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JUTE AND GLASS FIBER REINFORCED CASHEW NUT SHELL LIQUID (CNSL) – FORMALDEHYDE (NOVOLAK) RESIN COMPOSITES, A STUDY

Anurag L Emanuel[1] Nisarg Prajapati[2] and Vijay Kumar Sinha[2*]

[1]*Bhailalbhai & Bhikabhai Institute of Technology, P.O Box 3, Mota Bazar, Vallabh Vidyanagar-388120, Gujarat, India.*

[2]*Industrial Chemistry Department, V.P. & R.P.T.P. Science College, Vallabh Vidyanagar-388120, Gujarat, India.*

ABSTRACT

Cashew nut shell liquid (CNSL) is a by-product of cashew nut processing industry and is a potential natural alternative to chemically derived phenol. It was reacted with formalin to form Novolak type phenolic resin, which is further used to prepare jute and glass fiber composites. The Novolak resin was characterized by FTIR spectroscopy. The molecular mass was determined by using GPC. Thermal stability was tested using thermogravimetric analysis (TGA). The composites prepared using the Novolak resin as matrix and jute fiber and glass fiber as reinforcing materials were tested for their mechanical and chemical resistance properties. Rockwell hardness, Izod-Impact Strength, flexural strength and flexural modulus and chemical resistance of these composites were compared and studied.

Keywords: CNSL, formalin, jute fiber, glass fiber, composite.

INTRODUCTION

Over the last few decades, there has been considerable development in the field of composite materials. Today, modern composite materials constitute a significant proportion of the engineered materials ranging from everyday products to sophisticated niche applications. Lightweight corrosion resistance materials such as fiber-reinforced composites could provide an important contribution to the safe economical development of resources for structural applications. If renewable resources are used for preparation of composites then it has many added advantages ranging form cost effectiveness to proper management and reduction in industrial wastes and byproducts.

Cashew nut shell liquid (CNSL) a by-product of cashew nut processing industry is essentially a mixture of phenolics extracted from the shells of the cashew nut and is a good natural alternative to chemically derived phenol. The major constituents of CNSL are cardanol, anacardic acid, cardol and 6-methyl cardol [1]. Among these, anacardic acid is the major component of CNSL. Anarcardic acid gets decarboxylated on heating to give cardanol or 3-pentadecadienyl phenol. The side chain containing C15 could be (CH2)14-CH3, (CH2)7-CH=CH-(CH2)5-CH3, (CH2)7-CH=CH-CH2-CH=CH-(CH2)2-CH3 or (CH2)7-CH=CH-CH2-CH=CH-CH2-CH=CH2. Cardanol is a potential renewable source for the synthesis of a variety of specialty polymers. Many patents and reviews have been published on cardanol-based polymers [2].

Cardanol is a phenolic compound having free ortho and para position, which can be used for the manufacture of a large number of phenolic resins for their versatile uses. Alfonso Maffezzoli and co-researchers [3] worked on synthesis, formulation and characterization of a thermosetting resin based on cardanol. This resin was used for fabrication of glass and natural fiber reinforced composites. They concluded that cardanol could be used effectively as a building block for the development of a thermosetting matrix for composite manufacture.

Nayak and Lenka [4] have reported the synthesis and characterization of a large number of resins using

a range of hydroxyl aromatic compounds, viz. formaldehyde/furfural and substituted aromatic compounds in the presence of acids and bases as the catalyst. Resins from natural resources such as CNSL have been successfully used in composite laminates and particleboards manufacture. They have good mechanical and physical properties. Moreover, they are low cost, readily available in abundance and are easy to process [5]. Cashew nut shell liquid has been used in the manufacture of phenolic resins, which finds application in air-drying or stoving enamels

[6, 7]. It also finds application in friction linings, paints and varnishes, surface-coatings, laminates, rubber compounding, cashew cements, polyurethane based polymers, surfactants, foundry chemicals and intermediates for chemical industries [8, 9, 10].

In 2011 Chrissamis and its co. worker reported the process for preparation of phenol formaldehyde resin using CNSL [11]. Mahanwar P.A., Kale D.D., [12] experimentally investigated the effect of replacement of phenol by CNSL on properties of Novolak and Resol resins. Menon et. al. [13] stated the method of production, composition and polymerization characteristics of CNSL as well as general feature of polymeric phenolic products and utilization pattern of CNSL based industrial application. Satyalaxmi stated that cardanol derived from CNSL is used to prepare glass fiber laminates using cardanol, water and succinic acid catalyst having good mechanical property and dimensional stability [14]. Composites fabricated using natural fibers such as jute, coir have potential to be an attractive alternative to synthetic fiber composites such as glass fiber composites.

