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A study on jute and glass fiber reinforced cashew nut shell liquid (resol) resin composites

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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 Resol type phenolic resin which is further used to prepare jute and glass fiber composites. Resol resin was characterized by FTIR spectroscopy. The molecular mass was determined by using GPC. The composites prepared using the Resol resin as matrix and glass fiber and jute fiber as reinforcing agents, were tested for their mechanical properties and chemical resistance. Rockwell hardness, Izod-Impact Strength, flexural strength and flexural modulus and chemical resistance of these composites were compared and studied.

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KEYWORDS

CNSL;
Formalin;
Jute fiber;
Glass fiber;
Composite.

INTRODUCTUION

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 from cost effectiveness to proper management and reduction in indus-

trial wastes and byproducts.

Cashew nut shell liquid (CNSL) is a by-product of cashew nut processing industry. CNSL 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^[1,2]. Among these, anacardic acid is the major component of CNSL. Anacardic 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. CNSL is a

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potential renewable monomeric source for the synthesis of a variety of specialty polymers. Many patents and reviews have been published on CNSL based polymers^[3].

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^[4] 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 can be used effectively as a building block for the development of a thermosetting matrix for composite manufacture. 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^[8-10].

In 1984, Gunci chemicals industry Co.Ltd., patented the process for preparation of phenol formaldehyde resin using CNSL^[11]. P.A.Mahanwar, D.D.Kale,^[12] experimentally investigated the effect of replacement of phenol by CNSL on properties of Novalak 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. Sathyalakshmi stated that cardanol derived from CNSL is used to prepare fast curing phenolic resin by reacting cardanol, formaldehyde and adipic acid catalyst^[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. 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 ad-

vantage 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 agents 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 and its molecular mass was determined using GPC.

EXPERIMENTAL

Material

The basic chemicals used for the experimental purpose were of laboratory grade. Raw CNSL procured from Vellow. Chem. Industry, Vitthal Udyognagar, Gujarat, was according to Indian standards IS-840-1964. The specifications are given in TABLE 1. The free phenol content of CNSL was estimated in laboratory^[25]. 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. Liquor ammonia was used as catalyst. Solvents and chemicals used for the synthesis purpose were of laboratory grade and were used after routine purification.

Synthesis of resin

Synthesis of Resol type resin was carried out using CNSL, formaldehyde as starting materials and liquor ammonia as catalyst. The ratio of free phenol and form-

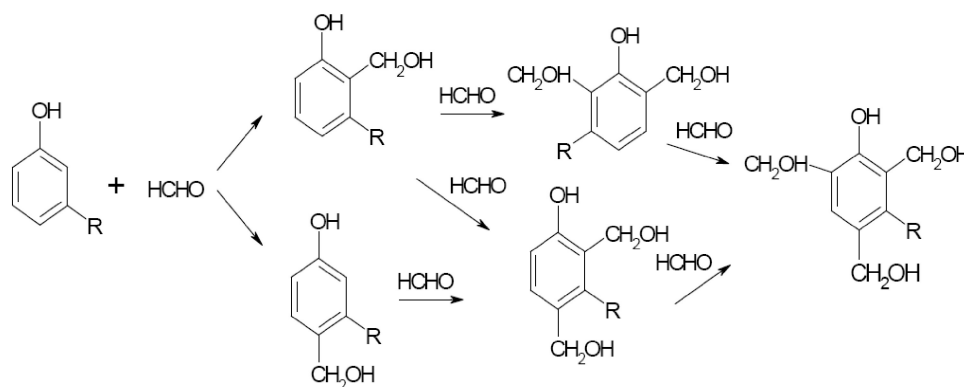
TABLE 1 : Specification for untreated CNSL as per IS-840-1964

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
	Iodine value	
7.	Wijis method	270
	Catalytic method	375
8.	Polymerization time in minutes	4

aldehyde was kept 0.8:1 and 5% liquor ammonia 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

complete removal, the temperature was again raised slowly until 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 (FTIR) and the molecular mass was determined by the help of gel-permeation chromatography (GPC).



