Polyurethane adhesive system from biomaterial-based polyol for bonding wood

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Abstract

Polyester polyols for use in the preparation of polyurethane (PU) adhesives were synthesized from potato starch and natural oils by a transesterification reaction. These polyester polyols were combined with an aromatic adduct based on toluene 2,4-diisocyanate to form a PU adhesive. Both the polyols and the PU adhesives were characterized by means of FTIR spectroscopy. The adhesive performance of the PU adhesives in bonding wood was evaluated by lap shear tests. The effect on adhesion of variation of NCO/OH ratio and hydroxyl value were studied. The change in lap shear strength before and after exposure to cold water, hot water, acid, and alkali were evaluated. Development of bond strength to wood was determined by means of tests at regular intervals, and also curing time required for different adhesive formulations were determined. The PU adhesive derived from natural products was found superior to the commercially available adhesive.
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1. Introduction

The performance and behavior of adhesive systems for wood depend on a wide range of variables, such as smoothness of substrate surfaces, pH, presence of extractives, and amount of debris [1]. The bonding mechanism of the adhesive to the wood substrate can include covalent bonding, weaker forces such as van der Waals forces and hydrogen bonding, or mechanical interlocking [2,3].

Adhesives based on urea–formaldehyde and phenol–formaldehyde are commonly used [4–6], but are very sensitive to hydrolysis [7,8] and stress scission [9]. These adhesives also produce health hazards because of the formaldehyde they release [10]. To overcome such problems, scientists are trying to develop new polymeric adhesives [11,12]. Polyurethane (PU) is a class of polymer that is used in coatings, elastomeric items, foams and adhesives [13]. PU adhesive has developed a reputation for reliability and high performance [14]. Its applications include footwear, packaging, automotive components, and furniture assembly [13]. Properties of PU adhesives can be tailor-made to fit the application due to the great variety in raw materials that can be used to formulate PUs [15].

Although for many years researchers have been trying to develop PU coatings [16] and interpenetrating networks from oils [17], many different types of PUs have been made from synthetic chemicals [18,19]. In our laboratory, an attempt has been made to develop a PU adhesive that is at least partially made from the natural materials potato starch and edible or non-edible, plant-derived oils. Because the hydroxyl functionality of the polyol plays an important role in the formation of PU adhesives, polyols having different hydroxyl values were prepared. This was done by means of glycosylation of starch, followed by transesterification with oil to yield polyol. The NCO/OH ratio and the hydroxyl values were varied, and the influence of these two factors on adhesive characteristics for wood bonding was studied. Lap shear strength was measured and the development of adhesive bond strength was determined as a function of regular time intervals up to maximum strength. Chemical resistance of various PU adhesive formulations was also evaluated.

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2. Experimental

### 2.1. Materials and methods

Starch was extracted from potatoes and freed from amylopectins by means of extraction with toluene [20]. Argemone oil was extracted from seeds in a Soxhlet apparatus with hexane as solvent. Castor oil was purchased from the local market. Both the oils were purified before use by a reported method [21]. The toluene 2,4-diisocyanate (TDI)-based adduct, containing 13.5% free NCO, was supplied by Marigold Coatings Pvt. Ltd., Vithhal Udyognagar, Gujarat, India. The chemicals and solvents used in the synthesis work were of laboratory reagent grade.

2.2. Glycosylation of starch

300 milliliter of ethylene glycol and 0.5% (w/w) sulfuric acid were mixed in a three-necked flask equipped with a stirrer, thermometer well, nitrogen inlet, and vacuum line. The mixture was heated with constant stirring at 80°C under nitrogen atmosphere and reduced pressure (125 mmHg) to remove traces of water. Then 10 g of starch was added and the mixture was heated at 110–120°C for 1 h. After this, barium hydroxide was added to neutralize the remaining H_2SO_4. The pale yellow, viscous glycol glycoside was separated from the barium sulfate precipitate by filtration. The unreacted ethylene glycol was distilled off at 150°C and reduced pressure of 125 mmHg. The glycol glycoside so prepared, a mixture of α-D glycol glycoside and β-D glycol glycoside [22], was used to synthesize polyols. The yield of product obtained was 270 g. The reaction is shown as Scheme 1.