*Corresponding author: *vijay_sinhain@yahoo.com*

The natural fibers are thermally less stable and absorb atmospheric moisture more compared with synthetic fibers. But, as far as cost is concerned natural fibers have a clear advantage over synthetic fibers [15].

The above literature survey encouraged us to prepare phenol-formaldehyde resin using CNSL as the starting material and use it in fabrication of composites made up of reinforcing materials like jute and glass fiber. Then to carry out a comparative study on mechanical properties of the composites based on reinforcing agents used. The raw CNSL was first examined for its free phenol content [16] and based on this, CNSL-formaldehyde resin was prepared. The resin thus prepared was characterized using FTIR, its molecular mass was determined using GPC and thermal stability of the resin was determined by TGA.

EXPERIMENTAL

Material:

The basic chemicals used for the experimental purpose were of laboratory grade. CNSL procured form Vellow. Chem. Industry, Vitthal Udyognagar, Gujarat was according to Indian standards IS-840-1964. The physical specifications are given in Table: 1. The free phenol content of CNSL was estimated in laboratory [16]. The free phenol available to react with formaldehyde in raw CNSL was found to be 21%. Formaldehyde in the form of 37% formalin was obtained from S.D. fine chemicals. Hexa Methylene Tetra Amine (HMTA), oxalic acid was procured form Merck USA. Solvents and chemicals used for the synthesis purpose were of laboratory grade and were used after routine purification.

Table-1: Specification for untreated CNSL as per IS-840-1964

Sr. No	Properties	Value
1.	Specific gravity, 30°C	0.950-0.970
2.	Viscosity at 30°C, centipoises	550
3.	Moisture content (% by weight)	1.0
4.	Matter soluble in toluene (% by weight)	1.0
5.	Loss in weight on heating (% by weight)	2.0
6.	Ash content (% by weight)	1.0
7.	**Iodine value** Wijis method Catalytic method	 270 375
8.	Polymerization time in minutes	4

Synthesis of resin:

Synthesis of resin was carried out using CNSL and formaldehyde as starting materials with oxalic acid as catalyst. The ratio of free phenol to formaldehyde was kept at 1:0.8 and 0.5% oxalic acid was taken.

The raw material was taken in a round bottom flask equipped with a reflux condenser a thermometer pocket and a mechanical stirrer. The reaction mass was heated slowly and maintained at reflux temperature. Viscosity of the reaction mass steadily increased as the reaction progressed. After 2 hours water formed due to condensation reaction was removed under vacuum. After removal of water the temperature was raised again slowly till it reached 230°C. It was maintained at this temperature until 18"-21" long threads of resin were obtained. The resin at this point was of dark reddish brown color. The mass was cooled down and stored in an airtight container. Formation of resin was confirmed by spectral analysis and its molecular mass was determined by the help of gel permeation chromatography. Further, the resin contained relatively very less amount of water and other volatile matter into it, nearly 12% as confirmed by its thermogram. Upto 380°C the polymer is not decomposed, confirming its high temperature applications.

Preparation of composites:

Composites were prepared using jute and glass fiber as reinforcing agents. For fabrication of composites, Compression molding machine was used. Acetone was used as diluent.

For glass fiber and jute, the composites were prepared by hand lay up technique. 12 ply for glass fiber and 14 plys for jute 10cm wide and 20cm long were stacked one over other after applying resin with brush. The solvent was removed by sun drying and then taken for compression molding. The dried plys were put in between two Teflon release sheets, which were again placed between two steel plates. The whole system was then subjected to compression molding at 170°C and 70 Kg/cm^2 for 30 minutes. HMTA was used as curing agent and the cured composites were cooled under pressure before they were taken out for testing.

Measurements:

All the mechanical and chemical tests of the prepared composites were conducted according to ASTM methods as listed below using five test specimens for each test.

Flexural strength and flexural modulus test:

The flexural strength is the ability of the material to withstand bending forces applied perpendicular to the longitudinal axis. The stress induced due to flexural load is combination of compressive and tensile stresses. ASTM D-790 procedure was used to measure the flexural strength of the composites using Universal Instron testing machine model no.1111. The crosshead speed was 100 mm/min.

