The product is urea–melamine-formaldehyde copolymer resin adhesive. The material is widely applied in the production of plywood and particle board with better bond strength and water resistance. Urea-melamine-formaldehyde resin performs nicely. Urea-phenol-formaldehyde copolymer adhesive has also been developed for the production of plywood and particle boards. The adhesive strength and water resistance of the product are between those of PF resin and UF resin bonded materials.

RESORCINOL BASED PHENOL-FORMALDEHYDE RESINS

Resorcinol based adhesive was first introduced in 1943. The polyhydroxy phenols are, in general, much more reactive than the monohydric phenol, since the second hydroxyl group enhances the activity of benzene ring. Probably the only polyhydric phenol used commercially in phenol-formaldehyde resins is resorcinol i.e. m-
dihydroxy benzene. Resorcinol-formaldehyde resins cure at room temperature because of its high reactivity and are prepared with only a part of formaldehyde. For complete cure, the balance of the formaldehyde is added at the time of application of the resin adhesives. Later it was found that the most important properties of the resorcinol-formaldehyde adhesive can be retained, and the costs can be reduced, if some of the costly resorcinol is replaced by ordinary phenol. The usual replacement is up to one half the molecular proportion of total phenolic constituents. It may be possible to replace more than one half but during the process of room temperature setting, often gelation becomes progressively slower. The cost reduction is the motive for mixing phenol to resorcinol resin glues but the principal point is that the resins remain adequately active for hardening at lower temperature.

Resorcinol-formaldehyde glues, although quite expensive, cure at room temperature or at slightly elevated temperature to provide water-proof products. Mixture of phenol and resorcinol based resins as well as resorcinol-phenol- formaldehyde copolymer resins have been in the use for the production of exterior grade of plywood and structural timber products.

Commercially, resorcinol adhesives are available in two components as a dark reddish liquid (50-70% solid) resin with a powdered, or at times with a liquid hardener. This hardener is usually a mixture of paraformaldehyde and fillers. The paraformaldehyde is selected for control of glue mix working life and curing efficiency. Filler such as nutshell flour's siliceous fiber etc. are used to provide suitable consistency to the mix, to form a fibrous reinforcement for the adhesive films and to control thixotropic behavior. Once the resin and the hardener portions
are mixed, the usable life of the adhesive mix is limited. The viscosity increases as
the reaction continues until the adhesive becomes non-spreadable. This time is
generally termed as ‘pot life’ and is generally determined at controlled temperature
with the aid of timing device.

Since the adhesive mixer produce exothermic reaction, the temperature of adhesive
mixes increases and the cross-linking reaction proceeds more rapidly thereby
reducing the pot life considerably. It is always advisable to remove the heat as it is
generated by stirring and cooling rapidly at or below room temperature. Resorcinol
adhesives cure at 27°C or higher, but usually are not recommended for use below
27°C. The advantage of room temperature setting of resorcinol resins over acid
catalyzed room temperature setting adhesives are several. Whereas a PF resin
requires very strong acid catalyst for curing at room temperature while resorcinol-
formaldehyde (RF) and phenol-resorcinol-formaldehyde (PRF) resin cure at nearly
neutral pH [6.5 to 7.0 (RF) and 7.0 to 7.5 (PRF)]. These limits are between pH 6 and
9, a range which is not at all harmful to wood. RF and PRF resins are mostly used as
special purpose adhesives in the assembly gluing of wood and wood products. These
adhesives withstand exposure to weather better than most timbers themselves. They
comply with the highest requirements of all specification and have outstanding
durability under most severe conditions. These adhesives are also suitable to bond
treated wood. Further, it is feasible to treat timber or plywood and then glue the
assemblies to the desired size and shape.
LIGNIN BASED PHENOL-FORMALDEHYDE RESIN

