

Synthesis and Characterization of Vegetable Oil Based Polyurethane Derived from Low Viscous Bio Aliphatic Isocyanate: Adhesion Strength to Wood-Wood Substrate Bonding

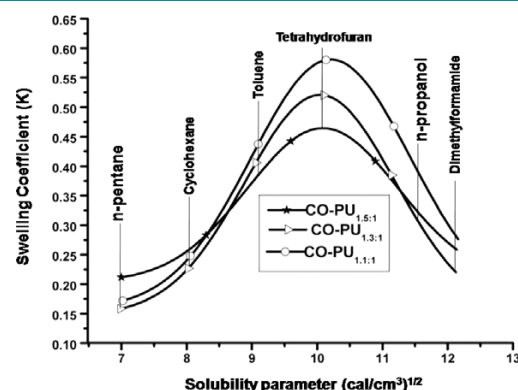
Swarnalata Sahoo^{*,1,2}
Hemjyoti Kalita²
Smita Mohanty^{1,2}
Sanjay Kumar Nayak^{1,2}

¹ Central Institute of Plastic Engineering and Technology (CIPET), Chennai, Tamilnadu, 600032, India
² Laboratory for Advanced Research in Polymeric Materials, LARPM, CIPET, Bhubaneswar, Odisha-751024, India

Received August 22, 2016 / Revised February 18, 2017 / Accepted March 13, 2017

Abstract: In the current study, biobased polyurethane (PU) adhesives at three different stoichiometric ratios of hard (NCO) to soft segment (OH) (1.1:1, 1.3:1, 1.5:1) were prepared by reacting castor oil (CO) based polyol with partially biobased polyisocyanate (PBPI) in the presence of dibutyltin dilaurate (DBTDL) as catalyst. The synthesis of PU adhesive films such as CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} was confirmed by Fourier transform infrared (FTIR) spectroscopy. The effect of stoichiometric ratios on the bonding strength of wood-to-wood substrate was studied using lap shear strength test. The change in lap shear strength of PU adhesive films subjected to acid and alkali solution was tested. The chemical resistance, surface properties and wetting energies of PU adhesive films were evaluated using scanning electron microscopy (SEM) analysis and contact angle measurement. Thermal stability and activation energy of the films were determined employing thermogravimetric analysis (TGA). The experimental result showed that CO-PU_{1.3:1} exhibited higher adhesive strength, whereas CO-PU_{1.5:1} exhibited higher thermal stability.

Keywords: biobased polyurethane, adhesive, activation energy, TGA.



1. Introduction

Synthesis of polyurethane (PU) based adhesive from renewable resources, such as vegetable oils has been one of the major efforts currently being practised world wide as an alternative to the petrochemical resource. Moreover, with increasing environmental awareness and new legislation rules, there have been several attempts to reduce the carbon foot print and improve the sustainability.¹ Commercially, PU based adhesives are synthesized from soft segments polyester/polyether polyol (OH) and hard segments as isocyanate (NCO) at different stoichiometric balance. These adhesive possess excellent adhesion properties, flexibility, high cohesive strength and low temperature performance.^{2,3} One part PU adhesive for different substrates like aluminum, steel and wood has created new possibilities for development of new ecofriendly adhesive system for various applications like packaging, forest products, coatings, automotive, footwear, and adhesive for furniture industry.⁴ Most of the wood adhesives have the downside in terms of their high cost and limited durability.

The formaldehyde and phenol formaldehyde based adhesives have been widely utilized for the bonding of wood substrates. However, these adhesive have inherent drawbacks of high sensitivity to hydrolysis and stress scission. As reported

by many authors, polyacrylate based adhesive are also used for bonding wood substrates.⁵⁻⁷ Several reports pertaining to polyacrylate adhesive displaying shorter pot life, high cost and limited durability have been discussed.⁸ To overcome such issues, in particular to decrease the cost of adhesive and produce highly durable polymeric based adhesive systems, recent focus has been diverted to the synthesis of PU adhesive derived from synthetic polyol and isocyanates.^{9,10} The effect of petroleum products to the environment and the depletion of petroleum have aimed the search for alternative renewable sources for the synthesis of vegetable oil based polyols. The raw materials based on renewable resources such as starch cellulosic wastes,¹¹ agricultural wastes,¹² saw dust¹³ and vegetable oils had been utilized for polyol synthesis. Among these, vegetable oils have advantages for the production of polyol due to its versatilities and technical feasibility. CO is an abundant vegetable oil that can be used for the development of biobased PU due to its inherent triglycerides of hydroxyl fatty acid. The hydroxyl functionality of CO plays an important role in the development of PU adhesives. Hence, CO has been receiving considerable research interest as polyol for the development of green PU adhesive due to its easy availability, low cost and presence of high fatty acid.^{14,15} One of the most important factors that predominates PU synthesis of PU synthesis from castor oil is its inherently high stability under heat and humidity. Furthermore, PU adhesives prepared from castor oil produces superior lap shear strength and easy to handle due to

*Corresponding Author: Swarnalata Sahoo (sahoo.swarnalata@gmail.com)

its adequate viscosity as compared to petroleum based polyols as reported by Silva *et al.*¹⁶ Moreover, PU adhesives are getting more demanding due to its low volatile organic contents, good adhesion property and highly resistant to environment.¹⁷