2.3. Alcoholysis of oil with glycol glycoside

A calculated amount of oil and 1.5 g of lithium hydroxide was placed in a 1-l, three-necked flask. The flask was equipped with nitrogen inlet, thermometer well, and mechanical stirrer. The mixture was heated to 80°C, and the required amount of glycol glycoside was added to it at a reduced pressure of 125 mmHg. The reaction mixture was constantly stirred as the temperature was raised to 210–230°C. The reaction was continued at this temperature for 1 h. Then it was allowed to cool to about 100°C, after which the vacuum was released and the resultant polyol was allowed to cool to room temperature. The reaction is shown as Scheme 2. Both argemone-oil-based polyols and castor-oil-based polyols were synthesized in this way. The polyols thus produced did not require any further purification. Being hygroscopic in nature, they were stored in an airtight container.

Scheme 1.
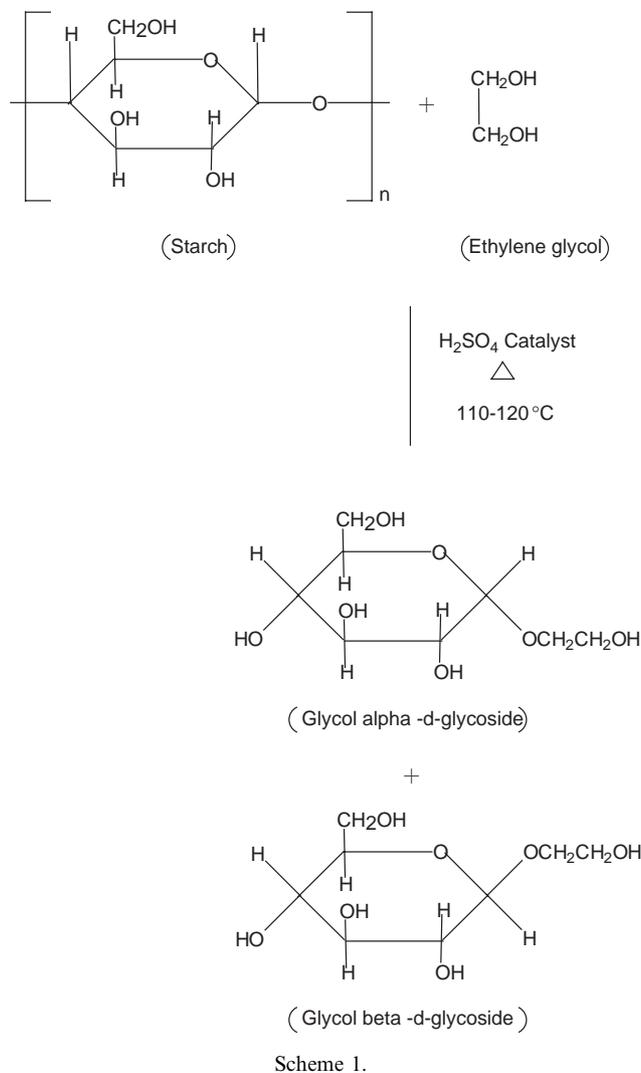
Polyols having varying hydroxyl values were synthesized by varying the ratio of glycol glycoside to oil. Hydroxyl values of the polyols were determined by the acetic anhydride and pyridine method [23]. Table 1 lists the hydroxyl values, acid values, moisture contents and percentages of non-volatile matter for the various polyols synthesized.

2.4. Wood preparation

As per the ASTM 906 requirements, the teak wood pieces were cut into strips measuring $25 \times 300 \times 3$ mm^3. They were polished with sandpaper of grit no. 60 (250 μm).

2.5. Adhesive preparation

The adhesive was prepared in a clean, dry, 150-ml beaker. The TDI-based adduct was added in the required amount to the previously weighed polyol

(Glycol glycoside)

+

(Oil)

LiOH
120-230°C

(Polyol)

+

Scheme 2.

Table 1
Properties of synthesized polyols

Serial no.	Hydroxyl value (mg of KOH/g)	Acid value (mg of KOH/g)	% moisture content	Percentage non-volatile matter (at 120°C for 1 h) (%)
Castor oil-based polyols				
1	200	0.5	0.5	98.6
2	300	0.3	0.2	98.5
3	400	0.9	0.3	97.8
4	500	0.4	0.4	96.5
Argemone oil-based polyols				
1	100	0.8	0.3	97.2
2	200	0.4	0.5	98.0
3	300	0.6	0.4	98.0
4	400	0.3	0.3	97.6

component to give the desired NCO/OH ratio. The mixture was well stirred with a glass rod for about 1 min and was then applied to the surfaces.

