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Liquefied *Nicotiana tabacum stalks* derived Polyurethane Wood Adhesives as a New Particle Board Adhesive System

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ABSTRACT

Bio-based polyol (ester, ether) are used for the preparation of polyurethane (PU) adhesives, which were synthesized from tobacco stem and nontraditional oil by transesterification reaction. These prepared polyols were reacted with isocyanates adduct to form a PU adhesive, where different NCO/OH ratios were used to give various compositions. The polyols and PUs were characterized by FTIR spectroscopy and further TGA was used for the analysis of thermal properties. The tobacco stem based PU adhesives had comparable or better adhesive properties in terms of lap shear strength than the commercial adhesives. The effect of the NCO/OH ratio on adhesive characteristics on wood bonding was also evaluated by lap shear tests. The change in lap shear strength before and after exposure to cold water, hot water, acid, and alkali were evaluated. The resultant formulated PU adhesive from agricultural waste was comparable to the commercially available adhesive.

Keywords: Adhesive for wood, Lap shearing strength, *Nicotiana tabacum* stalks based polyol, Chemical resistance

INTRODUCTION

Lignocellulosic materials, including agricultural waste and forestry residues are mainly composed of cellulose, hemicelluloses, and lignin [1] which typically contains two or more hydroxyl groups per molecule. These hydroxyl groups provide the sites for reaction in many chemical modification works involving these types of natural polymers, in particular cellulose.

A number of research have been conducted to evaluate the performance of liquefied agricultural waste in varying application such as foam, adhesive, and coating. [2-12]. However, the liquefaction process is typically carried out at prominent temperature and in the presence of an acid catalyst. The liquefied wood and agricultural residue contain depolymerized products from the cellulose and hemicelluloses molecules as well as from low molar mass oligomers [13-15].

With respect to the liquefied agricultural waste, wood and bark at high temperatures and pressures to used solvolysis in glycols [16,17]. Most of these studies had used agricultural waste such as sawdust [18], switch grass [19], straw [20], bagasse [21], banana-bamboo and crop residue [22-24] as a starting material. Since tobacco waste is very much similar to other waste in terms of chemical composition [25], which encourages us to do practices for preparing polyol by liquefying tobacco stem and further utilize in PU application.

According to hypothesis liquefaction of the stem is the first objective of the present attempt by means of what we have a product that contain high reactive hydroxyl group, which has potential to use as precursors in the formulation of PU adhesive.

The properties of polyurethane adhesive produced were analyzed and the adhesive was then applied onto the wood substrate. The glue bond integrity of the bonded wood was evaluated for its shear strength. The chemical resistance of various PU adhesive formulations was also evaluated.

MATERIALS AND METHODS

Material

Tobacco stem was collected from local farm and ground the stem with help of ball-mill up to 20 – 80 mesh was the raw material. p-toluenesulfonic acid (PTSA), (recrystallised before use) and sulfuric acid (S.D. fine chem. Ltd., Mumbai, India) were used as catalyst. Poly Ethylene glycol (S.D. fine chem. Ltd., Mumbai, India) and acetone (Merck, Mumbai, India) were used as glycolysing reagent and as solvent respectively. Double filtered castor oil (having hydroxyl value 165), tobacco seeds oil, and Pongamia glabra oil (karanja oil) as purchased from the local market. All the oils were purified before use by a reported method [26]. The toluene 2, 4-di isocyanate (TDI)-based adduct, containing 13.3% (± 0.4%) free NCO, was supplied by Gads fine chem. ltd, Ahmadabad, Gujarat, India. DBTDL (Merck) was used as catalyst.