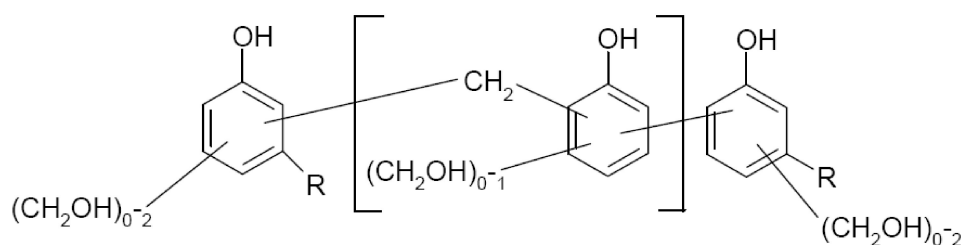
Reaction scheme

The Cardanol is CNSL which is essentially a phenol will take part in the reaction. The condensation reaction of Cardanol with formaldehyde using base catalyst will initially give a mixture of o- and p-methylol Cardanol, which being more reactive than cardanol will result in formation of di- and trimethylol derivatives.

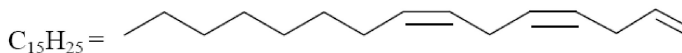
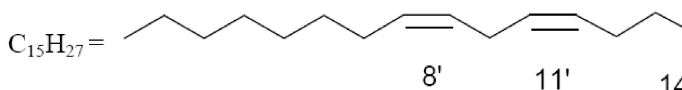
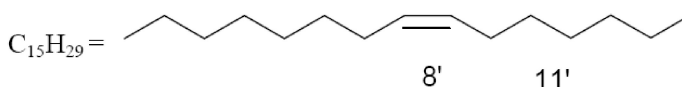
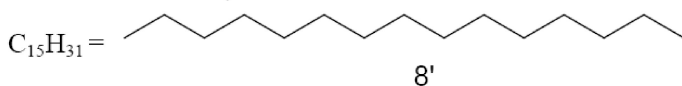
The methylol groups undergo self-condensation to

form polynuclear compounds in which phenolic nuclei are linked by methylene groups. The product obtained by the condensation reaction of Cardanol with formaldehyde using base catalyst will give a complex mixture of mono and polynuclear Cardanol with methylene bridges. The structure of such a component can be represented as:

Preparation of composites



Where R stands for,



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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 10 plies 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 plies 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. The temperature was kept 190°C for 1 hour and the pressure of 70 Kg/cm² was applied. The resin got heat cured. It was then cooled under pressure before they were taken out for testing. The jute fiber reinforced composites were 0.4 cm (4 mm) thick and the glass fiber reinforced composites were 0.5 cm (5 mm).

Measurements

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 = 120 mm

Width = 12.5 mm

Thickness = 0.5 mm for glass fiber and 0.4 mm for jute fiber composites

Support Span = 75 mm

Flexural strength = $3PL / 2bd^2$

Where,

P = Breaking load (Kg)

L = Support span (mm)

b = width of the specimen (mm)

d = thickness of the specimen (mm)

Flexural modulus can be determined by using the following equation:

Flexural modulus = $PL^3 / 4bd^3y$

Where,

P = Breaking load (Kg)

L = Support span (mm)

b = width of the specimen (mm)

d = thickness of the specimen (mm)

y = beam deflection (mm)

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 = 60 mm

Width = 12.5 mm

Thickness = 0.5 mm for glass fiber and 0.4 mm for jute fiber composites

Chemical resistance

ASTM D 543-67 procedure was used to measure the chemical resistance property of the composite specimen. The test specimen were immersed for 7 days at room temperature i.e. 35°C. After seven days weight gain, swelling, delamination etc. were observed.

RESULTS AND DISCUSSION

The results obtained after testing the composites for their mechanical properties are shown in the tables. The results of Resol resin based sawdust composites are shown in TABLE 2 and wood flake composites are shown in TABLE 3.

