

Biomaterial Based Novel Polyurethane Adhesives for Wood to Wood and Metal to Metal Bonding

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Polyurethane adhesives made from synthetic chemicals are non-biodegradable, costly and difficult to find raw materials from local market. To avoid solid pollution problem, cost effectiveness and easy availability of raw materials, biomaterials based polyurethane adhesives are used in current industrial interest. Direct use of castor oil in polyurethane adhesive gives limited hardness. Modification on active sites of castor oil to utilize double bond of unsaturated fatty acid and carboxyl group yields new modified or activated polyols, which can be utilized for polyurethane adhesive formulation. In view of this, we have synthesized polyurethane adhesives from polyester polyols, castor oil based polyols and epoxy based polyols with Isocyanate adducts based on castor oil and trimethylolpropane. To study the effects of polyurethane adhesive strength (i.e. lap shear strength) on wood-to-wood and metal-to-metal bonding through various types of polyols, cross-linking density, isocyanate adducts and also to compare adhesive strength between wood to wood and metal to metal surface. These polyols and polyurethanes were characterized through GPC, NMR and IR-spectroscopy, gel and surface drying time. Thermal stability of PU adhesives was determined under the effect of cross-linking density (NCO/OH ratio). The NCO/OH ratio (1.5) was optimized for adhesives as the higher NCO/OH ratio (2.0) increasing cross-linking density and decreases adhesion. Lower NCO/OH ratio (1.0) provides low cross-linking density and low strength of adhesives.

Keywords: *adhesive, castor oil, polyurethanes*

1. Introduction

Generally the adhesives based on polyurethanes used by a wide range of application like woodworking, furniture building/ restoration, boat building/ repair, cabinet making and millwork, stone working, tile and other masonry, light aircraft building/ repair, crafts, and many others. With respect to the different composition and applied methods as well as versatility in polyurethane chemistry, various types of polyurethane adhesives are available in market. Polyurethane adhesives are normally contains a number of urethane group in the molecular backbone or formed during use without consideration of the chemical composition of the chain. So, typical polyurethane adhesive may contain in addition of urethane linkage, aliphatic and aromatic hydrocarbons, esters, ethers, amides, and urea and allophanate linkage, which are responsible to change the final properties^{1,2}. Also the performance of adhesives related to its physical properties i.e. viscoelastic and surface free energy, therefore the relationship

between composition and properties are great importance³. These adhesives are normally consisting of polyols, isocyanates and some compositions of the other materials.

For many years researches have been trying to develop the properties of polyurethane adhesives for different application area via, modification and combination of various polyols as well as isocyanates adducts. Modification in hydroxyl terminated polyols based polyurethane has been studied extensively as they could be effectively used as adhesive^{4,5}. Extensive reports are available on use of polyurethane inter penetrating network (IPN's) and semi inter penetrating network (semi IPN's) as adhesives⁶⁻⁹. The developments of environment friendly and high performance polyurethane adhesives for automobiles assemblies have been studied¹⁰. Polyurethanes adhesive properties also studied under the effects of different kinds of polyether, curing agents and moisture contents on adhesion surface¹¹.

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Effects of moisture and temperature on PU adhesives for wood substrate also studied¹².

The behaviour of a wood and metal adhesive system are depending upon a wide range of variables like surface smoothness of substrates, environment that are related to change in temperature, humanity as well as other physical and application parameters.

The bonding mechanisms of polyurethanes adhesives are different on wood and metal surface. Wood bonding deals with the complex chemistry through celluloid hydrogen bonding i.e. Vander walls forcers, while metal bonding takes a part through the polarity of metal substrate i.e. orientation of polar group. Generally for wood-to-wood bonding urea and phenol formaldehyde based adhesives are available, but some of these are sensitive towards hydrolysis and also cleavage due to stress i.e. normally observed in plywood¹³⁻¹⁸. To strengthen the mechanical properties of plywood, polyurethane adhesives give good results and recently introduced¹⁹. Some disadvantages such as shorter pot life, durability and higher cost observed in acrylate based adhesives^{20,21}.

Polyurethane adhesives made from synthetic chemicals are non-biodegradable, costly and difficult to find raw materials from local market. To avoid solid pollution problem, cost effectiveness and easy availability of raw materials, biomaterials based polyurethane adhesives are used in current industrial interest²²⁻²⁵. Direct use of castor oil in polyurethane adhesive gives limited hardness. Researcher has proposed modification on active sites of castor oil to utilize double bond of unsaturated fatty acid and carboxyl group yields new modified or activated polyols, which can be utilized for polyurethane adhesive formulation. Castor oil based polyurethanes are extensively used in coatings, IPNs, telecommunications, as insulators in electrical

industries, foams and adhesives²⁶⁻³⁰. The adhesive properties of polyurethane from modified castor oil or its derivatives are studied under the different variation in composition³¹⁻³³.