2.6. 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. The two coated pieces of wood were placed together to form an area of overlap measuring $25 \times 30 \, \text{mm}^2$. A load of about 1 kg was placed on the joint and kept there for 24 h. After cure, the wood joints were conditioned at room temperature (30°C) and $50\% \pm 5\%$ relative humidity (RH) for 7 days. These wood joints were subjected to lap shear tests on a Zwick Universal Test Machine Model 1445 as per ASTM D 906.

2.7. Determination of effect of NCO/OH ratio on adhesive performance

To determine the effect of NCO content on adhesive performance, TDI-based adducts were mixed with one randomly selected polyol in various proportions. Argemone oil-based polyol with a hydroxyl value of 300 mg

Table 2
Effect of NCO/OH ratio on adhesion

NCO/OH ratio (argemone oil-based polyol with hydroxyl value of 300 mg of KOH/g)	Average lap shear strength $(N/m^2 \times 10^5)$
1.0	34.3 ± 0.8
1.1	38.4 ± 0.9
1.2	41.2 ± 0.4
1.3	50.9 ± 0.4
1.4	48.1 ± 0.4
1.5	48.1 ± 0.5
1.6	44.2 ± 0.3
1.7	41.1 ± 0.5

Table 3
Statistical significance of difference between NCO/OH = 1.3 and other ratios

Comparative ratios	p-value
Ratio 1.3 vs. ratio 1.0	2.59×10^{-12}
Ratio 1.3 vs. ratio 1.1	5.31×10^{-11}
Ratio 1.3 vs. ratio 1.2	1.19×10^{-11}
Ratio 1.3 vs. ratio 1.4	2.61×10^{-07}
Ratio 1.3 vs. ratio 1.5	2.29×10^{-06}
Ratio 1.3 vs. ratio 1.6	5.03×10^{-10}
Ratio 1.3 vs. ratio 1.7	7.30×10^{-12}

of KOH/g was selected for this purpose. The lap shear test results for this series are presented in Table 2. The student *t*-test, appropriate for small sample sizes [24,25] was carried out to evaluate the statistical significance of the difference between the sample with the NCO/OH ratio 1.3 and samples with other ratios. The *p*-values are listed in Table 3.

2.8. Determination of effect of hydroxyl value on adhesive performance

To determine the effect of hydroxyl value on adhesive performance, a series of polyols with different hydroxyl values were made from the oils. For this series, the NCO/OH ratio was held constant at 1.3, the value found to be given the best performance in earlier (Table 2) lap shear tests. The lap shear test results for this series are presented in Table 4.

2.9. Gel time

The gel time, 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. Gel times of various adhesive formulations are shown in Table 5.

Table 4
Lap shear strength of different adhesives

Hydroxyl value	Average lap shear strength $(N/m^2 \times 10^5)$	Mode of failure
Argemone oil-based polyols		
100	30.3 ± 1.4	C + A
200	38.2 ± 0.7	C + A
300	50.9 ± 0.4	A
400	59.8 ± 0.9	A
500	63.1 ± 1.7	S
Castor oil-based polyols		
200	33.3 ± 0.4	C + A
300	45.0 ± 0.8	A
400	56.8 ± 1.0	A
500	61.7 ± 1.2	S

C—Cohesive failure of adhesive.
A—Adhesive failure of adhesive.
S—Failure of wood substrate.

Table 5
Gel time

Hydroxyl value (mg of KOH/g)	Gel time (min)	
	Argemone oil-based polyols	Castor oil-based polyols
100	60	—
200	54	48
300	45	37
400	37	28
500	28	19

2.10. Chemical resistance

Wood pieces bonded with the adhesives prepared from different polyols were immersed in cold water (30°C) for 1 day, after which they were taken out, dried at room temperature (30°C and 50% ± 5% RH) for 1 day, and subjected to lap shear tests. A separate group of bonded wood pieces was immersed in hot water at 100°C for 1 h; another group in water of pH 2 (acid) at 80°C for 1 h; and another group in water of pH 10 (alkali) at 80°C for 1 h [11]. Also, one of the most commonly used (in India) adhesives for wood joints, Fevicol® brand for wood-to-wood bonding, was also analyzed for chemical resistance. After that, the lap shear strength was determined as described earlier. The results are presented in Tables 6 and 7.

