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Synthetic resins and their properties in respect of development of jute based composite boards

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Abstract

Synthetic resins play an important role for preparation and sustenance of composite industry. Preparation of synthetic resins in standard protocol is readily available in literature. However, the standardization and stability of both urea formaldehyde and phenol formaldehyde resins has the paramount importance to develop suitable composite board. An attempt therefore made to synthesis these resins through a rational approach. The developed resins were subjected to preparation of medium density particle board and it has been revealed that higher resin viscosity causes ball formation with fibrous mass at the time of blending; however resin viscosity of 250 – 300(cP) is found suitable for making fibreboard. 0.75 board density can meet the BIS specification for fiberboards (IS 12406). In this experiment the fibreboards need to have a density of 0.74 g/cc and a resin content of about 12% to produce boards conforming to BIS specification. It is also observed that the dry process generated fibres have a better l/b ratio compared to wet-process generated fibres.

Highlights

- Synthesis of PF and UF resins were made through a rational approach
- Higher resin viscosity causes ball formation with fibrous mass at the time of blending
- Resin viscosity of 250 300(cP) is found suitable for making fibreboard
- Dry process generated fibres have a better l/b ratio compared to wet-process generated fibres

Keywords: Synthetic resin, phenol formaldehyde, urea formaldehyde, phenol formaldehyde, Composite board

The use of economical agro-based renewable natural fibres such as jute, sisal, coir and bamboo in preparing composites by using various thermoplastic and thermosetting resins have successfully proven their high qualities in various fields of technical application in recent years (Mishra *et al.* 2001; Coutinho *et al.* 1997; John and Gatenholm, 199, Rout *et al.* 2001; Mishra *et al.* 2001; Sanadi *et al.* 1995; Mondal *et al.* 2015, Ray *et al.* 2013; Ray *et al.* 2014) Synthetic resin is typically manufactured using a chemical polymerization process. This process

then results in the creation of polymers that are more stable and homogeneous than naturally occurring resin. Since they are more stable and are cheaper, various forms of synthetic resin are used in a variety of products such as plastics, paints, varnishes, and textiles. There are various kinds of synthetic resins; acetal resins, amino resins, casein resins, epoxy resins, emulsion polymers, hydrocarbon resins, polyamide resins, polyesters rubber resins etc. The classic variety is epoxy resin, manufactured through polymerization, used as a



thermoset polymer for adhesives and composites. Epoxy resin is two times stronger than concrete, seamless and waterproof. Polyamide resin is another example of synthetic resins. Polyamide resins are products of polymerization of an amino acid or the condensation of a diamine with a dicarboxylic acid. They are used for fibers, bristles, bearings, gears, molded objects, coatings, and adhesives. The term nylon formerly referred specifically to synthetic polyamides as a class. Because of many applications in mechanical engineering, nylons are considered engineering plastics. Resins are valued for their chemical properties and associated uses, such as the production of varnishes, adhesives, lacquers, paints, rubber and pharmaceutical uses. The applications of synthetic resins are seen in some important industries like paint industry, adhesive industry, the printing ink industry, the textile industry, the leather industry, the floor polish, paper, agricultural industry etc. As it can be seen that there is an enormous scope of application of resins hence it is one of the major field to venture.

Resins for Particle board

Particleboard or chipboard is manufactured by mixing wood particles or flakes together with a resin and forming the mix into a sheet. Resin, in liquid form, is then sprayed through nozzles onto the particles. There are several types of resins that are commonly used. Amino, formaldehyde based resins are the best performing when considering cost and ease of use. Urea Melamine resins are used to offer water resistance with increased melamine offering enhanced resistance. Phenol formaldehyde is typically used where the panel is used in external applications due to the increased water resistance offered by phenolic resins and also the colour of the resin resulting in a darker panel. Melamine Urea phenolic formaldehyde resins exist as a compromise. To enhance the panel properties even further the use of resorcinol resins typically mixed with phenolic resins are used, but this is usually used with plywood for marine applications and a rare occasion in panel production. Another interesting but little used synthetic binder is polyisocyanate.

Urea and melamine resins are also known as amino resins and are the reaction products of amino and amido groups with aldehydes, most commonly formaldehyde. The reaction causes formaldehyde to condense with the amino/ amido compound to form methylol derivatives which upon further heating form the cured, colourless resin. These resins as well as phenol-formaldehyde resin can be cured rapidly in the presence of catalysts with the application of heat. As noted, the resins are built up by condensation polymerization.