In the current investigation, the synthesis of PU adhesives at three different stoichiometric ratio (1.1:1, 1.3:1, 1.5:1) were carried out using CO based polyol and biobased PBPI. Subsequently, the formulation of PU adhesive was confirmed using FTIR analysis. Further, the interfacial adhesion between the PU adhesives and wood substrate was studied using lap shear strength test. The chemical resistance of PU adhesives subjected to acid and alkali solution was evaluated using lap shear strength and SEM analysis. The surface properties and wetting energy of PU adhesive films were studied using contact angle measurement. Furthermore, to determine the thermal stability of developed PU adhesive films, TGA analysis was carried out. Additionally, the decomposition activation energy (E_a) of thermal degradation of the films was determined by employing COATS and RED-FERN model.

2. Experimental

2.1. Materials

Partially bio based polyisocyanate (PBPI) (Tolonate TM X FLO 100) was supplied by M/s. Vencorex Chemical, Frances. Castor oil (CO) was purchased from M/s.SD Fine chemicals, Kolkata. The CO was dried at 100 °C for 4 h and the corresponding hydroxyl value (160 mg KOH.g⁻¹) was calculated as per ASTM D standard D-1957. The catalyst dibutyltin dilaurate (DBTDL) was kindly supplied by M/s. Sigma Aldrich, Germany, Chemie GmbH Eschenstrasse, Taufkirchen bei Munchen and was used

as received. Acetone of Analytical Reagent grade was purchased from M/s Mohapatra Scientific, Odisha, India and was used without purification.

2.2. Synthesis method of polyurethane adhesives

Three stoichiometric ratios (NCO/OH) such as 1.1:1, 1.3:1, and 1.5:1 were taken for the synthesis of corresponding PU adhesives viz. CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} respectively. The synthesis was carried out in a three necked flask equipped with a stirrer, reflux condenser, thermometer and nitrogen inlet in which a weighed quantity of CO and PBPI in presence DBTDL catalyst were charged. The reaction process was carried out at 70 °C with continuous stirring for 45-55 min. To achieve an appropriate viscosity, the PU adhesives were diluted with acetone. Further, the solution was casted on a glass plate at room temperature to produce PU adhesive films of thickness 35 μm for further characterization. The complete reaction mechanism is shown in Figure 1.

2.3. Characterizations

2.3.1. Fourier transform infrared analysis (FTIR)

The spectra of PU adhesive films were obtained using FTIR (Nicolet 6700, Thermo Scientific, USA) equipped with omnic software with attenuated total reflectance (ATR) attachment. The analysis was taken on each sample with 64 scans over the wavelength range of 4000 to 400 cm⁻¹.

2.3.2. Lap shear test

The wood substrate was prepared according to the standard ASTM D 906 and polished with sandpaper of grit no. 60. The prepared adhesive solution of approximately thickness 0.1 mm was applied on both pieces of the wood strips using a brush on 25×30 mm² area of overlap. Over the contact area of wood pieces, a load of 2-3 kg was applied and left overnight. Subsequently, the wood joints were kept at room temperature for 10 days strength of wood joint specimens was tested using lap shear strength test. Five replicate samples were taken for each test and the data reported are the average of five.

2.3.3. Scanning electron microscope (SEM) analysis

SEM analysis was conducted to evaluate the morphology of PU adhesive films treated with acid and alkali solution. A comparative account of the films without treatment was also studied. The films were sputter coated with gold and the palladium mixture to make the surface conductive prior to analysis. Further, the films were inserted in into SEM (EVO MA 15, Carl Zeiss, Germany) instrument and the corresponding micrographs were taken for analysis and interpretation.

2.3.4. Contact angle

The contact angle measurement and the wetting energy of all synthesized PU adhesive films with different stoichiometric ratio were performed using Phoenix SEO instrument. The contact angle of PU adhesive films was measured using distilled water as a probe liquid under room temperature.

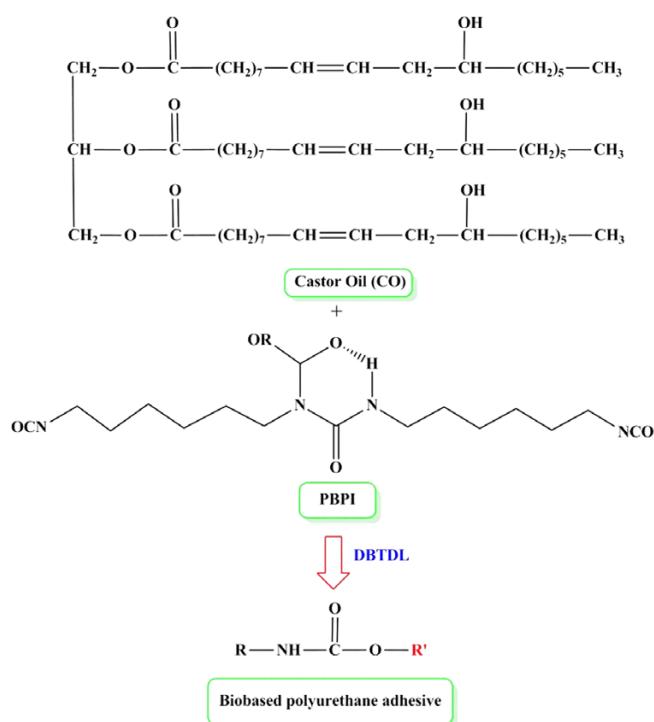


Figure 1. Reaction mechanism of bio based polyurethane adhesive synthesis.