For Flexural test, the dimensions were as follows:

- Length = 12 cm
- Width = 2 cm
- Thickness = 0.5 cm for glass and 0.4 cm for jute fiber.
- Support Span = 7.5 cm

Flexural strength = 3PL / 2bd2

Where,

P = Breaking load (Kg)

L = Support span (cm)

b = width of the specimen (cm)

d = thickness of the specimen (cm)

Flexural modulus can be determined by using the following equation:

Flexural modulus = PL3 / 4bd3y

Where,

P = Breaking load (Kg)

L = Support span (cm)

b = width of the specimen (cm)

d = thickness of the specimen (cm)

y = beam deflection (cm)

Hardness testing:

Hardness is defined as resistance of material against permanent deformation. The Rockwell hardness was measured according to ASTM D-785. The sample size was 25mm X 25mm and the hardness was measured using hardness tester TSE testing machine.

Impact testing:

Impact resistance is ability of a material to resist breaking under shock loading or ability to resist the fracture under stress applied at high speed. The impact properties indicate toughness of material. The tests were carried out according to ASTM D 265.

For Izod impact strength the dimensions were as follows:

- Length = 7.5 cm
- Width = 1.25 cm
- Thickness = 0.5 cm for glass and 0.4 cm for jute fiber

Chemical resistance:

ASTM D 543-67 procedure was used to measure the chemical resistance property of the composite specimen.

RESULTS AND DISCUSSION

The results obtained after testing the composites for their mechanical properties are shown in the tables. The results of novolak resin based glass fiber composites are shown in table: 2 and jute fiber composites are shown in Table: 3.

Reaction conditions:

CNSL being a phenolic material reacts with formaldehyde at 90-95°C. The reaction is a condensation polymerization and water is formed as a byproduct. The reaction takes two hrs to complete and viscosity of the reaction mass steadily increases. Water formed and the unreacted formaldehyde if any should be removed from the reaction mass. If not removed excessive foaming occurs which is difficult to control as the temperature is raised above 100°C. Moreover, if unreacted formaldehyde is present then it will result in gelling/curing of the resin. Therefore, water and unreacted formaldehyde should be removed completely before raising the temperature of the reaction mass above 100°C. After complete removal, the temperature is raised to 230°C and maintained until 18"- 20" long resin threads are obtained. During the whole process the reaction mass is continuously stirred to evenly distribute heat.

Resin Analysis and Characterization:

The characterization of resin was done by using Fourier Transform Infrared Spectroscopy (FTIR). IR spectrum of CNSL based Novalak resin is shown in figure-1. The band in the region 3416.45 cm-1 indicates the presence of hydroxyl group. The peaks at 3070 cm-1 and 2920.75 cm-1 are assigned to C-H stretching and Methylene stretching respectively. The peaks at 1580 cm-1 and 1695.01 cm-1 is due to the vibration of the aromatic –C=C– linkages. The peak at 1451.76 cm-1 is due to bending vibration of –CH2. The peak at 1102.71 cm-1 is due to the in plane C-H bending of phenyl ring. The presence of band at 911.68 cm-1 is due to a trans double bond in aliphatic side chains of cardanol moiety. The peak at 719.38 cm-1 is due to the meta substituted aromatic benzene ring.

The molecular weight of the resin was confirmed using GPC (figure-2). The number average (Mn) molecular weight was found to be 3981. The weight average (Mw) molecular weight was found to be 11252. The peak molecular weight PMwt was found to be 12225.

Thermal stability was confirmed by using thermogravimetric analysis. The resin contained relatively very less amount of water and other volatile matter into it, nearly 12% as confirmed by its thermogram (figure-3). Upto 380°C the polymer is not decomposed, confirming its high temperature applications.