Urea-formaldehyde (UF) Resin

Urea-formaldehyde resins are the most prominent examples of the class of thermosetting resins usually referred to as amino resins (Williams, 1991; Updegraff, 1990). Urea-formaldehyde adhesives are the most widely used resin in the particleboard industry due primarily to their low cost and ease of application. Binders or adhesives are the second major constituent of a particleboard. About 90% or more of the worlds' particleboard production is made with UF resins. The properties offered by these resins are adequate for bonding particles in products intended for interior applications (e.g. in sub floor and furniture core stock). Many improvements, along with a continuous reduction in their cost have kept urea-formaldehyde adhesives in a leading position during the past several decades. Further research in producing yet better properties will help urea resins retain their market position in the field of wood particleboard manufacture.

Synthesis of UF Resin

Urea itself is the most prominent member of the amino resins with the chemical formula:

Urea adhesives are condensates of urea and formaldehyde, HCHO (formalin), which have been advanced in polymerization to a degree that still allows almost complete dispersion in water at solid contents of about 50-65%. Mole reaction of approximately 1.5 to 2 of formaldehyde to one of urea is common for urea-formaldehyde resins, which can be produced in dispersion or spray-dried forms.

The simplest reaction product of urea and formaldehyde is brought about when equimolar proportions of urea and formaldehyde are used. This reaction produces a type of "building block" for urea adhesives called monomethylol urea:

$$NH_2 - CO - NH_2 + HCHO \rightarrow NH_2 - CO - NH.CH_2OH$$

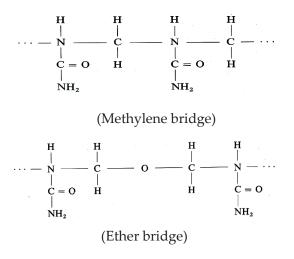
(monomethylol urea)

Under proper conditions, the reaction results in the attachment of the formaldehyde to a nitrogen of the urea molecule. If the molar ratio of the formaldehyde to urea is increased to 2:1, then dimethylol urea, another type of "building block" for urea-formaldehyde adhesives, will result:

$$NH_2$$
-CO-NH₂ + 2 HCHO \rightarrow HO.CH₂NH-
CO-NH.CH₂OH
(dimethylol urea)

Formaldehyde is again attached to the nitrogens of the urea molecule. Both monomethylol urea and dimethylol urea can be produced in aqueous solutions using an alkaline catalyst.

Polymerization (curing) of the monomeric "building blocks," described above, is believed to involve different and complex mechanisms depending upon the reaction conditions and the molar ratio of formaldehyde and urea used. Analysis of intermediate condensates in the polymerization process of urea-formaldehyde resins indicates the presence of methylene and ether bridges between the urea molecules :



The polymerization may, for instance, advance through the formation of an intermediate compound called methylene urea.

$$N = CH_2$$

$$|$$

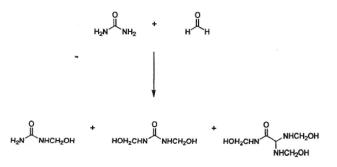
$$C = O$$

$$|$$

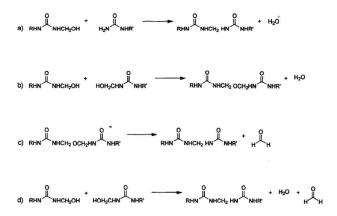
$$NH_2$$

(Methylene urea)

In the presence of dilute acids, the intermediates will subsequently condense to generate a linear polymer utilizing one of the bridges indicated above. Terminal groups may exist as amide ($-NH_2$), methylol ($-CH_2OH$) or azomethine ($-N=CH_2$). Direct determination of the molecular size in crude urea resins points to a relatively low degree of polymerization (compared to, for instance, thermoplastic adhesives). During transition from monomeric to polymeric state whether under the influence of heat, catalyst, or both, the urea resins split out water of condensation.



Formation of mono-, di- and trimethylolurea by the addition of formaldehyde to urea.



The urea resins manufactured for particleboard industry are either essentially monomeric or, at most, only slightly advanced in polymerization. The low degree of polymerization is necessary to provide solubility of resin product in the initial stage of application. Available urea-formaldehyde resins contain the reactive terminal groups enabling them to condense further in an acid environment under the influence of heat.