2.3.5. Crosslink density (ν_c) and average molecular weight between two cross link points (M_wC)

Crosslink density (ν_c) and average molecular weight between two crosslinks (M_wC) of all PU adhesives were determined by the equilibrium swelling method using Flory-Rehner Eq. (1).

$$M_wC = \frac{\rho_p \left\{ (\phi_p)^{\frac{1}{3}} - \frac{\phi_p}{2} \right\}}{[\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2]} \quad (1)$$

Where ρ_p indicates the density of the polymer and ϕ_p indicates the volume fraction of the polymer in the swollen state. χ is the polymer solvent interaction parameter.

The polymer solvent interaction parameter can be calculated by using the following equation, $\chi = \beta + \frac{V_s(\delta_p - \delta_s)^2}{RT}$

$$\chi = 0.34 + \frac{V_s(\delta_p - \delta_s)^2}{RT} \quad (2)$$

where, δ_p and δ_s are the solubility parameters of the polymer and solvent respectively in $(\text{cal}/\text{cm}^3)^{1/2}$ and β is the lattice constant whose value is 0.34, V_s is the molar volume of solvent (cm^3/mol), R is the gas constant, 1.983 (cal/molK) and T is the temperature, K.

$$\nu_c = \rho_c / M_wC \quad (3)$$

$$\theta = \frac{1}{2M_wC} \quad (4)$$

where θ is the degree of crosslinking between two points.

$$\text{Volume fraction } \phi = \frac{M_p / \rho_p}{(M_s / \rho_s) + (M_p / \rho_p)} \quad (5)$$

where M_s =mass of solvent in the swollen polymer film at equilibrium (in grams)

M_p =mass of the dry weight of polymer at the initial state (in grams)

ρ_s =density of solvent (g/cm^3)

ρ_p =density of the respective polymer film (g/cm^3).

2.3.6. Thermogravimetric analysis (TGA)

TGA of PU adhesive films was performed under air from room temperature to 600 °C at a heating rate of 10 °C/min analysis using Q50 series of Thermal Analyzer (TA) instrument. Corresponding activation energy (E_a) of each film was calculated by employing COATS and REDFERN method.

3. Results and discussion

3.1. Fourier-transform infrared analysis

The FTIR spectra of synthesized PU adhesive films at three different compositions CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} has been displayed in Figure 2. The occurrence of characteristic band at 2260 cm^{-1} confirmed the presence of unreacted isocyanate group in CO-PU_{1.5:1} film. However the absence of peak at 2260 cm^{-1} in CO-PU_{1.1:1} and CO-PU_{1.3:1} adhesive film confirmed the

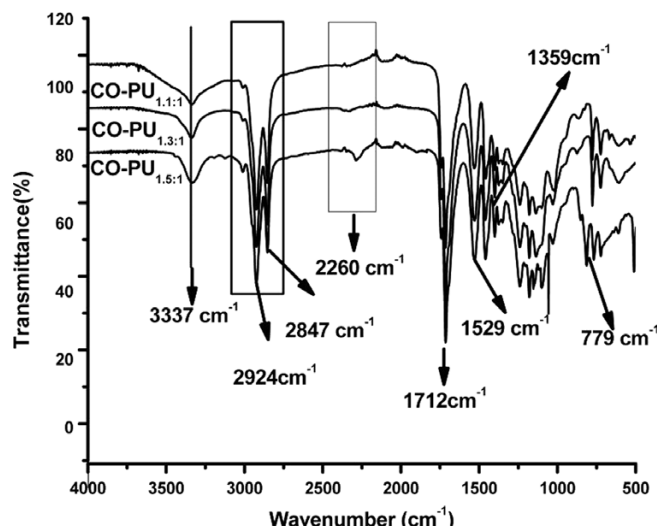


Figure 2. FTIR spectrum of castor oil based polyurethane adhesive films at different ratio of NCO:OH.

fact that isocyanate groups were completely reacted with hydroxyl group. The disappearance of the broad hydroxyl group at 3400 cm^{-1} in all three PU adhesive films showed that the OH group is completely utilized during polymerization which confirms the formation of PU. The band at 1712 cm^{-1} appeared in all three synthesized PU films due to carbonyl stretching. The band at 1529 cm^{-1} observed due to the combination of CN stretching and NH bending and at 1359 cm^{-1} appeared due to -CH bending in alkanes in all PU films. In addition, the peak appeared at 779 cm^{-1} observed due to the presence amide groups. The other characteristic bands at 3337 cm^{-1} and 1575 cm^{-1} were observed due to -NH stretching and bending vibrations in the polymer chain of all three synthesized PU adhesive films.^{18,19} These results confirmed the reaction between castor oil based polyol and partially biobased polyisocyanate.