In the view of this the present work describe the performance of castor oil based novel polyurethane adhesive system for wood to wood and metal to metal bonding by using polyester polyols, castor oil-polyester polyols and epoxy-polyester polyols with different isocyanate adducts having different NCO/OH ratio. The polyester polyols (PO) were synthesized from Adipic acid and ethylene glycol with different stoichiometric proportion. Castor oil-polyester polyols (CO) were synthesized through the transesterification reaction between castor oil and polyester polyols (PO). The epoxy polyester polyols synthesized from Diglycidial ether of bis-phenol A (DGEBA) and polyester polyols under maintain the physical condition. The polyols and polyurethanes adhesives were characterized by FTIR spectroscopy. The adhesive strength (Lapshear strength) of these polyurethanes were measured under the effects of chain length, isocyanate adducts, cross linking density and types of polyols to determine the effects of cross-linking density on thermal stability, gel and surface drying time on polyurethane adhesives.

2. Experimental

2.1. Materials

Adipic acid and Ethylene glycol were received from Samir-Tech Chem. P. Ltd. Vadodara, Gujarat, India. Refined castor Oil (Hydroxyl value 165, acid value 0.3) was received from Jayant Oil Mills, Vadodara Gujarat, India. Diglycidial ether of Bisphenol A

Table 1. Physical properties of isocyanate adduct.

Adduct based on TDI	% of free NCO	NCO equivalent	Specific gravity @ 30 °C	Ford Cup- viscosity @ 30 °C by BIV(sec)
R-60	7.48	561	1.36	325
R-90	8.0	525	1.33	320
TMP	12.50	336	1.02	210

Table 2. Characterization Data of polyols.

Polyols code	Acid value	Hydroxyl value (mgKOH/gm)	Hydroxyl equivalent	Non volatile content	Brookfield viscosity in Centipoises @ 50 rpm at 35 °C in Spind n° 1
PO3	≈0	103	545	99.5	1470
PO4	≈0	271	206	99.7	176
PO5	≈0	396	141	99.3	115
CO3	-	128	438	99.6	570
CO4	-	185	302	99.6	324
CO5	-	202	276	99.4	244
EP3	-	89	627	99.2	1000
EP4	-	186	301	99.1	510
EP5	-	239	233	99.2	405

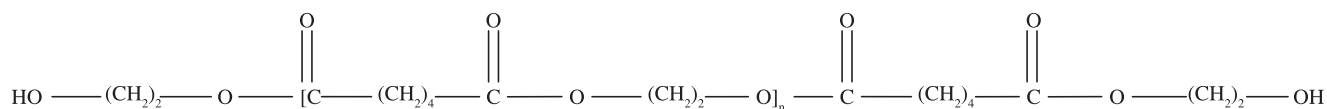


Figure 1. Structure of polyester polyol (PO).

(DGEBA Epoxy equivalent weight - 200) was received from Atul Industries Valsad, Gujarat, India. Triethyl amine and dibutyltindilurate (DBTDL) was obtained from Marck, U.S.A. Isocyanate adducts based on castor oil derivatives (R-90, R-60) received from N.K. Polymers Ahmedabad, Gujarat India and Trimethylol propane based isocyanate adduct received from Grand polycot Padra Gujarat India. These adducts were characterized for their physical properties shown in Table 1.

2.2. Synthesis of polyols

2.2.1. Hydroxyl terminated polyester polyols (PO)

A mixture of Adipic acid (1 molar) and ethylene glycol (3, 4 and 5 equivalent respectively for PO3, PO4 and PO5) was heated in under the blanket of N₂, in three necked flask equipped with stirrer, thermometer, column and gas inlet initially at 150 °C and raised up to 230 °C over the period of 10 hours. The water-glycol azeotrop is continuously removed from the top of the column at 105 °C and collected in receiver. Finally

the by-product water removed was facilitated by vacuum. The extent of Polycondensation reaction (esterification) was monitored by acid value determination. The reaction was stopped at the zero acid value, the excess ethylene glycol was distilled out by vacuum distillation and the light yellow product was cooled and the acid value was determined. The hydroxyl value of polyol was determined by acetic anhydride-pyridine method³⁴. The structure and characterization data of the polyols presented in Figure 1 and Table 2 respectively.

2.2.2. Castor oil based novel polyols (CO)

Castor oil based novel polyols were synthesized by the ester exchange reaction of castor oil with polyester polyols. Castor oil (1 molar) and polyester polyol (1 equivalent) derived from Adipic acid and ethylene glycol was charged in three-necked flask equipped with mechanical stirrer, thermometer and reflux condenser. The reaction mixture was heated at 180-200 °C. The completion of reaction was determined by observing separation of resin layer (unreacted

Table 3. Polyurethane adhesives compositions.