Phenol- Formaldehyde Resin

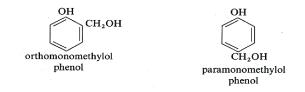
Phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. Phenolformaldehyde adhesives are the second most widely



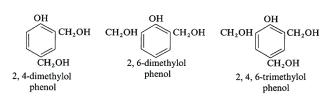
used binders in the production of particleboard. They are not nitrogen-containing and have some basic performance differences with urea-formaldehyde resins. Phenolic resins, unlike urea- formaldehyde, are durable, exhibiting resistance to breakdown in both cold and hot water. Phenolics are not attacked by weak acids or alkali and are resistant to common organic solvents. These adhesives also show good resistance to higher temperatures. However, phenolformaldehyde adhesives are at a disadvantage compared to urea binders in a number of respects including solids content, storage life, cure speed, tack characteristics, compatibility with additives including wax emulsions, and cost. Furthermore, they impart colour to the resulting board.

There are many ways for phenol and formaldehyde to combine in this condensation process, with products being either thermosetting or thermoplastic. The manner in which phenol and formaldehyde can combine depends on many factors such as type and amount of catalyst, the reaction pH, the molar ratio of phenol to formaldehyde, the time and temperature of the reaction, and the use of various additives. The thermosetting products of phenol and formaldehyde reaction are formed when formaldehyde is used in molar excess in an alkaline medium.

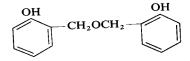
The first reaction between phenol and formaldehyde can generate products such as ortho- or paramonomethylol phenol:



These can subsequently react with more formaldehyde to yield di-and tri- methylol phenols :

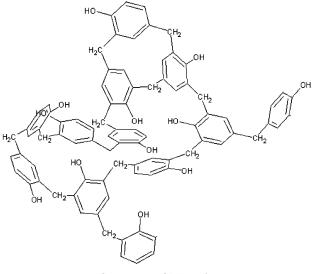


In the ensuring reaction, a methylol group of one molecule reacts with a second phenolic molecule, splitting off water, to form a dihydroxydiphenylmethane type of compound or, it can react with a methylol group attached to another phenolic molecule, splitting off water and producing a dihydroxydibenzylether such as :



In either alkaline or acid environments this ether splits off formaldehyde to form a methylene-linked compound, with the formaldehyde becoming available for further reaction.

In the production of thermosetting phenolic resins, the molar ratio of formaldehyde to phenol usually ranges from 1: 1 to 3: 1. Catalysts employed for these resins are usually strong alkali (e.g., sodium hydroxide) although ammonia is also frequently used. Since the reaction between phenol and formaldehyde involves condensation polymerization, the weight of the cured resin will be less than the combined weights of reactants by the amount of water split off. This amount of water released is proportional to the extent of polymerization and number of cross links. Condensation proceeds slowly at room temperature and rapidly at elevated temperatures.



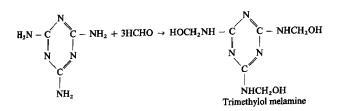
Structure of PF-resin

Melamine-Formaldehyde Resin

MF is the most durable and most expensive of the amino resin class. It is not usually used by itself in the manufacture of wood particleboard. Since it offers better moisture and heat resistance than the urea-formaldehyde resins, it is sometimes used in conjunction with ureas to upgrade the binder. Melamine-formaldehyde resins are synthesized in two stages with a 1:(2–12) molar ratio of melamine to formaldehyde. Various methylol derivatives of melamine are formed during the first stage at a temperature of 80°-90° C and pH 8.5; the second stage involves subsequent polycondensation of the products in an acid medium. For example, the reaction mixture must be cooled to 50°-60° C and a certain quantity of acid added to produce melamine-formaldehyde resins with the highest industrial value.

Melamine-formaldehyde resins are amorphous white products that are readily soluble in water but insoluble in organic solvents. The methylol groups in the resins undergo esterification with alcohols, primarily *n*-butanol and methanol, to impart to them hydrophobic properties, solubility in organic solvents (during the preparation of varnishes), and the ability to combine with plasticizers. Melamineformaldehyde resins are cured at high temperatures, or at room temperature in the presence of slightly acidic catalysts

The basic raw materials required for the manufacture of melamine- formaldehyde are melamine and formaldehyde. Melamine (2, 4, 6- triamino-1, 3, 5-triazine) entered the field of commercial production in 1939 in the United States. It is a white crystalline chemical which can be produced from calcium cyanamide.