Methods

Hydroxyl values and acid values of the polyol were obtained according to the Indian standard methods. The viscosity of the polyols was determined using a Brookfield viscometer (RVT standard, Spindle No. 2 at 100 rpm). The color of the polyols was obtained by using the Gardner color comparator. To study the molecular weight of depolymerized product GPC was performed using Perkin Elmer turbo matrix-40. THF was used as mobile phase at a flow rate of 1 ml/min. IR Spectroscopy of Fourier Transform Infrared (FT-IR) was done to identify the functional groups and chemical bond of prepared polyol using a Perkin Elmer Spectrum GXFTIR spectrophotometer. The infrared spectrum was recorded in the 4000–500 cm^{-1} range. Thermal analysis on the products was performed using Mettler Toledo thermo gravimetric analyzer (TGA) model (TGA/STDA 851e). The weight loss of samples during temperature ranging from 45˚C to 700˚C was measured under nitrogen flow 10 ml/min with a heating rate of 10_C/min. The moisture content was determined by means of a Karl–Fischer titrator. Lap shear strength of adhesives was measured using single-lap shear joints of two wood specimen on Universal Testing Machine (UTM), LR 30 K Plus, Lloyd Instruments Ltd., Hampshire, U K, at pulling rate of 5.0 mm/min.

Pretreatment and glycolysis

Tobacco stem was cut into small pieces, dried in the sun for 24 hour, and ground up to 18-mesh with the help of Boll mill. The resulted powder form mill was refluxing using H_2SO_4 and NaOH (1.25% M/m) for 2.5 hour. Thus resulted purified form of powder used as base material for value added polymeric material.

A three-necked flask equipped with stirrer, nitrogen inlet, a contact thermometer heaving accuracy of ± 0.5ºC, vacuum arrangement, and reflux condenser was charged with 150 ml of polyethylene glycol along with PTSA 0.5% (w/w) as a catalyst. Trace of moisture was removed by heating the mixture to 85ºC in a nitrogen atmosphere and reduced pressure (125 mmHg). 5 g of purified tobacco stems powder was added and the mixture was heated at 145-150ºC for 2.5 hour. (Scheme-1). The remaining catalyst was neutralized with barium hydroxide, and light brown viscous liquid was extracted from the residue with acetone by vacuum filtration using Whattmanfilter paper (No.1). Acetone was distilled under vacuum and un-reacted ethylene glycol was distilled off at 150ºC under reduced pressure of 125 mmHg. Thus the obtained product contained α and β-D glycosidei [16]. The percentage conversion of feed to the glycoside and the color of the obtained product were determined. The glycoside product so obtained was used without further purification to synthesize the polyols.

In order to find the percentage conversion of feed to glycoside, residue obtained after glycolysis was washed with acetone until all the glycoside was extracted from the residue and dried in a vacuum oven for 24 hour, at 70ºC. The dried residue was stored in a desiccator. The percentage conversion (w/w) of feed was calculated according to the following equation.

$$\%\ \text{Conversion (I)} = \frac{(w_0 - w)}{w} \times 100$$

Where W_0 = weight of the initial dry tobacco stem.

W = mass of the residue obtained after the liquefaction.

Synthesis of polyol

A calculated amount of castor oil and 0.6% (w/w) of lithium hydroxide was taken in 500 ml three-necked flask equipped with a nitrogen inlet, contact thermometer, mechanical stirrer, and vacuum arrangement. The heterogeneous mixture was heated to 80°C under reduced pressure of 125 mmHg and required amount of glycoside was added to it. The reaction temperature was raised to 220-230°C and the reaction mixture was stirred at this temperature for 1 hr. (Scheme – 2). Then it was cooled to 90°C and vacuum was released and the obtained polyol was allowed to cool to room temperature. Being hygroscopic in nature, polyol was stored in an airtight container [27].

The ratio of glycoside to oil was varied to obtain polyol of different hydroxyl values. To obtain the required hydroxyl value, greater amount of glycoside was added, which resultantly contributed to decrease in viscosity of polyols. The synthesized polyols were tested for hydroxyl value, acid value, moisture content, NVMs, viscosity, color and specific gravity (Table 1).