In recent years, the need for conservation to meet the expanding requirement for the materials, and the urge for more economical production method in the face of higher operating costs, have added additional incentive to exploiting more efficiently the lignin containing wastes from the pulping and wood using industries. For the pulp and paper industry, the most profitable use of lignin would be as a component of finished paper. Lignin consisting of 20 to 30% by weight of the dry weight of wood is a high molecular weight polymer. It is the most important non-cellulosic portion of the wood and is the resinous binder for the cellulosic fiber. It has structural properties similar to phenolic resins. The structure of lignin is still only completely unknown and the term lignin, cannot be considered to be the designation of a constitutionally defined compounds, it is rather a collection term for a group or system of high molecular amorphous compounds that are chemically very closely related in the same sense as any other natural high molecular products such as cellulose, hemicelluloses, starch and proteins. Lignin may perhaps be defined as that incrusting material of the plant, which is built up largely of methoxylated p-hydroxy phenyl propane stones with varying degree of oxidation of their side chains, but how these building stones are fused together is still unclear. Lignin has been defined by Brauns as ‘that incrusting material of the plant which built up mainly, if not entirely, of phenyl propane building stones, it carries the major part of the methoxyl content of the wood, it is unhydrolyzable by acid, readily oxidizable, soluble in hot alkali and bisulphite, and readily condenses with phenol and thiocompounds.’
Studies have shown that the substitution of phenol with lignin, lignin rich materials and acid hydrolyzed wood which is enriched in lignin have resulted in replacement of 30 to 60% of phenol in PF resin adhesive but the results are generally less satisfactory than those achieved by the use of tannins. It has been reported that investigations carried out in Canada on a 100% lignosulphonate based adhesive have given satisfactory results. A process has recently been reported wherein high molecular weight lignin derivatives are copolymerized with PF resin, replacing up to 40% of resin in adhesive mix without undue effect on wood failure or durability. Wood flour and coconut shell flour have been shown to be satisfactory extenders for PF resin adhesives. During hydrolysis especially in the presence of phenol, the lignin in coconut shell flour (CSF), wood flour and other similar lignocellulosic materials is dispersed and the hemicellulosic and the cellulose converted at least partially into simple sugars and aldehydes. These products of hydrolysis can be expected to react with phenol and/or formaldehyde during subsequent resin formation. The process is applicable to both hardwood and softwood and other lignocellulosic materials such as coconut husk, coconut husk pith and coconut shell. It has been observed that CSF may also be dispersed by alkali treatment. Yoshihiro and Naoki prepared lignin based phenol formaldehyde (LPF) resin adhesives. Lignin based adhesives (LRF) from a mixture of RF and LF was the best of the other lignin-based adhesives. About 80% of the
resorcinol resin can be replaced by high molecular weight lignin. Arthur et. al have carried out the reactivity test of lignin with formaldehyde in order to identify potential lignins to partially replace phenol in phenol–formaldehyde resin adhesives. Sulphite lignins were found to be the best with reference to rate of reaction and capacity of reaction. Fast curing copolymer resins of phenol–formaldehyde and chemical extract from agriculture and forest residue was prepared. The copolymer provided superior bond quality for plywood in comparison to the common phenolic resins especially at the short press time in the preparation of veneer flake board laminates of 2mm thickness.