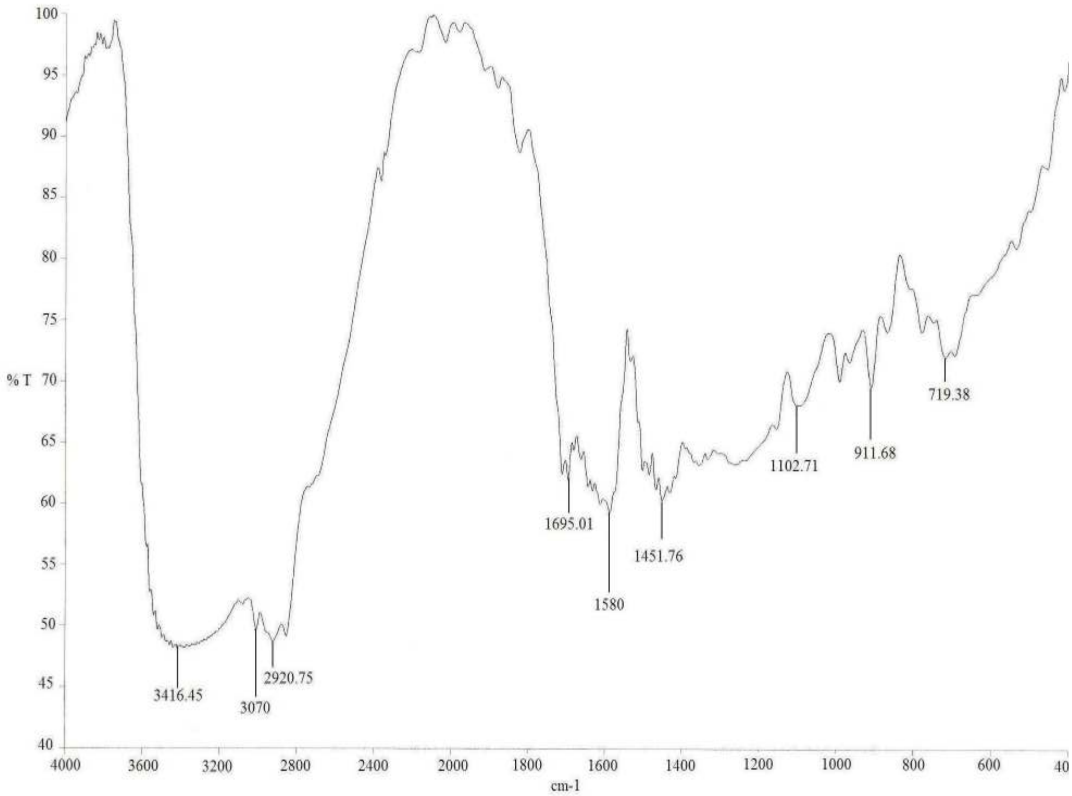
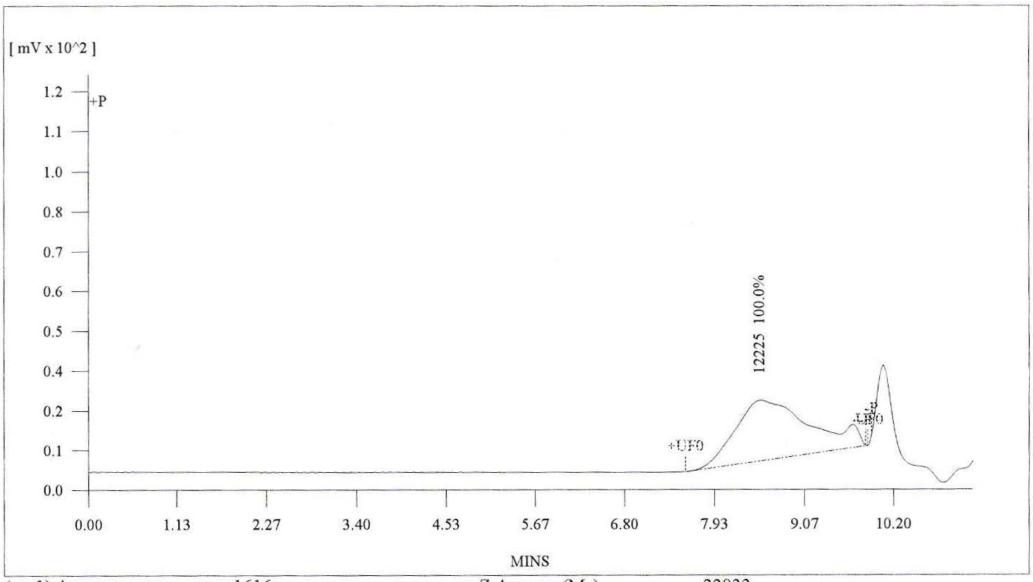