Table 1: Physicochemical properties

Sample Coade	Hydroxyl value (mg KOH/gm)	Acid value (mg KOH/gm)	Viscosity (mPa s)(25 ^{0}C)	Moisture (Wt %)	Nonvolatile matter (120 ^{0}C, 1 h) (Wt %)	Colour (gardner)
CAS-1	211	2.31	682	0.5	98.8	17
CAS-2	303	2.03	322	0.2	98.04	17
CAS-3	407	1.93	310	0.1	98.0	18
CT-1	208	2.3	185	0.3	99.2	18
CT-2	306	2.28	171	0.12	99.3	16
CT-3	401	2.5	169	0.2	98.7	18
CK-1	202	2.49	195	0.31	98.01	17
CK-2	298	2.19	187	0.2	98.12	17
CK-3	399	2.3	177	0.15	97.8	18

Wood preparation

As per the ASTM 906 requirements, the teak wood pieces were cut into strips measuring 25 × 300 × 3 mm. They were polished with sandpaper of grit no. 60 (250 mm). Dust was cleaned from the wood samples using a nylon brush and the wood specimens were dried at 110°C for 24 hour before use.

Adhesive Preparation

Adhesive were prepared by using different synthesized polyols. Castor-oil based polyol as well as blends of tobacco-seeds-oil and Pongamia-glabra-oil (karanja oil) with Castor-oil based polyol were used to prepare the adhesives. In a clean dry glass beaker, calculated amount of polyol (based on the hydroxyl equivalent), TDI (based on the NCO equivalent) and catalyst were added to obtain different NCO/OH ratios from 0.8 to 1.9. The content was mixed thoroughly for 1 min and used (Scheme – 2).

Wood bonding and testing

The adhesive solution described above was applied with a brush to both pieces of wood to a thickness of 0.1 mm. (heaving less than 1% moisture). The two coated pieces of wood were placed together to form an area of overlap measuring 25 × 30 mm^2. A load of about 1 kg was placed on the joint and kept there for 24 hour. The joints obtained with adhesives of different NCO/OH ratio were cured at ambient temperature for 1–10 days (Relative Humidity: 50% 74%). The bonded wood joints were tested for lap shear strength using universal testing machine (with pulling rate 5.0 mm/min and error of 72.0 MPa) as per ASTM D 906 and based on the experience of different types of failure obtained in wood adhesives the locus of failure was determined by manual observation as shown (Figure 1). Five experimental determination of beach specimen were repeated and the results were averaged.

RESULTS AND DISCUSSIONS

Glycolysis

p-Toluenesulfonic acid (PTSA) used as a catalyst for glycolysis gave better results compared to sulfuric acid. The yield of glycoside was 94% when PTSA was used but it reduced to 80% when sulfuric acid was taken as a catalyst. Sulfuric acid also suffered the disadvantage of lower yield, because the decomposition of cellulose in the feed was fast when sulfuric acid was used whereas PTSA gave a good yield even at higher temperatures. Optimum conditions for reaction were 150 min and 150°C resulting in maximum yield. Decrease in conversion was observed with increasing either temperature or time there after because of decomposition of the cellulosic part of the mixture, which ultimately increased the content of decomposed solid in the form of residue.

Characteristic data of viscous polyols

The physicochemical characteristics of the obtained product were evaluated in the sense of, the hydroxyl number (I_{OH}) that is running between 200 to 400. The acid value less than 2.5 for all the prepare polyols. Light brownish yellow-to brown-coloured polyols were obtained having non-volatile matter content higher than 98% by weight (Table 1). A sudden decrease in viscosity observed in some polyols may be attributed to the resulting long and semi-cross-linked structure in polyol. A polyol having a lower amount of glycoside added to the oil so as to control the hydroxyl value results in more crosslinking of the fatty-acid chain. On the other hand, increasing the hydroxyl value requires more glycoside to be added which results in hindrance of the cross linking and more amount of fatty chain gets reacted to hydroxyl of glycoside which in turn results in long and semi-cross-linked structure ultimately decreasing the viscosity of polyol.

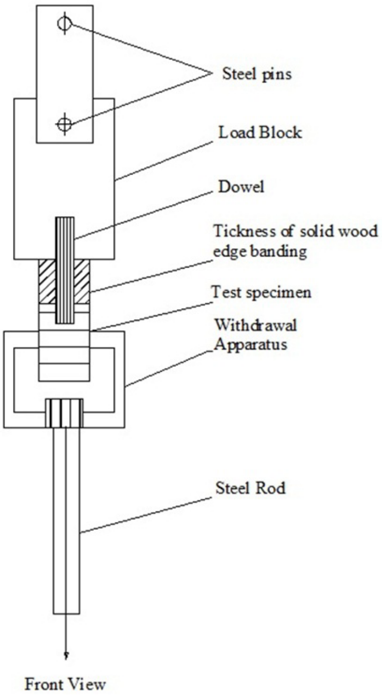

Figure 1: Universal testing machine.