	Isocyanate adduct	Ratio NCO/OH	Amount of adduct in gms @ 5 gm of polyol
PO3	R-90	1.0	04.80
PO4	R-90	1.0	12.74
PO5	R-90	1.0	18.52
PO3	R-90	1.5	07.20
PO3	R-90	2.0	09.50
CO3	R-90	1.0	05.90
CO4	R-90	1.0	08.60
CO5	R-90	1.0	09.45
CO4	R-60	1.0	09.25
CO4	TMP	1.0	05.50
EP3	R-90	1.0	04.15
EP4	R-90	1.0	08.70
EP5	R-90	1.0	11.18
EP5	R-60	1.0	12.00
EP5	TMP	1.0	07.15

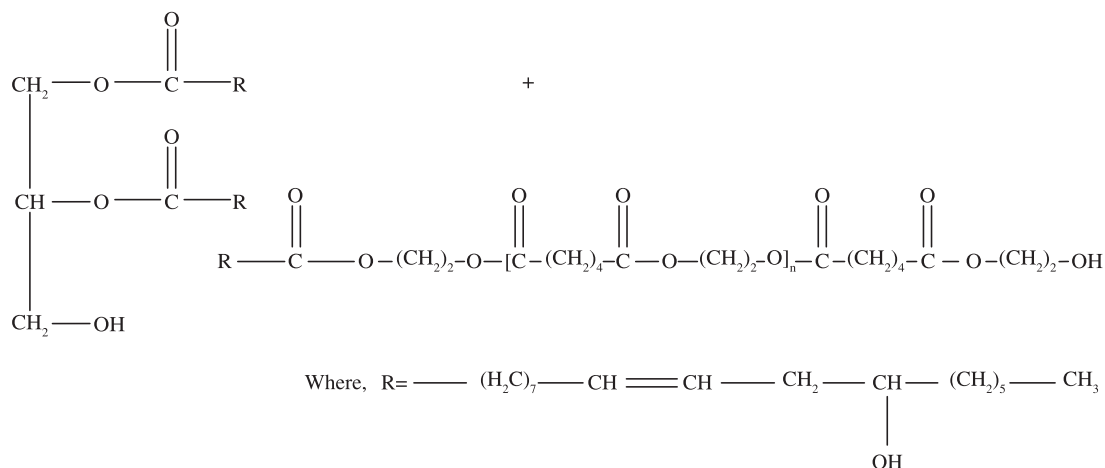


Figure 2. Structure of castor oil-polyester polyol (CO) (Mixture).

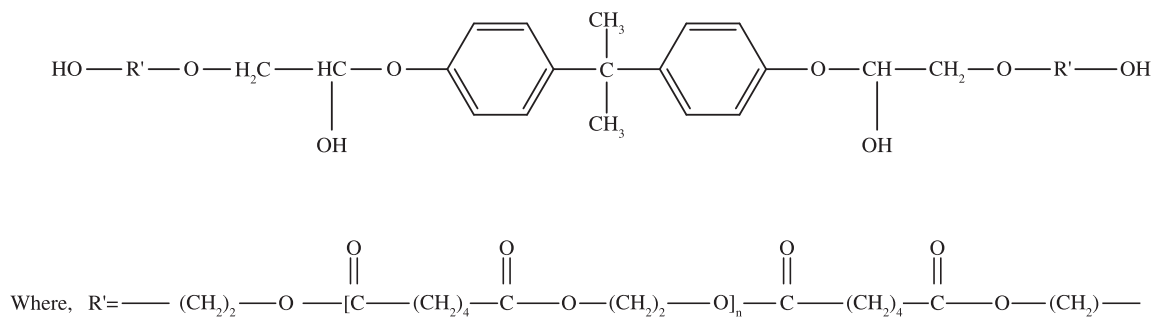


Figure 3. Structure of epoxy-polyester polyols (EP).