3.2. Gel time

Gel time and tack free time of polyurethane adhesive films (CO-PU_{1.1:1}, CO-PU_{1.3:1}, CO-PU_{1.5:1}) were studied during the polymerization reaction at constant stirring using a magnetic stirrer in the presence of DBTDL catalyst. The progress of reaction was observed with the measurements of curing parameters such as surface drying time, tack free designation drying time and hard drying time and the corresponding values are summarized in Table 1. The analysis showed that with increasing NCO/OH ratio (1.1:1 to 1.5:1), curing time decreased as well as the reaction became faster. This might be due to the presence of higher NCO content in matrix with higher cross linking reaction. It has been concluded that the surface drying time, tack free designation drying time and hard drying time decreased with increasing stoichiometric ratio by monitoring the reaction condition at which the gelation reaction occurred.¹⁹⁻²¹ Hence, it can be concluded that the adhesive composition CO-PU_{1.5:1} cured faster at a gel time of 30 min and surface drying of 4 h compared to other composition. This might be due to the presence of higher stoichiometric ratio (1.5:1) with higher reactive NCO group. All the samples have a hard drying time of overnight nearly equal to 24 h.

Table 1. Gel time, surface drying time, tack free designation drying time and hard drying time of PU adhesives at different composition

Samples	Different molar ratio	Gel time (min)	Surface drying time (h)	Tack free designation drying time (h)	Hard drying time (h)
CO-PU _{1.1:1}	1.1:1	45	6	8	O/N
CO-PU _{1.3:1}	1.3:1	40	5	6	O/N
CO-PU _{1.5:1}	1.5:1	30	4	5	O/N

3.3. Lap shear test

The lap shear strength of PU adhesives at various compositions is displayed in Table 2. As observed from the table the shear strength of developed PU adhesives CO-PU_{1.1:1}, CO-PU_{1.3:1}, CO-PU_{1.5:1} was determined by lap shear test and was found to be 32, 40 and 19 N/m²×10⁵, respectively. It has been demonstrated that with the increase in NCO content in stoichiometric ratio, the adhesive performance improves up to stoichiometric ratio 1.3:1, but beyond a critical value the stiffness increases with increasing stoichiometric ratio which indicated decrease in the adhesive strength. Hence excellent bonding strength has been found in the stoichiometric ratio of CO-PU_{1.3:1} adhesive while lower bonding strength observed in CO-PU_{1.1:1} and CO-PU_{1.5:1} adhesive as represented in Table 2. This behaviour is primarily due to the presence of strong chemical bonding between any free NCO in the adhesive and the OH groups present in the substrate of wood surface. Similar observation was reported in Patel *et al.*²² Moreover, the lap shear strength of CO-PU_{1.3:1} adhesive was found to be 2–4 times greater than the commercially available adhesives.²³ Hence, it can be concluded that PBPI can be utilized to develop PU adhesives with desirable properties. At a lower stoichiometric ratio based PU adhesive (CO-PU_{1.1:1}) the entire isocyanate group has been utilized which does not leave enough free NCO groups to react with the wood surface. On the other hand, at a higher stoichiometric ratio based polyurethane adhesive (CO-PU_{1.5:1}) excess of isocyanate penetrated within the top layer of wood surface which provides higher strength between the adhesive and the substrate as compared to the strength within the substrate which in turn results in failure.

The variation of lap shear strength of PU adhesives as a function of no. of days is represented in Table 3. As observed from Table, it is evident that the PU adhesives prepared at various compositions show a consistent increase in the shear strength with increase in the duration of exposure for 10 to 40 days beyond which there was no applicable increase in the shear strength. This might be due to the ongoing cross linking process during storage as the acetone gets removed from the films upon increase in the time period. This ability of strength of adhesive to hold the substrates before reaching the ultimate strength of the adhesive is known as the green strength of the polymer.²⁰ Further, the composition at NCO:OH ratio of 1.3:1 exhibited optimum strength as compared with other composition.

Table 2. Lap shear strength of PU adhesives at variable concentration of NCO:OH ratio

NCO/OH ratio	Sample type	Lap shear strength (N/m ² ×10 ⁵)
1.1:1	CO-PU _{1.1:1}	32
1.3:1	CO-PU _{1.3:1}	40
1.5:1	CO-PU _{1.5:1}	19

Table 3. Lap shear strength of PU adhesives as a function of no. of days

No. of days	Lap shear strength (N/m ² ×10 ⁵)		
	CO-PU _{1.1:1}	CO-PU _{1.3:1}	CO-PU _{1.5:1}
10	32	40	19
20	39	50	25
30	47	69	37
40	46	69	37

3.4. Contact angle

The contact angle values have been obtained by the sessile drop method to measure the surface properties of PU adhesives.^{24,25} Distilled water has been used as a probe liquid to drop onto the surface of the PU adhesive films. From the Table 4, it has been found that the contact angle of PU adhesive films at three different stoichiometric ratio slightly increases with the increase in stoichiometric ratio. This might be due to the increased crosslinking density in the system with the increasing stoichiometric ratio. It has also been observed that the value of contact angle slightly increases with decrease in work of adhesion (95.6 to 86.8 J). Wenzel *et al.* have reported that the samples with higher contact angle having lower wetting energy.²⁶ Furthermore, the test results reported in table showed that the PU adhesive film surface is hydrophilic in nature. As wetting energy is the important factor in the adherence of the two materials, it is necessary to observe the wetting energy value which was found to be decreased with the increase in molar ratio of PU adhesive. High wettability on the surface of CO-PU_{1.1:1} has been observed at smaller contact angle of 71.72° which indicated that the fluid spreads over an area for a given fluid volume and low wettability on the surface of CO-PU_{1.5:1} is primarily due to higher contact angle.²⁷