Resin Properties for Particle board preparation

Availability of better synthetic resins has largely been responsible for this development of wood particleboard industry. Urea and phenolic resins have been able to meet many requirements imposed by the manufactures. The need for custom formulating resins based on a large number of factors is now well established. Some of the more important properties of resins are as follows:

Viscosity

Resin viscosity is affected by a number of variables including temperature. Increased ambient temperatures result in lower viscosities for both urea and phenolic resins (2.12). Tests on resin viscosity, under appropriate conditions, can reveal information pertinent to its age, quality, and, in many cases, wetting characteristics. Tests can further reveal changes in density, stability, solids content, and molecular weight. It is generally recommended that the resin viscosity be in the 100 to 500 cp at 20°C for particle board production.

Solids content

In particleboard production, the solids content should be high enough such that upon completion of the blending operation, excessive amounts of water have not been added to the wood furnish. The solids content, on the other hand, cannot be excessively high since the resin becomes too viscous, causing problems associated with high resin viscosity already mentioned. The solids content of resins supplied to the particleboard industry is about 65% for urea-formaldehyde and 40-50% for phenolic resins.

Tack

Tack is refers to the ability of the adhesive to develop a certain amount of adherence on contact. With the development of caulless production lines and other modifications in the manufacture of particleboard, proper tack development has become a critical requirement.

Cure

The cure rate of the resin obviously influences the rate of production. Much research and development has been devoted to reducing the time required in the hot press. Sharp reductions in press time have been achieved. The use of slow curing resins leads to an uneconomical underutilization of the hot press and thereby of the rest of the equipment in the particleboard plant. However, the rate of cure of a given resin must not be so fast as to produce precure before the full pressure is applied to the mats. Further, good resins will not stick to the cauls or platens once cured.



Formaldehyde release

The odour of formaldehyde is pungent and, when excessive, is considered a serious nuisance. All urea- and phenol- ; formaldehyde adhesives release varying amounts of formaldehyde during hot pressing and later from the products utilizing such binders.

Storage life

Storage life is very important in particleboard production because the adhesives are stored in large quantity and eventually used over a period of time. During this period, it is imperative that the resin properties essential for quality board production not be adversely altered. The resin must have storage integrity such that no rapid viscosity build-up occurs. In addition, its other essential properties, e.g., cure speed and tack characteristics, must not change substantially from the time it is manufactured to the time it is used by the board plant. The temperature of the environment in which the resin is stored has a substantial influence on its storage life. Commercial resins have a storage life of a number of months if kept under relatively cool temperatures.

Working life

The working life begins in particleboard manufacture when catalysts and additives are added until the particle mats are being consolidated under full pressure and heated in the hot press. The resin suppliers and manufacturers, based largely on experience, usually provide the board plant with information on the length of the working life yielded by their resin under various circumstances encountered in the plant. To avoid the hazard of facing a short working life, continuous mixing systems (catalyst and resin) can be very helpful since in this type of arrangement no appreciable amount of time elapses before the mats reach the hot press.

Additive compatibility

In particleboard manufacture, a number of additives are often incorporated into the board structure to enhance its performance under certain circumstances. Additives include sizing agents, fire retardants, insect repellents, and fungicides. It is, therefore, essential that the adhesives' properties and curing mechanism are not adversely affected when these compounds are added. Furthermore, the efficiency of the adhesive must not suffer with the addition of additives. The current generation of urea- and phenol-formaldehyde adhesives generally meets these requirements.

Flow

This property refers to the ability of the resin to retain its fluid state in the early moments of hot pressing when the mat has been subjected to intense heat and pressure. A resin with good flow properties continues to wet new particle surfaces and generally permits particle movement in the mat before it is solidified by polymerization.

Bonding efficiency

The resin used for particle board preparation must be an efficient *binder*. The type of resin employed and the techniques of application used are principal factors affecting bonding efficiency. Although the influence of the latter on bonding efficiency is evident, the former can affect efficiency by a number of variables such as the amount used, resin viscosity, solids content, and the temperature during application.