Influence of NCO/OH ratio on adhesive performance

A calculated amount of hydroxyl equivalent of polyol, and isocyanate are mixed with each other to avoid free hydroxyl or isocyanate groups. The lap shear test results for this series are presented in Table 2. Increasing the ratio up to 1.3 showed an increase in bond strength which decreased after the ratio of 1.4. This may be attributed to the chemical bond between any free NCO in the adhesive and the substrate surface. A lower NCO/OH ratio utilizes all of the isocyanate which does not leave enough free isocyanate to react with wood; on the other hand, excess of isocyanates penetrates in wood top layer which results in more strength of adhesive bond as compare to the substrate which in turn results in the substrate failure.

Table 2: Effect of NCO/OH ratio on adhesion

NCO/OH ratio	Avg. lap shear strength MN/m2(±2)	Locus of Failure
0.8	18	CF
1.2	27	CF
1.1	33.6	CF+AF
1.3	37.3	CF+AF
1.4	37.3	CF+AF
1.5	31	SF
1.6	23	AF

Effect of hydroxyl value on adhesive

Strength of adhesive was found to increase linearly with increase in hydroxyl content of the polyol Table 3. As the hydroxyl content of the polyol was increased, the reactive sites available to the isocyanate also increased resulting into increase in crosslinking density of the prepared PU adhesive which gave more compact network structure formation to the adhesive. Table 4 shows the adhesion strength of adhesives produced from castor-oil-based polyols and blend of castor-oil-polyol with tobacco- seed-oil-polyol and Pongamia-glabra-oil polyol. As the hydroxyl content of castor oil increased from 200 to 400, the adhesive strength increased from 25 to 43.5 MPa. The results also indicate that the adhesives produced from blends of castor-oil polyol and other two polyols, showed the same trend of increase in strength. Locus of failure of adhesives from hydroxyl value up to 300 was cohesive or mixed (cohesive adhesion failure). The hydroxyl value 400 heaving resulted in adhesion failure due to higher amount of cured polymer which increased the attraction between the adhesive material as compare to the attraction between adhesive and wood.

Table 3: Strength of different polyol-based adhesives

Hydroxyl value	Average lap shear strength (N/m^{2}x 10^6)	Failure mode
CAS polyols		
200	21.22	CF
300	33.89	CF+AF
400	43.2	AF
CT polyols		
300	40	CF
400	29	CF+AF
CK polyols		
300	29	CF
400	25.8	CF

CAS: Castor oil based polyols
CT: Blend of castor-oil-polyol with tobacco- seed-oil-polyol
CK: blend of castor-oil-polyol with Pongamia-glabra-oil polyol (karanja oil).

Table 4: Lap shear strength of adhesives

Sample Code	Avg. lap shear strength MN/m2(±2)	Locus of Failure
CAS-1	25	CF
CAS-2	34	CF+AF
CAS-3	43.2	AF
CT-1	34	CF
CT-2	41	CF+AF
CT-3	28	CF+AF
CK-1	31	CF
CK-2	29	CF
CK-3	26	CF

Gel time

(Table 5) shows the gel times of various adhesive formulations, or pot life, is important for an adhesive system from the point of view of its application. Gel time is the maximum length of time the system remains in sufficiently fluid condition to be applied to a substrate.

Table 5: Gel time.

Adhesive	Gel Time (min)
CAS-1	46
CAS-2	37
CAS-3	25
CT-1	49
CT-2	44
CT-3	35
CK-1	52
CK-2	43
CK-3	34

Chemical resistance

The chemical resistance of prepared adhesives before and after treatment with acid, alkali, cold water and hot water shows in (Table 6). Adhesives were having well resistant against water and moderate resistance to acid. Adhesive strength decreased after treating specimens with alkali due to the effect of alkali on lignin of the wood substrate. During the alkali treatment lignin from wood got dissolved with alkali which caused uneven contact of adhesive surface with substrate and also loosening of the chemical interlocking between wood and adhesive resulting in bond weakening.