3.5. Swelling and crosslink density of PU adhesive films at various concentrations

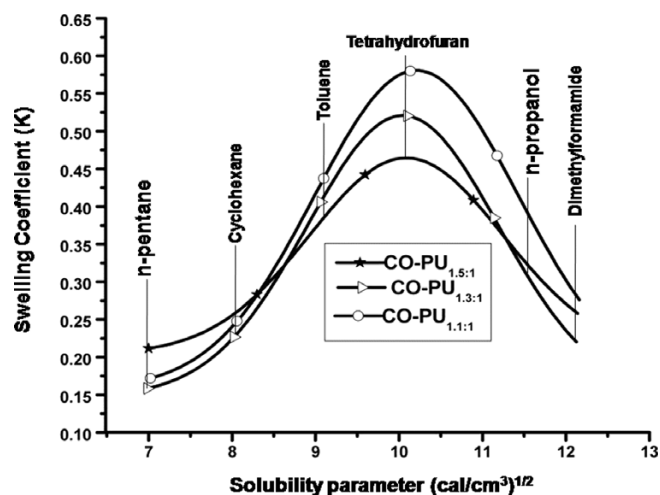
The swelling properties of three synthesized polyurethane adhesive films (CO-PU_{1.1:1}, CO-PU_{1.3:1}, CO-PU_{1.5:1}) were evaluated to determine the parameters such as solubility parameter, swelling coefficient (K), cross linking density (ρ_c), degree of cross linking (ρ_c) and the molecular weight between two cross linking points (M_wC) and the corresponding results are presented in Table 5. To observe the swelling coefficient of the PU, the

Table 4. Contact angle, wetting energy and work of adhesion of PU adhesive films at various concentrations

Samples	CO-PU _{1.1:1}	CO-PU _{1.3:1}	CO-PU _{1.5:1}
Contact angle θ (°)	71.72	73.96	78.84
Wetting energy (J/m ²)	22.83	20.11	14.07
Work of adhesion (J)	95.63	92.9	86.8

Table 5. Molecular weight between cross linking points, degree of cross linking and cross linking density of PU adhesives

Sample type	Density of polymer (g/cc)	Volume fraction of polymer (ϕ_p)	$M_w C$ (g/mol)	$\varrho_c \times 10^{-3}$ (mol/cm ³)	$\varrho_c \times 10^{-3}$ (mol/cm ³)
CO-PU _{1.1:1}	0.9	0.01	435	1.1	2.1
CO-PU _{1.3:1}	1.1	0.02	257	1.9	4.2
CO-PU _{1.5:1}	1.2	0.03	181	2.7	6.6


Figure 3. Variation of swelling coefficient with solubility parameter of CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} adhesive films.

synthesized adhesive films were immersed in different solvents such as n-pentane, cyclohexane, toluene, tetrahydrofuran, n-propanol, and dimethyl formamide. The solubility parameters of the synthesized PU adhesive films were determined from the maximum point obtained by plotting the solubility parameter of the solvents versus the swelling coefficient as represented in the Figure 3. The corresponding solubility parameter was found to be $9.5 \text{ (cal/cm}^3)^{1/2}$. The analysis from Table 5 exhibited higher swelling of CO-PU_{1.1:1} compared to other synthesized PU adhesives due to the presence of lower NCO content in CO-PU_{1.1:1}. This was in accordance with the earlier reports observed in previous literatures.^{28,29} Moreover, ϱ_c and ϱ_c values were found to be increased with increase in stoichiometric ratio in PU adhesive. This revealed the formation of highly cross linked network in CO-PU_{1.5:1} as compared to CO-PU_{1.1:1} and CO-PU_{1.3:1} adhesive. This observation can be explained on the basis that a three dimensional net work was formed by the reaction between the OH groups in CO and -NCO groups in PBPI, which exhibited higher ϱ_c .

3.6. Effect on chemical Resistance using Lap shear strength and SEM analysis

The wood substrates bonded with three different types of polyurethane adhesives (CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1}) were prepared using CO based polyol and PBPI. The evaluation of chemical resistance of adhesive was studied in different applied in different chemical environment. The developed substrates bonded with PU adhesives were immersed in water having pH 2 (acidic) at 80 °C and also in water having pH 10 (alkaline) at 80 °C for 2 h. Subsequently the substrates were removed and dried at room temperature for the period of 1 day and then

Table 6. Lap shear strength of CO-PU_{1.3:1} adhesive before and after acid, alkali treatment