Reaction conditions

CNSL being a phenolic material reacts with form-

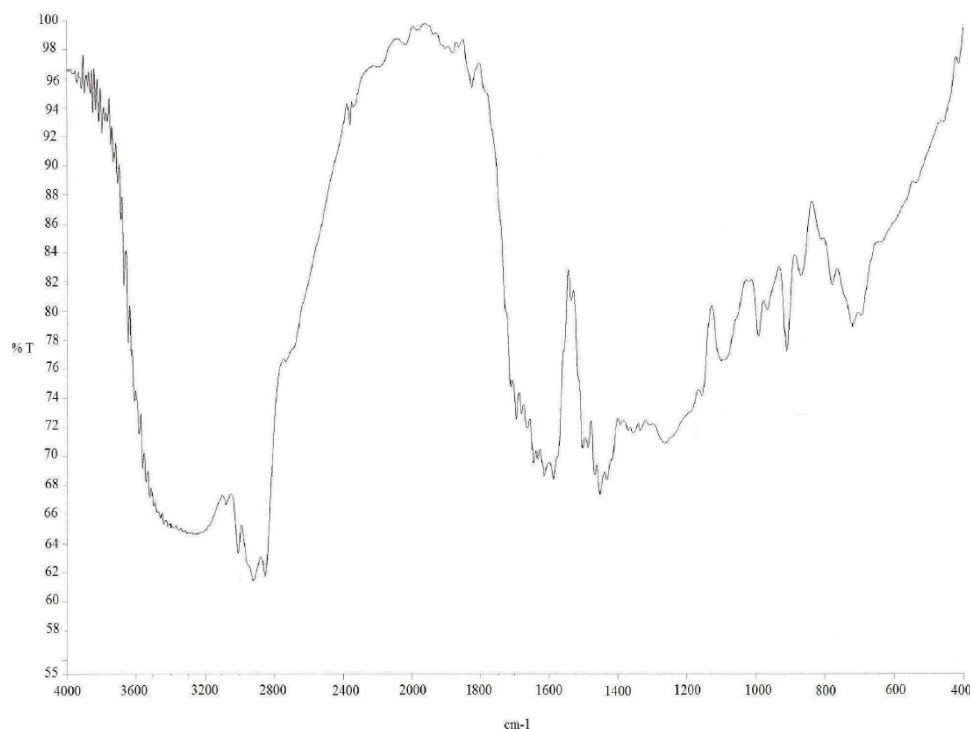


Figure 1 : IR spectrum of resol type CNSL-Formaldehyde resin

aldehyde 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 as the temperature is raised especially in Resol type 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 again raised to 230°C and maintained until 18"- 20" long resin threads are obtained. During the whole process the reaction mass should be continuously stirred to evenly distribute heat. If not done, it will result in localized heating and reaction mass will start bumping, finally resulting in gelling of the reaction mass.

Resin analysis

The characterization of resin was done by using Fourier Transform Infrared Spectroscopy (FTIR). IR spectrum of CNSL based Resol resin is shown in Figure 1. The band in the region 3300-3400 cm⁻¹ indicates the

presence of hydroxyl group. The peaks at 3010 cm⁻¹ and 2920 cm⁻¹ are assigned to C-H stretching and Methylene stretching respectively. The peaks at 1587 cm⁻¹ and 1620 cm⁻¹ is due to the vibration of the aromatic -C=C- linkages. The peak at 1452 cm⁻¹ is due to bending vibration of -CH₂. The peak at 1094 cm⁻¹ is due to the in plane C-H bending of phenyl ring. The presence of band at 911 cm⁻¹ is due to a trans double bond in aliphatic side chains of cardanol moiety. The peak at 721 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 3985. The weight average (Mw) molecular weight was found to be 11071. The peak molecular weight PMwt was found to be 12029.

Composite testing and comparison

Here our main aim is to study and compare the properties of the composites prepared using Resol 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 agent. The results obtained are shown in the TABLES 2 and 3.