REVIEW OF LITERATURE

The highest strength of adhesive joints bonding beech wood samples was obtained when phenol-formaldehyde adhesive contains 16-20 phr benzene sulphonylic acid as cross-linking agent and had pH between 0.12-1.39. The mechanical strength of the phenolic adhesive obtained using MgCO₃-water glass as fire proofing agent decreased by approximately 25%. ZnO was used as water proofing agent. The alkyl resorcinol-formaldehyde adhesives, DFK-1-AM and DFK-14, were prepared from crude shale phenols. The pot life at 20°C was 1.0 and 2.5–3.0 h and resistivity 100 at 30°C and 300-500 Mpa respectively. Resin useful as adhesives especially for corrugated paper board are prepared by condensing 1 mole ketone with 5.5–6.5 mole formaldehyde at pH > 8.5 until the free formaldehyde content is ≤ 4%, adding 0.15–0.4 mole urea and completing polymerization. The bonding strength of urea-formaldehyde resin was increased by the addition of oligomeric polyethylene glycol (PEG) or PEG–polypropylene glycol copolymer. Paraformaldehyde or α-
polyethylene fibers were used as hardeners for formaldehyde-phenol-resorcinol resin to check the evaluation of formaldehyde. Addition of cross-linking catalysts such as monobasic or dibasic ammonium salts to urea-formaldehyde resin reduces the curing time with good pot life. Adhesives containing mainly unmodified synthetic rubber latexes, poly (vinyl alcohol), extenders, fillers, polyisocyanate cross-linking agents and deliquescent compounds show excellent paste stability and form water proof bonds to wood. Modification of urea resin adhesive with melamine and phenol and aminoplast with isocyanate improved the strength and weather resistance of particle boards. The amount required and kind of reinforcing component affected the board quality. An adhesive useful for bonding cellulose containing materials and textiles is prepared by condensation of urea and formaldehyde in the presence of alkali and alkaline earth salts and adding cross linking controlling additives to obtain desired viscosity. The alkali lignin modified urea-formaldehyde resin was prepared by the polycondensation of urea with formaldehyde in an acid medium and the reaction of oligomer with alkali lignin at pH 9-9.5. The hot water resistance of the adhesive joints with veneer increased. Resins containing <0.40 % free formaldehyde, useful as wood adhesives, resistant to humidity and microorganism are manufactured by polycondensation of 1:0.8 urea-formaldehyde mix at 90-94°C, modification of the product with an sodium-lignosulphonate and optionally conditioning the product with insecticide and fungicide. Urea-formaldehyde resins hardened by acid catalysts especially useful in the manufacture of particle boards containing 0.5-25 % thermally unstable inorganic or organic peroxides have higher mechanical strength caused by gas pressure developed during hardening process. Binders giving particle boards
with high flexural and transverse tensile strengths and short press times contains urea-formaldehyde resin containing 0-2 % melamine and 0-5 % phenol, ammonium salt of (in)organic acids inert to curing compounds, urea and metal salts. Adhesives from lignin containing waste for the manufacture of wood based materials were prepared by Heinz. The process decreased the demand for phenol and improve environmental protection from discarded waste. Chemical modification of oligomeric formaldehyde-urea resin with sulphate lignin gave good quality binders for plywood and particle board manufacture. Physical and chemically modified lignins contributed better characterized to kraft-lignin-phenol-formaldehyde (LPF) resin compound with non-modified lignin especially for mechanical resistance. N-hydroxyl methyl caprolactam is used to modify phenol-formaldehyde resin to improve its elastic properties. Fire resistant adhesives for plywood were prepared from urea resins or urea-melamine resins using NH$_4$H$_2$PO$_4$ and powdered Al$_2$O$_3$. The plywood showed adhesive strength of 12 kg/cm$^2$ and acceptable flame proof performance. The strength and water resistance of particle boards were increased by using urea-formaldehyde resin containing chloroacetic acid as hardener and a complex of aluminium hydroxy pentabromide crystal solvate. Flame and heat resistant phenolic resin compositions containing vinyl chloride-vinylidene chloride copolymers with excellent adhesion, no residual smell, and low adhesion temperature were prepared and were useful as hot melt adhesives for felts, laminates and resin bonded grinders. Phenol resins with high lignin content and acceptable viscosity were formulated from acid insoluble residue of wood hydrolyzed resin cure and dry adhesive strength properties of laminated blocks glued with phenolic resins having
phenolic replacement levels by lignin >50% were not significantly different from lignin free control sample. The use of aqueous extraction of tannin from spruce wood and lignin from spruce and beech wood with 1% aqueous NaOH solution in the preparation of phenolic resin, replacing phenols, has been made. Lignin extraction from pinewoods gave better results than those from beech wood. The method of concentration of tannins affected their reactivity with formaldehyde and good results were obtained by spray drying the tannin extraction. Wheat straw based particle boards were prepared by using isocyanate resin. The boards revealed good physical and mechanical properties and were complying with the requirements of the standard for the furniture particle boards. Fire resistant particle boards were prepared from urea-formaldehyde resin containing oligomeric epichlorohydrin-phosphoric acid dimethylamide copolymer and monomeric product of phosphoric acid with cyanoguanidine and urea as the fire proofing agents. Recently, wood particle boards were prepared by press curing a mixture of wood particles with portland cement as the binder. The boards have a bending strength of 98 Mpa. Phenol-formaldehyde resin mixed with self-emulsifying polyisocyanate was used to prepare wooden fiberboard. The particle board could be removed from the press plate without trouble. Manufacture of lignocellulosic composite particle products using lignin as an additives has been successfully carried by Pukis et. al. Ready to use resin-wax emulsion adhesive was prepared by heating thermosetting phenol-formaldehyde resin with a wax emulsion adjusted to pH within one unit to that of the phenolic resin, and then cooling to room temperature. Preparation of adhesives based on tannin extracts for fabrication of wood particle boards have been carried out by Garro and Juan.
Adhesives for the manufacture of low-density particle boards consisted of polymethylene polyphenylene isocyanate (-NCO contents 0.5-5 %) and prepolymers of polypropylene polyols with 0.5-3 cross link density. Manufacture of wood based cement-bonded boards, utilizing wood chips and industrial waste was undertaken by Vladimir et. al. These included wood chip/wood dust cement boards (Arbolite), excelsior cement boards (fibrolite) and cement bonded particle boards. The bending strength of the manufactured cement bonded particle boards and excelsior cement boards are up to 182 and 1 Mpa respectively. Amino resins comprising of melamine containing 0.1-3 % (VS. Solid contents) and water soluble organic acids offered a short adhesion time for preparing particle boards. Water resistant and odorless boards showing storage ability on adhesives were prepared by using amino resin adhesive comprising 50-70 % (based on total solid), melamine-formaldehyde, methanol and alkali metal hydroxides (2.0-40 % based on formaldehyde) as catalyst. Gypsum slurry obtained by adding CuSO4·0.5H2O powder in water has been used as binder for manufacturing particle boards from wood chips by Kamatsu and Nezu. Formamide, hexamethylene tetramine and K2CO3 were evaluated as catalyst for phenol-formaldehyde resins in the manufacture of particle boards from beggasse. The gelling point of the resin decreased by 30-35%. The adhesive strength of the resin was 1.8 Mpa for all catalysts.

EXPERIMENTAL

MATERIALS AND METHOD

Phenol (CDH), Formalin (37%) (Qualigens), Urea (Nice), Resorcinol (Merck), NaOH were used as received.
PREPARATION OF PHENOL-FORMALDEHYDE RESIN

Specific mole ratio (by weight) of phenol and formalin, taken in a resin kettle, was mixed with the help of the mechanical stirrer. Meanwhile, 50% aqueous solution of sodium hydroxide was prepared on the basis of 5% relative weight of sodium hydroxide to the weight of phenol taken. Sodium hydroxide solution was added slowly with constant stirring and heating to the phenol-formaldehyde mixture. Since the reaction is exothermic, proper precaution was taken to maintain the temperature between 50 to 60°C by circulating cold water around the resin kettle for initial 30-40 minutes. The temperature was then raised to 80° - 85°C and mixture was further heated at this temperature. The addition of a drop from the condensing resin to the cold water checks the setting of the resinification on appearance of turbidity. Reaction mixture was condensed at this temperature for another three and a half hour after which the heating was stopped and the resin cooled.