Durability

The durability of adhesive bonds under exposure to outdoor conditions is vital in exterior particleboard. The durability of exterior particleboard is measured by the extent of its strength retention, thickness swell, and surface appearance over time. Standard urea resins offer very short durability in exterior situations while the phenolic resins perform a great deal better. Urea resins are durable in most interior applications where excessive levels of moisture and heat are not encountered.

Dilutability

The resins should be capable of being safely diluted with water. Dilution may be required in some cases to improve the quality of resin blending.

Colour

The most significant advantages of urea resin are that these are colourless. Generally, it is desirable to use an adhesive which does not impart colour to the resulting particleboard.

Cost

Cost is also important requirement that all resins must meet. Low cost is essential if any operation is to be economically viable.

Effect of resin viscosity

It is well known that resin viscosity determines the spreading efficiency of the resin on reinforcement fibres. Low viscous resin can flow and spread through the mass quickly, while high viscous resin causes ball formation at the time of blending.

Table 1: Effect of Resin Viscosity on Flexural
Properties of Fibreboard

	1				
Sample	Resin	Flexural	Flexural	Energy to	
	Viscosity	Strength	Modulus	Break (J)	
	(cP)	(MPa)	(GPa)		
Sample -A	200	13.22	1.43	0.95	
Sample -B	250	13.99	1.76	0.99	
Sample -C	300	14.20	1.82	1.02	
Sample -D	400	12.02	1.32	0.92	
Sample -E	500	11.23	1.35	0.92	

cP – Centi Poise; MPa-Mega Pascal; GPa-Giga Pascal; J-Joules

From the table 1, it is apparent that there is an increase in the mechanical properties of the board with increasing in the resin viscosity from 200 to 300(cP) and subsequently there is reduction in the mechanical strength beyond 300cP resin viscosity. High viscous resin could block in the reinforcement mass and subsequently there is non-uniform spreading of the resin. It can also lead to an uneven bonding between fibrous mass and resin that leads to reduction in the mechanical properties'. It is indicated that 300 cP resin viscosity is suitable to make strong fibreboard from jute biomass.

Effect of nature of resin

Ammayappan *et al.* (2016) reported that for medium density fibre boards, both Urea: Formaldehyde and Phenol: Formaldehyde phenol can be used. In order to assess the suitability of the both Urea: Formaldehyde and Phenol: Formaldehyde resin were used to develop fibre board at different concentrations i.e. 7 to 15%. It is apparent that at a board density level of 0.74 g/cc, the binder (Urea Formaldehyde or Phenol Formaldehyde) content of the board should be 12% or more to make the board conform to the BIS specification.

Table 2: Effect of Resin Content of the Board on itsMechanical Properties

Sl.	Resin		Flexural		Flexural		Internal	
No.	Content		Strength		Modulus		Bond	
	(%)		(M	Pa)	(GPa)		Strength	
	(70)		(111	- (1)			(M	Pa)
	UF	PF	UF	PF	UF	PF	UF	PF
1.	7	7	16.73	16.81	1.90	1.96	0.60	0.63
2.	9	9	22.01	23.39	2.14	2.17	0.72	0.76
3.	12	12	28.10	28.63	2.83	2.87	0.91	0.93
4.	15	15	28.26	29.02	2.89	2.91	0.92	0.95

Conclusion

Synthetic resins are materials with a property of interest that is similar to natural plant resins: they are viscous liquids that are capable of hardening permanently. Otherwise, chemically they are very different from the various resinous compounds secreted by plants. These resins are typically manufactured using a chemical polymerization process. This process then results in the creation of polymers that are more stable and homogeneous than naturally occurring resin. Since they are more stable and are cheaper, various forms of synthetic resin are used in a variety of products such as plastics, paints, varnishes, and textiles. There are various kinds of synthetic resins; acetal resins, amino resins, casein resins, epoxy resins, emulsion polymers, hydrocarbon resins, polyamide resins, polyesters rubber resins etc. The classic variety is epoxy resin, manufactured through polymerization, used as a thermoset polymer for adhesives and composites. From this study it is quite evident that that higher resin viscosity causes ball formation with fibrous mass at the time of blending; however resin viscosity of 250 – 300(cP) is found suitable for making fibreboard. 0.75 board density can meet the BIS specification for fiberboards (IS 12406). From this study it is found that the fibreboards need to have a density of 0.74 g/cc and a resin content of about 12% to produce boards conforming to BIS specification and can be exploited further for better economic to the composite board industry.

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