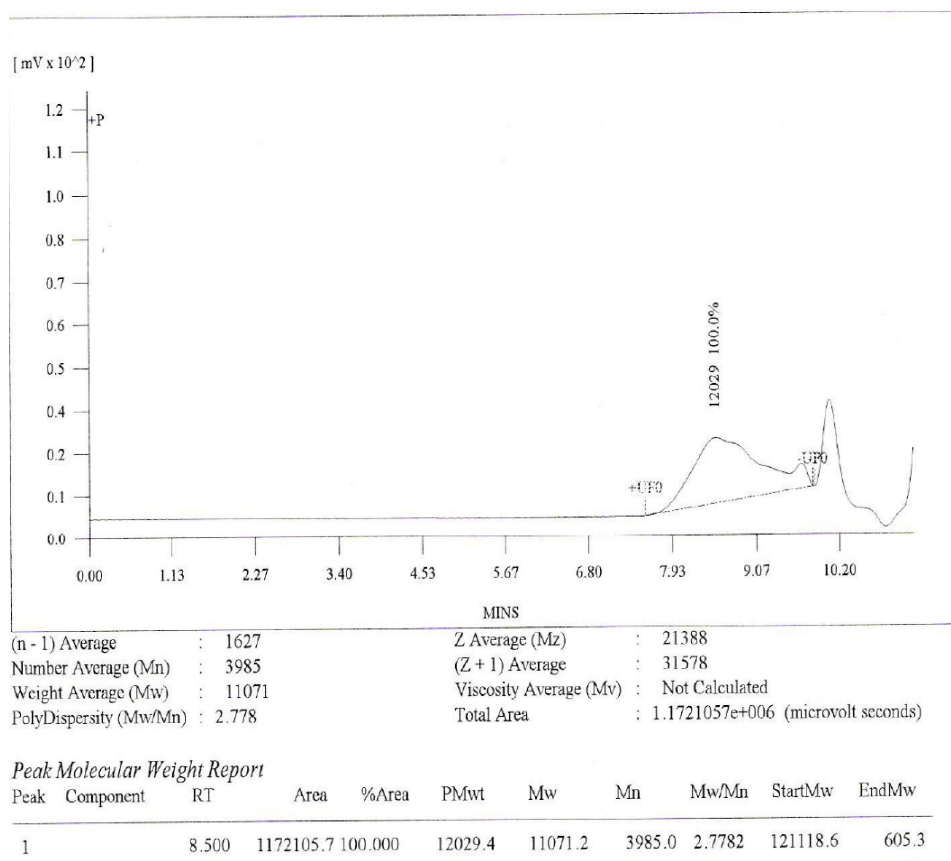


Figure 2 : GPC of resol type CNSL-Formaldehyde resin

TABLE 2 : Mechanical properties of glass fiber reinforced resol resin composites

% Resin	Rockwell hardness	Izod Impact Strength (joule/cm)	Flexural Load (Kg)	Flexural Strength (MPa)	Flexural Modulus (MPa)
20%	113	3.48	10.7	38.52	656.59
30%	115	4.28	14.3	51.48	1072.5
40%	119	4.78	19.9	71.64	2686.5
50%	119	4.82	20.1	72.30	2793.5

TABLE 3 : Mechanical properties of jute fiber reinforced resol resin composites

% Resin	Rockwell hardness	Izod impact Strength (joule/cm)	Flexural Load (Kg)	Flexural Strength (MPa)	Flexural Modulus (MPa)
30%	41	2.00	2.9	16.31	318.60
40%	59	2.68	5.3	29.81	698.72
50%	65	3.04	9.1	51.18	1999.49
60%	67	3.08	10.3	57.93	2263.16
70%	67	3.10	10.6	59.62	2329.10

Here, the weight of the reinforcing agent was kept constant and weight of the matrix (resin) was varied. As percentage of resin was increased, the mechanical properties also improved because binding between the reinforcing agent and matrix improved. At 40%, matrix ratio, glass fiber composites showed the best results

and jute fiber composites showed the best 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. This is because most of the resin above certain ratio was removed as excess resin on compres-

sion molding. 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. This can be attributed to the fact that jute absorbs moisture more and its moisture regain property is quite 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.

Common organic solvents like xylene, toluene, acetone, etc., water and concentrated mineral acids (25% V/V) like HCl, H₂SO₄, HNO₃ did not affect the composites, but the jute fiber composites showed little increase in weight about 1% to 1.5%. 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 3% 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 glass fiber with jute fiber composites the results obtained were quite 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 better chemical resistance. They showed better hardness, better impact strength and better load bearing capacity at low resin to substrate ratio. 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]. 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 re-

place 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 (1.29) and higher specific modulus (40GPa) of jute compared with those of glass fiber (2.5 and 30GPa respectively). Apart from much lower cost and renewable nature of jute, much lower energy re-

TABLE 4: Mechanical properties of glass and jute fiber (The values shown in the table are as reported by researcher^[18,19])

Property	Glass fiber	Jute fiber
Specific Gravity	2.5	1.3
Tensile Strength MN/m ²	3400	442
Young's modulus MN/m ²	72	55.5
Specific strength MN/m ²	1360	340
Specific modulus GN/m ²	28.8	42.7

quirement for the production of jute makes it attractive as a reinforcing fiber in composites.

CONCLUSION

Resol type resins, can be prepared using Cashew nut shell liquid (CNSL) and formaldehyde by using similar procedure as to phenolic resins. CNSL-formaldehyde resin can be used to prepare composites having competitive mechanical properties at low cost. 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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