Sample type	Lap shear strength (N/m ² × 10 ⁵)		
	CO-PU _{1.1:1}	CO-PU _{1.3:1}	CO-PU _{1.5:1}
Untreated	47	69	37
Acid treatment	31	50	25
Alkali treatment	23	46	19

characterized using lap shear test and SEM analysis.³⁰

The lap shear strength of their treated wood substrates along with those immersed in acid and alkali solution bonded with CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} adhesive has been depicted in Table 6. As observed from the table, it is evident that the treated CO-PU_{1.1:1} adhesive immersed in to acid and alkali solution exhibited a lap shear strength of 31×10^5 and 23×10^5 N/m² respectively which was comparatively less than that of the untreated sample (47×10^5 N/m²). Similarly, the lap shear strength of acid treated substrates bonded with CO-PU_{1.3:1} and CO-PU_{1.5:1} adhesive was found to be 50×10^5 and 25×10^5 N/m², which consequent to alkali treatment showed lap shear strength of 19×10^5 and 46×10^5 N/m². This behaviour of decrease in shear strength is due to the penetration of water molecules from acid and alkali solution within the PU matrix which breaks the molecular bonding between the adhesive and the substrate. Furthermore, as observed from the table, the samples immersed in alkali solution exhibited a greater decrease in the mechanical strength as compared with that of the samples immersed in acidic solution.

The micrograph images of the treated and without treated CO-PU_{1.3:1} adhesive subjected to acid and alkali solution is depicted in Figure 4. Structural effect of PU adhesive with alkali and acid treatment was observed in Figure 4(b) and 4(c). The analysis showed the dispersion of soft segment (white part) into the hard segment (black part) in treated and untreated PU adhesives. It was also observed that after the acid and alkali treatment of 2 h exposure, the pores and cavities were formed on the entire surface of films of PU adhesives which indicated the initiation stage of degradation of the adhesives. This can be attributed due to migration of acidic or basic solution in to the sample, which breaks the molecular bond and creates lower adhesion strength as compared to the untreated PU adhesive. In addition, it has also been observed that the more degradation was obtained in PU adhesive treated with alkali than of acid solution. This is due to the presence of alkali hydrolysable ester groups in the PU adhesive.³¹

3.7. Thermogravimetric analysis (TGA) of PU adhesive films at various concentrations

The effect of stoichiometric ratio on the thermal stability of

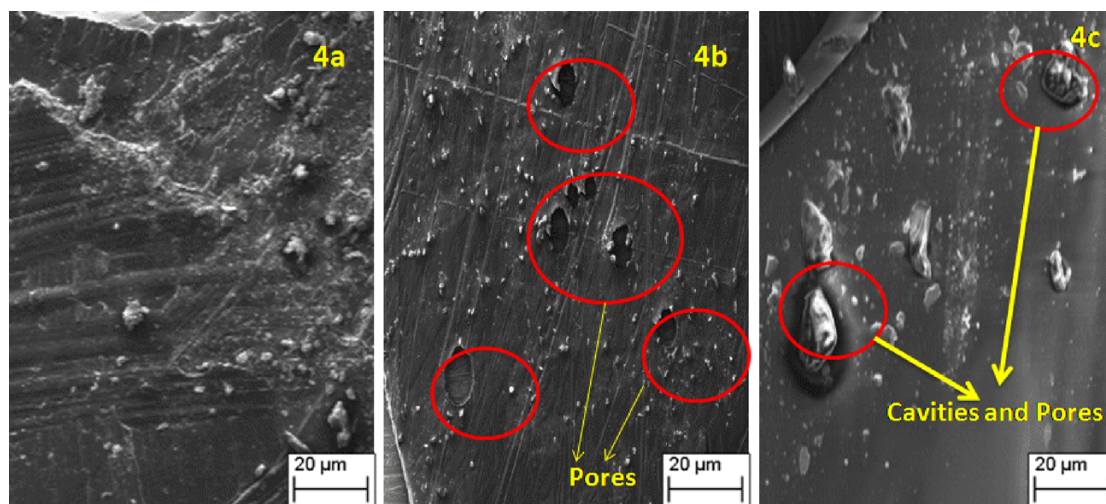


Figure 4. SEM images of CO-PU_{1.3:1} adhesive (a) untreated, (b) treated with alkali solution, and (c) treated with acid solution.