Table 6: Lap shear strength of different adhesives after soaking in chemicals

Sample Code	**Lap shear strength (MN/m^2(± 2) (before)**	**After treatment lap shear strength (MN/m^2(± 2))**			
		After acid treatment (1N HCl)	**After alkali treatment (1N NaOH)**	**After treatment with cold water (20–25 1^0C)**	**After treatment with hot water (80–90 1^0C)**
CAS-1	25	18	10	23	24
CAS-2	34	31	26	33.8	32
CAS-3	43.2	39	32	43.2	42
CT-1	34	29	24	34	33.5
CT-2	41	35	30	41	39
CT-3	28	25	19	25	27
CK-1	31	27	20	30	28.3
CK-2	29	23	17	29	27
CK-3	26	21	14	24	24

Comparison with commercial product

Comparison of one of the prepared adhesives showing the best performance was done with two of the widely used commercially available adhesives in India. As shown in (Table 7) the synthesized PU adhesives had comparable performance than the commercial adhesives which showed a good possibility to use synthesized adhesive in place of other available adhesives.

Table 7: Comparison with other adhesives

Product name	**Avg.lap shear strength MN/m^2 (± 2)**
Fevicol ™	25×10^5
Araldite ™	30×10^6
Synthesized adhesive	43.2×10^6

Instrumental Analysis

Figure 2 shows the FTIR analysis of adhesive prepared from castor oil based polyols, blend of castor and tobacco seed oil based polyol Figure 3 and castor and Pongamia-glabra-oil based polyol Figure 4. Broad absorption band around 3387 cm^{-1} is due to urethane NH linkage. Bands relative to 2857 cm^{-1} and 2927 cm^{-1} are due to alkyl C – H stretching of soft segment (fatty chain) of the polymer. Splitting of band at 1723 cm^{-1} indicates the H – bonded and non H – bonded carbonyl groups which overlap to give an asymmetrical absorption band. Band relative to 1064 cm^{-1} is attributed to C – N and bands at around 1544 and 1600 shows the conjugated double bonds of aromatic ring of the hard segment confirming the reaction of polyol with TDI. Thermo gravimetric analysis of prepared adhesives (Figure 5 and 6) showed almost identical thermal properties after their curing periods. TGA curve of adhesive obtained from CAS 300 and one of the blends (CT 2) has been shown. The obtained curves show that the samples were thermally stable until 100ºC and decomposition was observed at temperature of 110 ºC. Rapid weight loss was noted in decomposition step in range temperature 100-300°C with 86% decomposition. The second weight loss occurred in range 300-500ºC with lower amount of 11% decomposition. A first weight loss is detected around 45-100ºC, which is associated to the loss of volatile solvents and humidity. The second and most important weight loss is located at 100-150 ºC, consistent with the degradation of the adhesive. Furthermore, the weight loss also observed between 300 and 500ºC correlates with the degradation of adhesive.

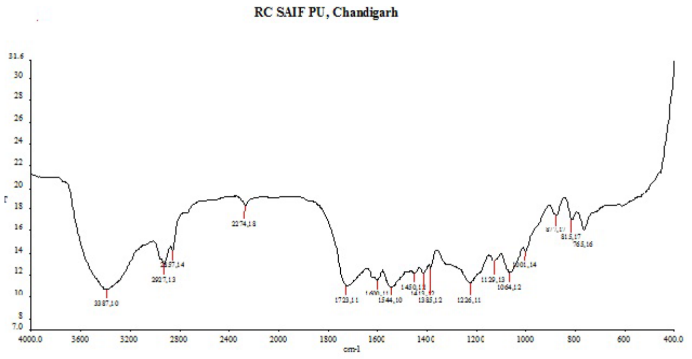

Figure 2: FTIR spectra of adhesives prepared from castor-oil-based polyol.