The pH, flow time, water tolerance, curing time and solid contents of the resin were measured and results are presented in Table 4.

PREPARATION OF UREA-FORMALDEHYDE RESIN

Urea and formalin were taken in a resin kettle in a specific mole ratio (by weight) and were mixed with the help of mechanical stirrer. To the solution was added 50% aqueous solution of sodium hydroxide till the pH of the mixture is adjusted to about 7.5. The reaction mixture was heated at 65° to 70°C till the dimethylol urea was formed (a few ml. of the solution in a test tube form white crystalline precipitates, when the sides of the test tube were scratched with the glass rod). The resultant product was then cooled and the pH of the reaction mixture was adjusted to 6 to 6.5
by the addition of 50 % acetic acid solution under constant stirring. The whole mass was heated again at 80° - 85°C till the start of the resinification (confirmed by the turbidity test). Condensation at this temperature was continued further for 30 minutes and then cooled to room temperature. The pH was raised to 7.5 by the dropwise addition of 50 % aqueous solution of sodium hydroxide.

The pH, flow time, water tolerance, curing time and solid contents of the resin were measured and results are presented in Table 4.

**PREPARATION OF PHENOL-RESORCINOL-FORMALDEHYDE RESIN**

Definite amount of PF resin was taken in a resin kettle and to it was added a known amount of resorcinol slowly with constant heating and stirring. The reaction mixture was heated between 55° to 60°C for about 50 minutes and then cooled to room temperature. The pH, flow time, water tolerance, curing time and solid contents of each resin were measured and results are presented in Table 4. The amount of resorcinol in PF resin and corresponding % PRF is tabulated as Table 5.

**PREPARATION OF LIGNIN-PHENOL-FORMALDEHYDE RESIN**

(i) **Formation of lignin formaldehyde (LF)** – The mother liquor containing lignin extract obtained after the digestion of the pine needles was concentrated and a definite amount of it was taken in the resin kettle. A known amount of formaldehyde was added; the pH of the mixture was adjusted 9.5 by the addition of aqueous 50 % NaOH solution with constant stirring. The reaction mixture was heated at 80°-85°C for about 4 hours and then cooled to room temperature.
(ii) **Phenol-formaldehyde (PF)** of best mole ratio (based on the properties of the particle boards) was prepared. Definite amount of lignin-formaldehyde resin and definite amount of phenol-formaldehyde resin were taken in a resin kettle and were mixed with the help of mechanical stirrer. The reaction mixture was heated between 55° - 60°C for about 24h and then cooled to room temperature. The composition of LF to PF in PLF corresponding to % PLF resin is detailed out in Table 6.

The pH, flow time, curing time and solid contents of each resin were measured and results are presented in Table 4.

**CHARACTERIZATION OF RESINS**

The resins were characterized with respect to the following properties.

1. **pH**: pH of each resin was measured with the help of pH meter.

2. **Viscosity**: Viscosity of the resin was measured at room temperature as a function of flow time with the help of B₄ cup.

3. **Solid contents**: Definite amount of resin was heated in a preweighed crucible at 100°C for one hour. After stipulated time, the resin was weighed again till the constant weight was obtained. Percent solid content of resin was determined from the following equation.

   \[
   \text{Percentage of solid contents} = \frac{W_1 - W_0}{W_1} \times 100
   \]

   Where \( W_1 \) and \( W_0 \) are the weights of resin before and after heating at 100°C respectively.

4. **Curing of Resin**: Curing of different resins was carried out as follows.
a. **Hot Curing (PF, PRF and PLF resins):** 5 ml. of the resin taken in a test tube, was placed in an oil bath maintained at 145°C. The sides of the test tube were scratched with the help of the glass rod till a string of the resin is formed. Time taken to form this string is noted.

b. **Hot Curing (UF resin):** UF resin requires the addition of ammonium chloride to avoid the fall of pH during application. To 20 gm. of UF was added 0.1 gm. NH₄Cl in 5 ml. of water and mixed thoroughly. 5 ml. of the resin solution was taken in a test tube and placed in boiling water. The sides of the test tube were scratched with the glass rod till the resin solidifies. The time taken for solidification was noted.

c. **Cold Curing (PRF resin):** Cold curing of PRF was carried out with the addition of formalin. To the known amount of the PRF was added a known amount of formalin, under stirring. The temperature of the mixture rises and the resin becomes solid. The time taken for solidification is noted. The results are presented in Table 7.

5. **Water Tolerance:** Water tolerance is the appearance of turbidity in the resin on addition of water to the resin.

**Water Tolerance of PF and PRF Resins:** Water from the burette is added slowly to 5 ml. of the resin (PF and PRF) taken in a beaker till the turbidity appeared. The amount of water required in proportion to the amount of resin taken gave the water tolerance of resin.