2.11. Study of green strength and curing time

Green strength is one of the important aspects for an adhesive, as it shows the ability of an adhesive to hold substrates together when brought into contact and before the adhesive develops ultimate bond properties when fully cured. For evaluation of green strength,

Table 6
Chemical resistance of argemone oil-based adhesives

Hydroxyl value (mg of KOH/g)	Average lap shear strength ($N/m^2 \times 10^5$) (before treatment)	Average lap shear strength ($N/m^2 \times 10^5$) (after treatment)			
		Cold water	Hot water	Acid, pH2	Alkali, pH10
100	30.3 ± 1.4	27.4 ± 1.1	24.5 ± 0.9	12.7 ± 0.6	7.8 ± 0.3
200	38.2 ± 0.7	38.2 ± 0.4	35.2 ± 0.7	20.5 ± 0.5	14.7 ± 0.6
300	50.9 ± 0.4	48.0 ± 0.8	44.1 ± 1.1	29.4 ± 0.6	19.6 ± 0.5
400	59.8 ± 0.9	58.8 ± 1.0	54.9 ± 0.8	39.2 ± 0.4	21.5 ± 0.5
500	63.1 ± 1.7[a]	60.0 ± 1.2	60.7 ± 1.1	47.1 ± 0.3	30.3 ± 0.9

[a] Wood pieces broke down cohesively.

Table 7
Chemical resistance of castor oil-based adhesives

Hydroxyl value (mg of KOH/g)	Average lap shear strength ($N/m^2 \times 10^5$) (before treatment)	Average lap shear strength ($N/m^2 \times 10^5$) (after treatment)			
		Cold water	Hot water	Acid, pH2	Alkali, pH10
200	33.3 ± 0.4	32.3 ± 0.4	29.4 ± 0.6	16.6 ± 0.4	9.8 ± 0.2
300	45.0 ± 0.8	45.0 ± 0.7	40.1 ± 0.8	28.4 ± 0.5	18.6 ± 0.3
400	56.8 ± 1.0	53.9 ± 1.8	49.0 ± 0.4	33.3 ± 0.8	25.4 ± 0.3
500	61.7 ± 1.2[a]	59.5 ± 1.2	57.8 ± 1.2	38.2 ± 0.3	31.3 ± 0.4
Fevicol®	20.2 ± 0.5	16.4 ± 0.3	6.0 ± 0.2	14.3 ± 0.2	12.1 ± 0.4

[a] Wood pieces broke down cohesively.

Table 8
Green strength and curing time

No. of days	Average lap shear strength ($N/m^2 \times 10^5$) (argemone oil-based adhesive)		
	Hydroxyl value 100	Hydroxyl value 300	Hydroxyl value 500
1	9.8 ± 0.5	20.5 ± 0.6	27.4 ± 0.4
2	12.7 ± 0.4	26.4 ± 0.8	37.2 ± 0.3
3	18.3 ± 0.3	27.3 ± 0.7	44.1 ± 0.4
4	22.5 ± 0.3	35.2 ± 0.5	56.8 ± 1.2
5	23.0 ± 0.9	42.7 ± 0.4	60.7 ± 0.9
6	28.4 ± 0.2	47.0 ± 0.6	63.1 ± 1.7[a]
7	30.3 ± 1.1	51.9 ± 0.6	
10	32.3 ± 0.8	50.9 ± 1.4	
13	33.3 ± 0.6	51.9 ± 1.1	
20	33.3 ± 0.9	51.9 ± 0.3	

[a] Wood pieces broke down cohesively.

Table 9
Comparison with other adhesives

Product	Average lap shear strength ($N/m^2 \times 10^5$)
A. Dunlop adhesive	12.0 ± 0.4
B. Fevicol®	20.2 ± 0.7
C. Araldite®	28.3 ± 0.9
D. Synthesized PU adhesive	63.1 ± 1.7[a]

[a] Cohesive failure of wood substrate.

argemone-oil-based polyols with hydroxyl values of 100, 300, and 500 were selected. In this series, the NCO/OH ratio was held constant at 1.3. Specimens were withdrawn and were subjected to lap shear tests at regular intervals (days). The results are presented in Table 8.