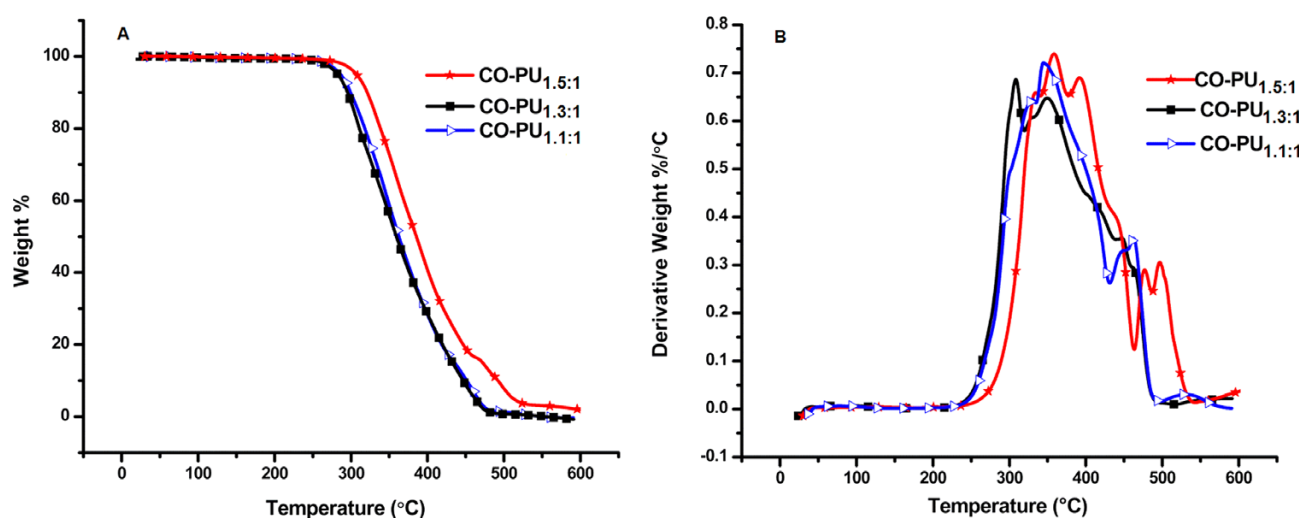


Figure 5. (A) TGA and (B) DTG thermogram of CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} adhesive film.

films of PU adhesives at three different compositions CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} was investigated by TGA analysis as shown in Figure 5(A) and 5(B). The data corresponding to TGA/derivative thermogravimetric (DTG) is depicted in Table 7. The investigation showed significant increased in the initial degradation temperature and the final degradation temperature of three synthesized PU adhesive from 314 °C to 323 °C and 476 °C to 482 °C respectively with increasing the stoichiometric ratio. DTG thermogram of all synthesized PU adhesive films showed three stages of degradation during the heating process and the same has also been reported in earlier reports.³²⁻³⁶ The first stage of degradation at three different composition of PU appeared at 314, 320 and 323 °C corresponding to CO-PU_{1.1:1},

CO-PU_{1.3:1}, and CO-PU_{1.5:1} respectively. This is predominantly due to urethane bond decomposition, which dissociates the isocyanate leading to the formation of alcohol, amines, aldehydes and CO₂.³³ The second stage degradation occurred at 367, 370, and 373 °C for CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} respectively through the decomposition of soft segments such as alkyl chain dissociation of the ester bond through chain scission, dehydrogenation of alkyl groups present in polyol.³⁵ Similarly, the third stage of degradation was obtained at 476, 480, and 482 °C corresponding to CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} respectively which is due to degradation of other segments of remaining structure of PU. As evident from the result, it has been concluded that all synthesized PU films exhibited the initial loss of mass above

Table 7. Parameters of PU adhesive films at various compositions

Sample	Degradation temperature (°C)			E_a-1 (kJ/mol)	E_a-2 (kJ/mol)	E_a-3 (kJ/mol)	Char residue
	1 st stage	2 nd stage	3 rd stage				
CO-PU _{1.1:1}	314	367	476	96	100	116	0.6
CO-PU _{1.3:1}	320	370	480	97	103	118	0.8
CO-PU _{1.5:1}	323	373	482	102	109	125	1.1

314 °C, which further reveals the fact that, the adhesion strength is stable up to 300 °C and beyond this temperature, the strength decreases. This might be due to the failure of adhesion strength between the adhesive and the substrates. Similar observation was reported by Li-Hong *et al.*³⁴ As it was expected, CO-PU_{1.5:1} adhesive film exhibits higher degradation temperature in all three stages as compared to CO-PU_{1.1:1} and CO-PU_{1.3:1} adhesive. Higher char residue was obtained for CO-PU_{1.5:1} adhesive film as compared to its counterpart thereby confirming its higher thermal stability. Similar findings have been reported by various workers.^{26,27} Furthermore, the corresponding decomposition activation energies such as E_a-1 , E_a-2 , and E_a-3 of CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} due to first, second and third stage of degradation respectively have been calculated using COATS and REDFERN method.²⁹ The E_a-1 of CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} adhesive was found to be 96, 97 and 102 KJ/mol respectively due to first stage of degradation. It can be concluded that the small difference between the E_a indicated the complex nature of thermal degradation. Similarly the E_a-2 of CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} adhesive was found to be 100, 103, and 109 kJ/mol respectively due to second stage of degradation and the E_a-3 of CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} was found to be 116, 118 and 125 kJ/mol respectively due to third stage of degradation. Thus, it has been concluded that the CO-PU_{1.5:1} exhibited higher E_a by confirming the lower mobility of the chains as compared to CO-PU_{1.1:1}, CO-PU_{1.3:1} adhesive films. This may be explained by similar facts that due to the high NCO content in CO-PU_{1.5:1}, the film exhibited higher cross linking density.

4. Conclusions

PU adhesives were successfully synthesized from castor oil at different stoichiometric ratios. The developed PU adhesive was confirmed by FTIR analysis which exhibited the reaction between castor oil based polyol and partially biobased isocyanate. The CO-PU_{1.3:1} adhesive showed excellent adhesion property on wood substrate compared to CO-PU_{1.1:1} and CO-PU_{1.5:1} adhesive. Further, the lap shear strength of CO-PU_{1.3:1} adhesive was found 2-4 times greater than the commercially available adhesives. Subsequently, all three PU adhesives showed good chemical resistance in acid solution than of alkali solution. To quantify the decomposition kinetics, E_a energy values for CO-PU_{1.1:1}, CO-PU_{1.3:1}, and CO-PU_{1.5:1} adhesive was calculated using COATS and RADFERN method, which reflected that the CO-PU_{1.5:1} adhesive is highly thermal stable by confirming the higher decomposition activation energy. Hence, it can be concluded that the castor oil based PU formulation can be effectively utilized as adhesive systems for wood substrates at optimum balance of NCO:OH ratio.