**Water Tolerance of UF Resin:** 10 ml. each of UF resin was separately taken in four beakers. To each of the beaker was added varying amount of water
under stirring. UF resin which settled first gave the least water tolerance to resin. The ratio of UF: H₂O required to settle the resin gave the water tolerance range of the resin.

RESULTS AND DISCUSSION

Formaldehyde-based adhesive systems are based on reacting formaldehyde with active hydrogen containing compounds such as phenol, urea or melamine (Fig.1). This family of thermosets has low flammability, high rigidity, good dimension stability and low cost. These systems are heat activated and are processed using compression or injection molding.

\[
\begin{align*}
(a) & : \text{HO} \quad \text{Phenol} \\
(b) & : \text{NH}_2\text{C} \equiv \text{NH}_2 \quad \text{Urea} \\
(c) & : \text{H}_2\text{N} = \text{N} = \text{N} = \text{H}_2 \quad \text{Melamine}
\end{align*}
\]

Fig.1: Formaldehyde can react with (a) phenol, (b) urea or (c) melamine to produce cured thermosetting resin.

PHENOL-FORMALDEHYDE RESIN

Phenol-formaldehyde resin based polymers are prepared by the condensation of phenol with formaldehyde. The reaction is catalyzed by acids or alkalies. The nature
of the product is dependent on the types of catalyst and the mole ratio of the reactants. Novolac resins are prepared by reacting a molar excess of phenol with formaldehyde (mole ratio 1.25:1) in the presence of an acid catalyst. In the present work resol resins are used and are prepared by the reaction of phenol with a molar excess of formaldehyde in the ratio of 1:1.5-2 under alkaline conditions. The mechanism of condensation of phenol, formaldehyde in the alkaline medium is represented as:

\[
\begin{align*}
\text{OH} & \quad \text{O}^- \\
\text{O}^- & \quad \text{H}^+ \\
\text{H—C—H} & \rightarrow \text{CH}_2\text{O}^- \\
\text{CH}_2\text{OH} & \quad \text{OH} \\
\text{O}^- & \quad \text{O}^- \\
\end{align*}
\]

The resulting o and p-methylol phenols are more reactive towards formaldehyde than the original phenol. They further react with formaldehyde resulting in the formation of di and trimethylol derivatives as shown below:

57
The above reaction is repeated forming the trinuclear phenols from the dinuclear phenol. Further heating of these initial reaction products results in the condensation and increase in the molecular weight. Condensation takes place between the methylol groups to form a methylene ether link (a) or between a methylol group and an active ortho and para hydrogen atom to yield a methylene link (b).

The amount of heating determines the final focus of the product e.g. whether the resin is less viscous (water soluble liquid), highly viscous (little or no water miscibility) or a grindable form. Hence, the product obtained by the reaction of phenol and
formaldehyde in the presence of alkali is a complex mixture of mono and polynuclear phenol in which the phenolic nuclei are linked by methylene groups. The general structure of resol can then be represented as:

\[
\text{UREA-FORMALDEHYDE RESIN}
\]

The preparation of urea-formaldehyde resin is sensitive to the change in pH. The pH is maintained and adjusted with proper addition of base or acid during the reaction. The mechanism of formation of resin follows two steps. The first step in the reaction between urea and formaldehyde is the formation of methylol urea. As urea is tetra functional, the initial reaction can lead to the formation of tetra methylol derivative of urea, if the ratio of formaldehyde to urea is high enough.
In this case, formation of methylol group slows the formation of another methylol therefore; the introduction of subsequent methylol groups is reduced gradually. For wood adhesives, reaction conditions, which leads mostly to the formation of dimethylol urea are employed.

The rate at which methylol urea (I) and (II) takes place, depends on the concentration, temperature, pH and the ratio of formaldehyde to urea (F/U). To control the reaction and to favour the formation of dimethylol urea, the conditions must be slightly alkaline and a pH of 7-8 is employed.

The methylol ureas are not adhesives. Condensation does not take place yet. Methylol present in dilute aqueous solution must be removed by means of distillation since it is toxic and could retard the hardening of the glue. The next step is the condensation of monomeric methylol urea to form polymer molecules. The resin is carried out at 90°-100°C and the reaction speed is controlled by the acidity of the medium. Best results are obtained at a pH of 4.5-5. As the reaction proceeds larger molecules with cross-linked structures are formed.

At a desired level, the reaction is arrested by neutralization (pH 7-8). If the reaction is allowed to continue, the cross linking will lead to gelatinization of the resin in the resin kettle. The condensation must, therefore, be closely watched and controlled at all the stages of production.