Figure-1: FTIR of Novolak type CNSL-Formaldehyde resin



(n - 1) Average	:	1616	Z Average (Mz)	:	22033
Number Average (Mn)	:	3981	(Z + 1) Average	:	32817
Weight Average (Mw)	:	11252	Viscosity Average (Mv)	:	Not Calculated
PolyDispersity (Mw/Mn)	:	2.826	Total Area	:	1.1772210e+006 (microvolt seconds)

Peak Molecular Weight Report

Peak	Component	RT	Area	%Area	PMwt	Mw	Mn	Mw/Mn	StartMw	EndMw
1		8.493	1177221.0	100.000	12225.0	11252.4	3981.1	2.8265	121118.6	574.5

Figure-2: GPC of Novolak type CNSL-Formaldehyde resin

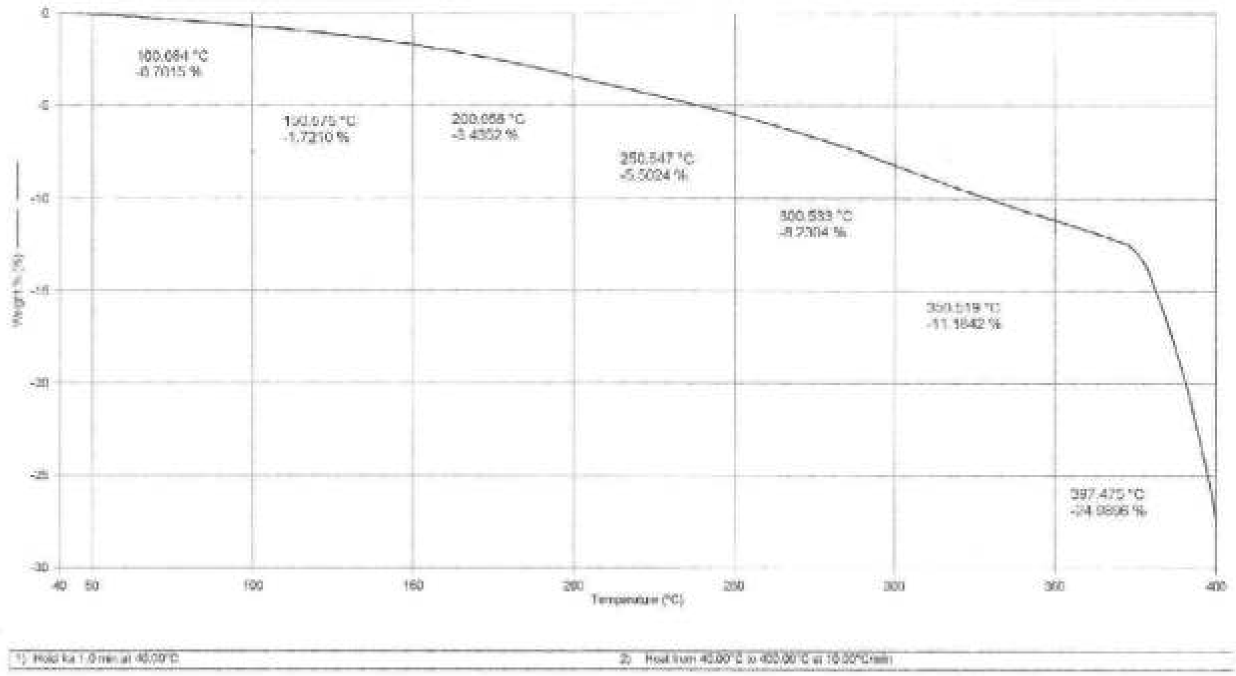


Figure-3: Thermogram of Novolak type CNSL-Formaldehyde resin

Composite testing and comparison:

Here our main aim is to study and compare the properties of the composites prepared using Novolak resin as the matrix and glass fiber and jute fiber as the reinforcing material.