References

- (1) H. Christian, K. Helmut, and M. O. Martin, *Polym. Int.*, **61**, 1048 (2012).
- (2) M. Modesti, A. Lorenzetti, F. Simioni, and G. Camino, *Polym. Degrad. Stab.*, **77**, 195 (2002).
- (3) K. D. Weiss, *Prog. Polym. Sci.*, **22**, 203 (1997).
- (4) K. Pietrzak, M. Kirpluks, U. Cabulis, and J. Ryszkowska, *Polym. Degrad. Stab.*, **108**, 1 (2014).
- (5) J. T. White, *Adhes. Age*, **7**, 19 (1981).
- (6) G. E. Myres, *Adhes. Age*, **10**, 31 (1988).
- (7) J. M. Dinwoodie, *J. Inst. Wood. Sci.*, **8**, 59 (1978).
- (8) D. Jia and X. Liang, *J. Polym. Sci., Part B: Polym. Phys.*, **132**, 817 (1994).
- (9) N. D. Ghatke and V. B. Phadke, *J. Appl. Polym. Sci.*, **11**, 629 (1967).
- (10) V. D. Athawale and S. L. Kolekar, *Polym. J.*, **30**, 873 (1998).
- (11) S. Desai, A. Emanuel, and V. Sinha, *J. Polym. Res.*, **10**, 275 (2003).
- (12) D. Mishra, *Int. J. Adhes. Adhes.*, **30**, 47 (2010).
- (13) C. H. Schilling, P. Tomasik, D. S. Karpovich, B. Hart, J. Garcha, and P. T. Boettcher, *J. Polym. Environ.*, **13**, 177 (2005).
- (14) D. D. Sandip, V. P. Jigar, and K. S. Vijay, *Int. J. Adhes. Adhes.*, **23**, 393 (2003).
- (15) J. D. Vivek and S. P. Hasmukh, *J. Am. Oil Chem. Soc.*, **86**, 383 (2009).
- (16) B. R. Silva Bianca, M. C. Santana Ruth, and M. C. Forte Maria, *Int. J. Adhes. Adhes.*, **30**, 559 (2010).
- (17) J. O. Metzger and M. Eissenm, *C. R. Chim.*, **7**, 569 (2004).
- (18) Md Z. Norazwan, Hj. A. Sahrim, and S. A. Ernie, *Int. J. Adhes. Adhes.*, **55**, 43 (2014).
- (19) M. F. Valero and A. Gonzalez, *J. Elastomers Plast.*, **44**, 433 (2012).
- (20) K. P. Somania, S. S. Kansaraa, N. K. Patelb, and A. K. Rakshita, *Int. J. Adhes. Adhes.*, **23**, 269 (2003).
- (21) S. Govindarajan and Y. Ning, *J. Biobased Mater. Bioenergy*, **8**, 457 (2014).
- (22) J. V. Patel and V. K. Sinha, *J. Sci. Ind. Res.*, **58**, 579 (1999).
- (23) A. K. Poha, L. C. Sinb, C. S. Foona, and C. C. Hocka, *J. Adhes. Sci. Technol.*, **28**, 1020 (2014).
- (24) R. M. M. Paiva, E. A. S. Marques, L. F. M. da Silva, and C. A. C. Ant6nio, *Materialwiss. Werkstofftech.*, **46**, 47 (2015).
- (25) H. Yoshida, R. M6rck, P. K. Knut, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **40**, 1892 (1990).
- (26) R. N. Wenzel, *J. Ind. Eng. Chem.*, **28**, 988 (1936).
- (27) Y. Yuan and T. R. Lee, *Surface Science Techniques*, G. Bracco and B. Holst, Eds., Springer-Verlag Berlin Heidelberg, 2013, Vol. 51, pp 1-34.
- (28) H. Yoshida, R. M6rck, P. K. Knut, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **40**, 1892 (1990).
- (29) P. S. Vasudev and W. G. Glasser, *J. Appl. Polym. Sci.*, **29**, 1831 (1984).
- (30) M. D. Banea, L. F. M. Da Silva, and R. D. S. G. Campilho, *J. Adhes.*, **91**, 331 (2015).
- (31) S. Desai, I. M. Thakore, and S. Devi, *Polym. Int.*, **47**, 172 (1998).
- (32) J. H. Saunders and K. C. Frisch, *Interscience*, XVI: 51 (1963).
- (33) C.-W. Chang and K.-T. Lu, *Prog. Org. Coat.*, **75**, 435 (2012).
- (34) L. H. Bao, Y. J. Lan, and S. F. Zhang, *Iran. Polym. J.*, **15**, 737 (2006).
- (35) M. A. Semsarzadeh and A. H. Navarchian, *J. Appl. Polym. Sci.*, **90**, 963 (2003).
- (36) A. Aboulkas and K. Elharfi, *Oil Shale*, **225**, 426 (2008).