Under acidic conditions, methylol ureas condense by elimination of water between either.

i. A methylol group and a free amine group (I) yielding a product containing methylene linkage (III)
ii. Two methylol groups (II) yielding product containing methylol ether linkage (IV).

iii. Or methylol ether linkage (IV), which by loss of formaldehyde condensed to III.

\[
\begin{align*}
&\text{HO}_2\text{H} - \text{C} - \text{N} - \text{CH}_2\text{OH} + \text{HN-} \quad \text{HO}_2\text{H} - \text{C} - \text{N} - \text{CH}_2\text{OH} + \text{HO}_2\text{H} - \text{NH} \\
&\text{(I)} \quad \text{H}_2\text{O} \quad \text{(II)} \quad \text{H}_2\text{O} \\
&\text{HO}_2\text{H} - \text{C} - \text{N} - \text{CH}_2\text{H} - \text{N} \leftarrow \text{HCHO} \quad \text{HO}_2\text{H} - \text{C} - \text{N} - \text{CH}_2\text{O} - \text{CH}_2\text{NH} \\
&\text{(III)} \quad \text{(IV)}
\end{align*}
\]

The product of the above kind still possesses methylol and amino groups. Thus condensation may continue to yield polymer methylene compounds. The general structure may be represented by:

\[
\begin{align*}
\text{HO}_2\text{H} - \text{C} - \text{N} - \text{CH}_2\text{H} - \text{N} \leftarrow \text{HCHO} \quad \text{HO}_2\text{H} - \text{C} - \text{N} - \text{CH}_2\text{O} - \text{CH}_2\text{NH} \\
\text{n}
\end{align*}
\]

Average molecular weight ranges from 200-500 corresponding to the value of ‘n’ in the above structure of about 1-5. The different steps in the formation of the resin are shown in Table 8.
### Table 8.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Raw material</th>
<th>State</th>
<th>Mole ratio F/U</th>
<th>Reaction</th>
<th>Semi product</th>
<th>Reaction</th>
<th>Product</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>Urea</td>
<td>White</td>
<td>1.5-1, 2.0:1</td>
<td>Addition</td>
<td>Mono-methylol urea and di-methylol urea</td>
<td>Condensation</td>
<td>UF resin</td>
<td>7.5 to 8.5</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>crystalline liquid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Addition**

Urea + Formaldehyde $\xrightarrow{\text{pH 7 to 8}}$ Methylolurea $\xrightarrow{\text{pH 5.5 to 6}}$ UF resin

**Condensation**

RESORCINOL BASED PHENOL-FORMALDEHYDE RESIN

Resorcinol i.e. m-dihydroxybenzene is trifunctional and it readily combine with formaldehyde to form methylene derivatives, with methylol groups occupying either the position ortho to both hydroxyl groups or ortho to one and para to the other

![Resorcinol derivative](image)

The reactivity of methylol derivative is so high that they cannot easily be obtained in the stable form as resoles as in the case of phenolics. The reactivity of resorcinol towards formaldehyde is such that the resins are formed in the absence of any catalyst. When two materials are heated together, the exothermic reaction proceeding...
vigorously to the thermoset stage unless carefully controlled. In these polymers, the resorcinol nuclei are joined together through methylene bridges to give complex molecule.

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{H}_2\text{C}_6\text{O}_H & + \\
\text{OH} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

The greater reactivity of resorcinol compared to phenol is due to the presence of two hydroxyl groups, meta to each others. The two groups reinforcing each other in their activation of the ortho and para positions of the benzene ring. Since the introduction of methylol groups onto the ring increases the activity of the ortho nuclear positions, it is, therefore, clear why resorcinol resins have so great tendency to react as long as there are active sites available.

**LIGNIN-PHENOL-FORMALDEHYDE RESIN**

The preparation involves the reaction of lignin with formaldehyde to give the product with hydroxyl groups of lignin reacting with formaldehyde. The resinous mass is mixed with the resin obtained from phenol-formaldehyde. The cross linking between the two leads to the formation of lignin based phenol- formaldehyde resin.
Characterization of Phenol-Formaldehyde, Urea-Formaldehyde, Phenol-Resorcinol-Formaldehyde and Phenol-Lignin-Formaldehyde Resins

Phenol-formaldehyde and urea-formaldehyde resins were prepared with varying ratio of phenol to formaldehyde and urea to formaldehyde respectively. Each resin sample was characterized with respect to pH, viscosity, water tolerance, curing time and solid content. The results are presented in Table 4.

The pH of phenol-formaldehyde resin for the F/P ratio varying between 1.74 to 2.44 is observed between 9.0 to 9.7 i.e. resin is alkaline which is due to the use of NaOH as the catalyst. For urea-formaldehyde resin, the pH of all the samples was maintained between 7 to 7.5 after the reaction is stopped, in order to avoid the process of further condensation. However, lower pH value (5.9 - 6.5) is required at the time of its use in the preparation of the board.

Viscosity measured in terms of flow time with B4 cup is found to vary with the change in F/P and F/U ratio in the resin. The flow time initially increases with increasing F/P and F/U ratios. At higher ratio it shows a decrease with both the resins. Flow time of 21 sec. is observed for PF resin of 2.44 F/P mole ratio while UF shows a flow time of 25 min. at F/U ratio 1.74. The PF resin with F/P ratios 1.97 shows the best water-tolerance (1:8.5) while at the maximum F/P ratio (2.44) the water-tolerance value is 1:6. In the case of UF, the higher water-tolerance (1:1.2) is observed for the lower F/U ratio (1.40) while at higher F/U (1.74) the value is 1:0.55. The better water-tolerance at lower ratio of both PF and UF resins may be due to the reason that since at lower ratios smaller amount of formaldehyde is used in
comparison to phenol and urea, which shows affinity for water. At higher ratios almost complete condensation takes place and as such the water-tolerance value decreases. Curing time for both PF and UF resin increases initially and decreases at higher F/P and F/U ratio. PF and resin of F/P 2.44 ratio shows a curing time of 11.32 sec. while UF resin a curing time of 152 sec at F/U =1.74. The solid content decreases with increasing F/P and F/U ratio.