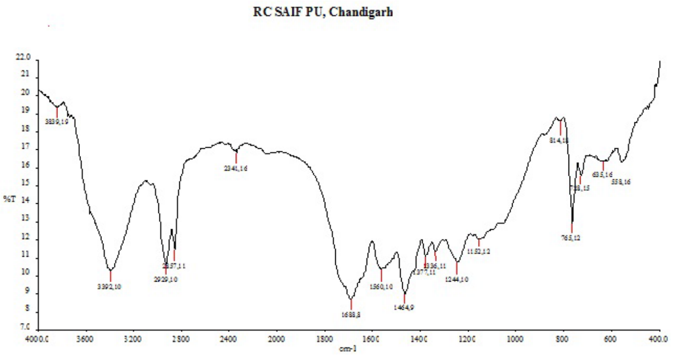

Figure 3: FTIR spectrum of adhesives prepared from blend of castor and tobacco seed oil -based polyol.

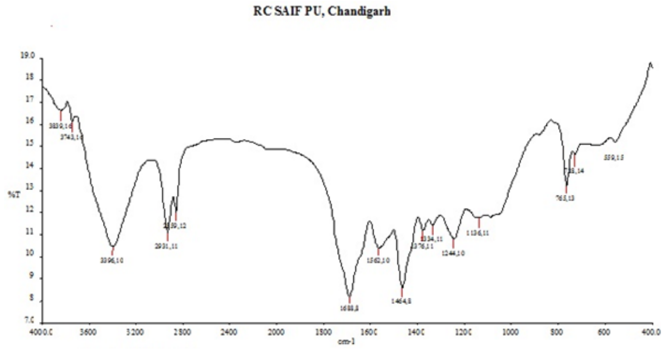

Figure 4: FTIR spectrum of adhesives prepared from blend of castor and Pongamia glabra oil (karanja oil)-based polyol.

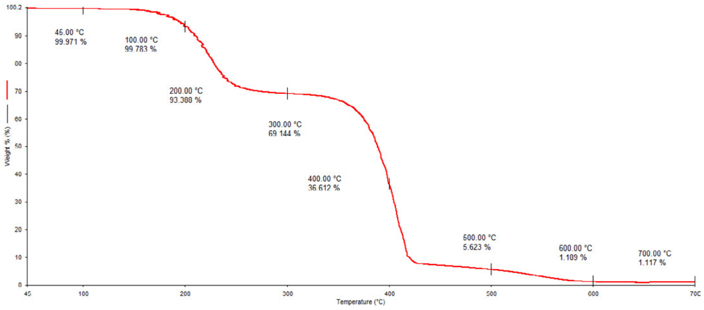

Figure 5: TGA for CAS 300.

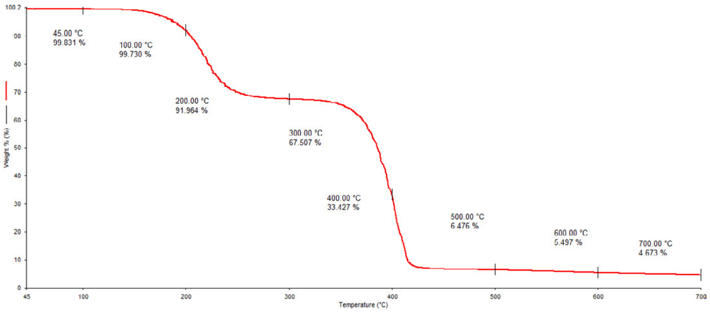

Figure 6: TGA for CT 2.

CONCLUSION

The prepared adhesive shows the comparable adhesive strength with commercially available adhesives used for wood joint. For the prepared adhesive, NCO/OH ratio of 1.3 and gel time of was found to be optimum in terms of adhesive joint strength and a linear increase in adhesive strength was found with increase in hydroxyl value of the polyol. The polyurethane adhesive prepared by us has good resistance to cold and hot water, moderate resistance to acids and weak resistance to alkali. The added advantage of the prepared adhesive was its synthesis from renewable resource, utilization of agricultural waste and possible economically viable production at industrial level.

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