The composites were prepared by varying the ratio between the matrix and the reinforcing material. In this study weight of the reinforcing material was kept constant and weight of matrix was varied. The results obtained are shown in the tables 2 and 3. As percentage of resin was increased, the mechanical properties also improved. At 40%, matrix ratio, glass fiber composites showed competitive results and jute fiber composites showed competitive results at 60% matrix ratio. As the percentage of matrix was increased above this, there was no marked improvement in the mechanical properties and the values were almost the same. The glass fiber composites showed better mechanical properties at lower percentage of matrix. On the other hand, jute fiber composites required higher percentage of matrix. For example, at 20% resin ratio, the jute fiber composites could not be formed and got easily delaminated. This can be attributed to the fact that jute absorbs moisture more and its moisture regain property is quiet high. Being hydrophilic and the matrix, hydrophobic, wetting of the fibers with the resin is poor, for which high resin consumption is required [17], which increases the cost, which to some extent is compensated because of very low cost of jute fiber compared to glass fiber.

Table-2: Mechanical properties of Novolak resin Glass fiber composites at different resin ratios

% Resin	Rockwell hardness	Izod Impact Strength *(joule/cm)*	Flexural Load *(Kg)*	Flexural Strength *(MPa)*	Flexural Modulus *(MPa)*
20%	113	4.38	10.3	44.28	754.77
30%	119	5.35	16.7	60.18	1252.50
40%	121	5.85	22.1	79.56	2983.50
50%	121	5.95	22.7	81.72	3064.50

Table-3: Mechanical properties of Novolak resin Jute fiber composites at different resin ratios

% Resin	Rockwell hardness	Izod Impact Strength *(joule/cm)*	Flexural Load *(Kg)*	Flexural Strength *(MPa)*	Flexural Modulus *(MPa)*
30%	41	2.50	4.10	23.06	450.43
40%	63	3.35	6.20	34.87	817.37
50%	67	3.80	10.3	57.93	2263.16
60%	68	3.85	11.2	63.00	2460.92
70%	68	3.85	11.5	64.68	2526.85

Common organic solvents, water and concentrated mineral acids (25% V/V) did not affect the composites, but the jute fiber composites showed little increase in weight about 0.4% to 1%. When the composites were immersed, in 25% NaOH solution the glass fiber composites remain unaffected but swelling was observed in the jute fiber composites and they gained about 2-2.5% weight. At lower resin ratio marginal swelling was observed in glass fiber composites, but the jute fiber composites got delaminated. Delamination was not observed above 40% resin ratio in case of jute fiber composites when immersed in 25% NaOH solution.

When we compare the mechanical properties of glass fiber with jute fiber composites the results obtained were quiet expected. The glass fiber composites clearly showed their superiority over jute fiber composites in the properties studied in the paper. As we can see from the results obtained that glass fiber composites definitely have better mechanical properties and they showed better hardness, better impact strength and better load bearing capacity than jute fiber composites. However, that is one way of looking at it. Although, the tensile strength and young's modulus of jute fiber is lower than that of glass fibers, the specific modulus of jute fiber is superior to that of glass fiber and when compared on modulus per cost basis, jute is far superior, as reported by one of the researchers [18, 19, 20, 21]. The properties reported by the researcher are as shown in the Table 4. The specific strength per unit cost of jute too approaches that of glass. Therefore where high strength is not a priority, jute may be used fully or partially to replace glass fiber. The need for using jute fibers in place of the traditionally used glass fibers partly or fully as reinforcing agent in composites stems from its lower specific gravity (1.3) and higher specific modulus (42 GPa) of jute compared with those of glass fiber (2.6 and 28 GPa respectively). Apart from much lower cost and renewable nature of jute, much lower energy requirement for the production of jute makes it attractive as a reinforcing fiber in manufacturing composites.

Table-4: Jute fibers and E-glass fibers properties (properties as reported by various researchers [18, 19, 20, 21])

Property	Glass fiber	Jute fiber
Specific Gravity	2.6	1.3
Tensile Strength *(MPa)*	2000	393-773
E-modulus *(GPa)*	76	26.5
Specific strength *(MPa)*	1360	340
Specific modulus *(GPa)*	28.8	42.7
Elongation at failure %	2.6	1.5-1.8
Moisture Absorption %	--	12
Cellulose/lignin %	--	63-70 /12

CONCLUSION

Novolak type resins, can be prepared using Cashew nut shell liquid (CNSL) and formaldehyde by using similar procedure as to prepare phenolic resins. CNSL-formaldehyde resin can be used to prepare composites having competitive mechanical properties. Glass fiber composites have better mechanical and chemical properties than jute fiber composites. But, in low-tech applications where high strength and stiffness is not the major concern jute fiber composite can replace synthetic fibers such as glass fibers and there by reducing the cost and making it more economical.

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