Different samples of PRF and PLF resins were prepared with varying percentage of resorcinol (15%, 20%, 25%) or lignin-formaldehyde (10%, 20%, 30%, 40%, 50 %) with respect to phenol-formaldehyde resin and characterized.

The pH of PRF resin does not vary much with rise in the percentage of resorcinol. It remains same (8.1) for 15% and 20% samples while for 25% PRF resin, pH lies at 8.3. Flow time and water-tolerance increases with increase in the percentage of resorcinol from 15 to 25 %. Maximum flow time (252sec.) and maximum water tolerance (1:8.5) is observed for 25% PRF resin. The curing time (13.54 min) and solid content (62.33 %) is also higher for this resin. Table 7 represents cold curing of PRF resin.

On determining the pH of the PLF resin, it was observed that pH remains almost same (9.1-9.2) for all percentages of PLF resin. The flow time increases with increase in percentage of PLF resin; the maximum (46sec.) is observed for 50% PLF resin. The curing time also increases with increasing LF percentage in PLF resin and the maximum (19.23min) is obtained for 50% PLF resin. Solid content also increases with increase in LF percentage upto 40% giving maximum (58.35 %) beyond which,
at 50% PLF, it falls to 54.51 %, which is due to relative amount of PF and LF present in the PLF composition.
### TABLE 1. PHYSICO-CHEMICAL CHARACTERISTIC OF PINE NEEDLES

<table>
<thead>
<tr>
<th>Physical Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Colour when dry</td>
<td>light brown</td>
</tr>
<tr>
<td>2. Length of the needles</td>
<td>15-20 cm.</td>
</tr>
<tr>
<td>3. Diameter</td>
<td>0.5 to 1.00 mm</td>
</tr>
<tr>
<td>4. Bulk density</td>
<td>0.05 g/cm³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Extractives:</td>
<td></td>
</tr>
<tr>
<td>4.47 % oven dry basis</td>
<td></td>
</tr>
<tr>
<td>4.81 % (in ether)</td>
<td></td>
</tr>
<tr>
<td>17.6 % (in alcohol: benzene 1:2 V/V)</td>
<td></td>
</tr>
<tr>
<td>2. Pentosan</td>
<td>13.3 %</td>
</tr>
<tr>
<td>3. Lignin</td>
<td>31.0 %</td>
</tr>
<tr>
<td>4. Holo-cellulose</td>
<td>70.5 %</td>
</tr>
<tr>
<td>5. Alpha cellulose</td>
<td>42.8 %</td>
</tr>
<tr>
<td>6. Ash</td>
<td>2.44 %</td>
</tr>
<tr>
<td>7. Hydrochloric</td>
<td>0.16 %</td>
</tr>
<tr>
<td>acid insoluble</td>
<td></td>
</tr>
</tbody>
</table>

- Calculated on extractive from oven dry basis

### TABLE 2. THERMOGRAVIMETRIC ANALYSIS OF PINE CELLULOSIC FIBERS.

<table>
<thead>
<tr>
<th>IDT (°C)</th>
<th>FDT (°C)</th>
<th>DT (°C) at every 10% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>250</td>
<td>458</td>
<td>296</td>
</tr>
</tbody>
</table>

### TABLE 3. WATER ABSORPTION STUDIES OF PINE CELLULOSIC FIBER FROM THE ATMOSPHERE AND IMMERSION IN WATER.

<table>
<thead>
<tr>
<th>Percent moisture absorption from atmosphere after</th>
<th>Percent water absorption by the sample immersed in water after</th>
</tr>
</thead>
<tbody>
<tr>
<td>24h 48h</td>
<td>24h 48h</td>
</tr>
<tr>
<td>3.5 6.0</td>
<td>221.5 225.5</td>
</tr>
</tbody>
</table>
TABLE 4. CHARACTERIZATION OF PF, UF, PRF AND PLF RESINS