2.12. Comparison with commercial adhesives

The best performing PU adhesive synthesized in our laboratory was compared with several commercially available adhesives commonly used for wood bonding. The adhesives used for this comparative study were A = Dunlop adhesive, Dunlop®, India; B = Fevicol®, Pidilite, India; C = Araldite®, Vantico AG, Basle, Switzerland; and D = PU adhesive synthesized in our laboratory. Adhesive D contained the argemone-oil-based polyol with a hydroxyl value of 500. Results are shown in Table 9.

3. Results and discussion

The data from Table 2 show the effect of NCO content on adhesive performance. As NCO content increases, adhesive performance improves up to NCO/OH = 1.3, but decreases thereafter. The small size of the

p-values (Table 3) obtained in the statistical analysis (Student t-test) indicate that the difference in lap shear strength between the sample with NCO/OH = 1.3 and the other samples is statistically significant.

The observed failure modes of samples in this series lead to speculation about the cause of the differences in adhesive performance. The mode of failure found is mainly cohesive at lower NCO/OH ratios (i.e. 1.0, 1.1 and 1.2). This is probably because the less crosslinked structure of PU with lower NCO content tends to fail cohesively within the adhesive material itself. At higher NCO content (i.e. 1.5, 1.6 and 1.7), the excess NCO that gets hardened after curing probably embrittles the adhesive layer of the lap joint, causing a mixed mode of failure (cohesive and adhesive modes on a single specimen). However, at NCO/OH = 1.3, the NCO, even though present in excess, apparently remained well-distributed within the PU to give a crosslinked network having good cohesion as well as good adhesive joint strength.

Thus, NCO/OH 1.3 found to give best bonding strength which is reported low [16] in the oil-based PUs when equivalent amount of NCO is used.

The data in Table 4 show the dependence of lap shear strength on hydroxyl value. Polyols having a hydroxyl value between 100 and 500, synthesized from castor oil and vegetable oil, were used in the adhesive formulation. The trend of increasing lap joint strength with increase in hydroxyl value is clear. At a hydroxyl value of 500, adhesive performance was found to be so good that the wood itself fractured. The observed trend is correlated solely to the crosslinking density in the adhesive. For low hydroxyl values, the polyol cannot crosslink much, and a resulting structure of the PU is poorly crosslinked, leading to a lower adhesive bond strength. On the other hand, a polyol with high hydroxyl value yields a densely crosslinked structure and a correspondingly better adhesive bond strength.

Table 5 shows gel times of different polyols. As expected, polyols with high hydroxyl values are able to form more crosslinks with NCO groups of the isocynate adduct. The formation of more crosslinks during the course of the curing lowers the gel time.

Tables 6 and 7 give an idea of the chemical resistance of PU adhesives. They show good resistance to cold and hot water. Acid decreases adhesive performance to some extent, while alkali has the most detrimental effect on adhesive performance. PU based on highly crosslinked polyester polyol had better chemical resistance than PU based on a less crosslinked structure.

Table 8 shows the correlation between hydroxyl value and green strength. Polyol having a hydroxyl value of 100 reaches 29% of its maximum strength in 1 day, and attains its maximum strength within about 10–13 days. Polyol having a hydroxyl value of 300 reaches 39.6% of its maximum strength in 1 day, and attains its maximum

strength within 7 days. Polyol having a hydroxyl value of 500 gives excellent results within 6 days, which leads to cohesive failure of the wood itself. These results point out that polyols with high hydroxyl values cure rapidly to give high initial and final adhesive bond strength in wood joints. By contrast, polyols with low hydroxyl values take longer to cure.

Table 9 compares the adhesive performance of joints prepared with commercially available adhesives to that of joints prepared with the adhesive synthesized in our laboratory. It was found that the adhesive synthesized in our laboratory had much better adhesive performance than the common commercial adhesives used for wood bonding in India.

4. Conclusions

1. The vegetable oil-based PU adhesive was found to give superior bonding properties to commercially available adhesives used for wood joints.
2. A NCO/OH ratio of 1.3 for the adhesive was found to be optimum in terms of adhesive joint strength. This (30%) excess NCO imparts better strength to the final PU adhesive. Higher NCO/OH ratios (above 1.3) showed reverse effects on adhesive performance.
3. As the hydroxyl value increased, bond strength increased due to formation of a more highly crosslinked structure.
4. The polyurethance adhesive prepared by us has good resistance to cold and hot water, moderate resistance to acids and weak resistance to alkali.
5. Use of polyol with a high hydroxyl value leads to better bond strength in shorter time.

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