<table>
<thead>
<tr>
<th>S.No</th>
<th>Resin</th>
<th>mole ratio/%</th>
<th>Flow Time (Sec)</th>
<th>Water Tolerance Resin:H₂O</th>
<th>Curing Time*</th>
<th>Solid Contents (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PF</td>
<td>F/P 1.74</td>
<td>29</td>
<td>1:6.5</td>
<td>11.55 min.</td>
<td>54.24</td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td>1.97</td>
<td>32</td>
<td>1:8.5</td>
<td>14.38 min.</td>
<td>56.35</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>2.20</td>
<td>25.5</td>
<td>1:5.5</td>
<td>12.32 min.</td>
<td>45.50</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>2.44</td>
<td>21</td>
<td>1:6</td>
<td>11.32 min.</td>
<td>42.23</td>
</tr>
<tr>
<td>5.</td>
<td>UF</td>
<td>F/U 1.40</td>
<td>21</td>
<td>10:12</td>
<td>175 sec.</td>
<td>49.67</td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td>1.55</td>
<td>27.5</td>
<td>10:7</td>
<td>189 sec.</td>
<td>47.51</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td>1.63</td>
<td>28</td>
<td>10:7.5</td>
<td>160 sec.</td>
<td>45.78</td>
</tr>
<tr>
<td>8.</td>
<td></td>
<td>1.74</td>
<td>25</td>
<td>10:5.5</td>
<td>152 sec.</td>
<td>46.22</td>
</tr>
<tr>
<td>9.</td>
<td>PRF</td>
<td>% 15</td>
<td>194</td>
<td>1:7</td>
<td>12.45 min.</td>
<td>54.22</td>
</tr>
<tr>
<td>10.</td>
<td></td>
<td>20</td>
<td>238</td>
<td>1:7</td>
<td>13.07 min.</td>
<td>58.63</td>
</tr>
<tr>
<td>11.</td>
<td></td>
<td>25</td>
<td>252</td>
<td>1:8.5</td>
<td>13.54 min.</td>
<td>62.33</td>
</tr>
<tr>
<td>12.</td>
<td>PLF</td>
<td>10</td>
<td>22</td>
<td>-</td>
<td>12.02 min.</td>
<td>46.35</td>
</tr>
<tr>
<td>13.</td>
<td></td>
<td>20</td>
<td>26</td>
<td>-</td>
<td>12.20 min.</td>
<td>48.05</td>
</tr>
<tr>
<td>14.</td>
<td></td>
<td>30</td>
<td>30</td>
<td>-</td>
<td>13.40 min.</td>
<td>53.41</td>
</tr>
<tr>
<td>15.</td>
<td></td>
<td>40</td>
<td>35</td>
<td>-</td>
<td>16.25 min.</td>
<td>58.35</td>
</tr>
<tr>
<td>16.</td>
<td></td>
<td>50</td>
<td>46</td>
<td>-</td>
<td>19.23 min.</td>
<td>54.51</td>
</tr>
</tbody>
</table>

* PF, PRF and PLF at 135°C-140°C
UF at 100 °C

TABLE 5. THE AMOUNT OF RESORCINOL IN PF RESIN AND CORRESPONDING % PRF

<table>
<thead>
<tr>
<th>S.No</th>
<th>PF (gm)</th>
<th>Resorcinol (gm)</th>
<th>% of resorcinol in PRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>30</td>
<td>10 (Cross linked)</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>

TABLE 6. THE COMPOSITION OF LF TO PF IN PLF CORRESPONDING TO % PLF RESIN

<table>
<thead>
<tr>
<th>S.No</th>
<th>LF (gm)</th>
<th>PF (gm)</th>
<th>% of LF in PRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>450</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>350</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
<td>250</td>
<td>50</td>
</tr>
</tbody>
</table>
### TABLE 7. COLD CURING OF PRF RESINS

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5</td>
<td>1</td>
<td>22</td>
<td>23</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>2.</td>
<td>5</td>
<td>2</td>
<td>22</td>
<td>24</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>3.</td>
<td>5</td>
<td>3</td>
<td>22</td>
<td>25</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>4.</td>
<td>5</td>
<td>4</td>
<td>22</td>
<td>23</td>
<td>1</td>
<td>24</td>
</tr>
<tr>
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<td>5</td>
<td>5</td>
<td>22</td>
<td>23</td>
<td>1</td>
<td>24</td>
</tr>
</tbody>
</table>

**20%**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of PRF 20% (ml)</th>
<th>Formalin added (ml.)</th>
<th>Initial Temp. °C</th>
<th>Change in Temp. °C</th>
<th>Difference in Temp. °C</th>
<th>Curing Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5</td>
<td>1</td>
<td>22</td>
<td>24</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>2.</td>
<td>5</td>
<td>2</td>
<td>22</td>
<td>25</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>3.</td>
<td>5</td>
<td>3</td>
<td>22</td>
<td>26</td>
<td>4</td>
<td>19</td>
</tr>
<tr>
<td>4.</td>
<td>5</td>
<td>4</td>
<td>22</td>
<td>26</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>5.</td>
<td>5</td>
<td>5</td>
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<td>24</td>
<td>2</td>
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</tbody>
</table>

**25%**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
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<td>1</td>
<td>22</td>
<td>25</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>2.</td>
<td>5</td>
<td>2</td>
<td>22</td>
<td>26</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>3.</td>
<td>5</td>
<td>3</td>
<td>22</td>
<td>27</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>4.</td>
<td>5</td>
<td>4</td>
<td>22</td>
<td>26</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>5.</td>
<td>5</td>
<td>5</td>
<td>22</td>
<td>26</td>
<td>4</td>
<td>22</td>
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</table>
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