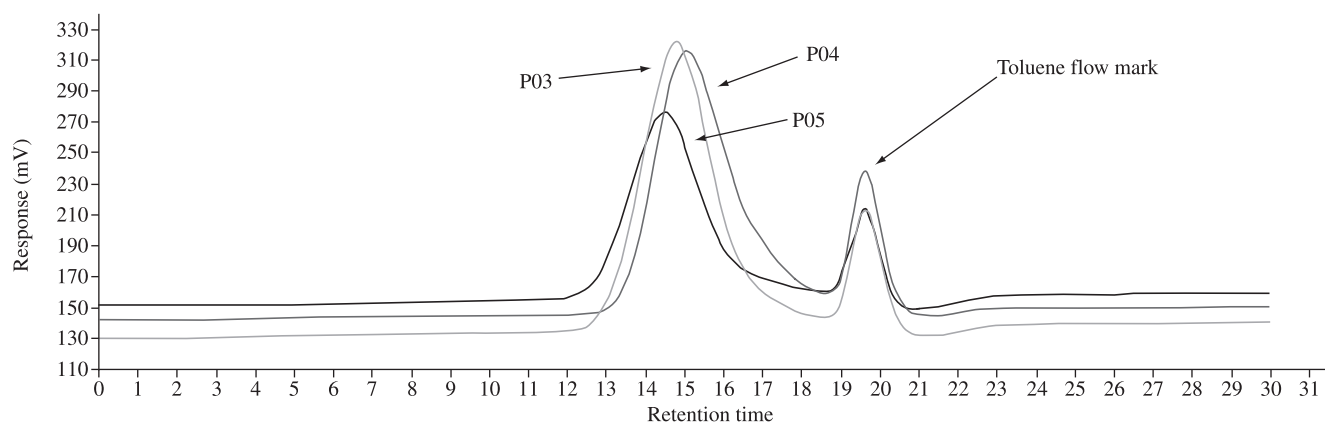


Figure 4. GPC of polyols.

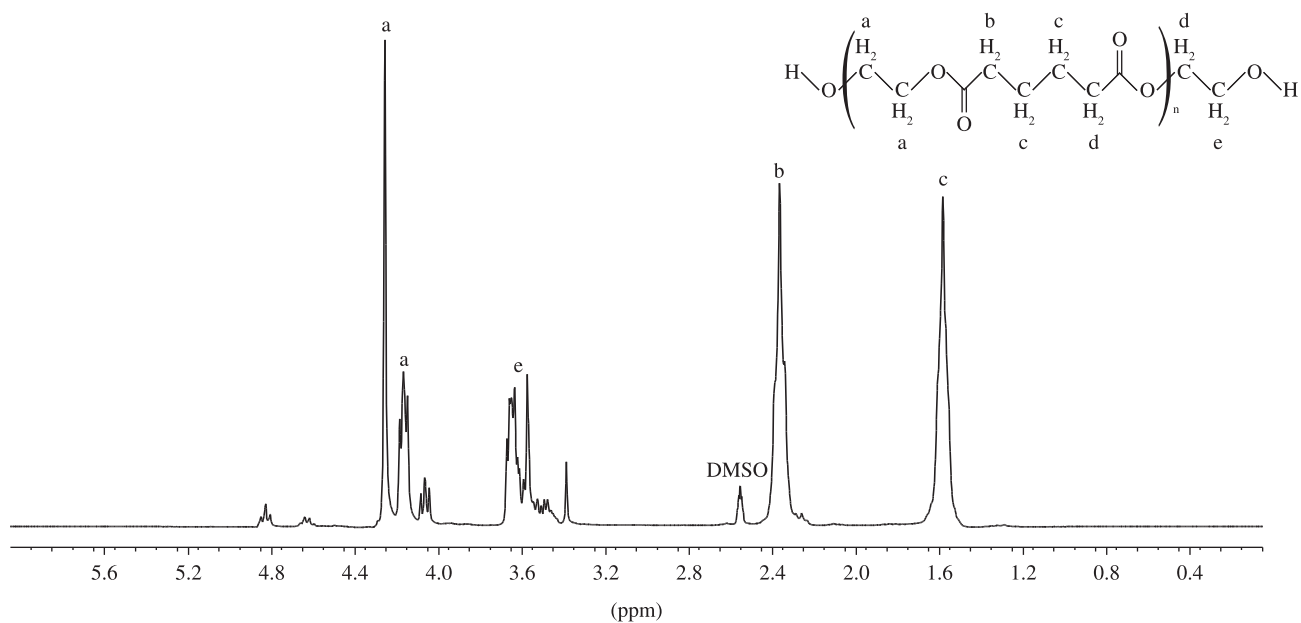


Figure 5. NMR spectra of polyol P03.

polyol). It was observed that the reaction took ~9 hours. Therefore all ester exchange reaction was carried out for 10 hours. At the end of the reaction hydroxyl value of the product was determined³⁴. The structure and characterization data of the polyols presented in Figure 2 and Table 2 respectively.

2.2.3. Epoxy based novel polyols (EP)

Novel epoxy based polyols were synthesized from Diglycidial ether of bis phenol A (1 molar) and polyester polyols (PO) derived (2 equivalent) were charged in the three necked flask containing 25 mL dioxane equipped with nitrogen inlet and water condenser along with 0.05 mole of triethyl amine catalyst, the reaction was reflux for 3 hours. Determining the epoxy equivalent weight monitored the extent of the reaction. The infinite value of epoxy equivalent indicates completion of the reaction. After the completion of the reaction dioxane was recovered by vacuum distillation and viscous liquid as epoxy based polyols free from dioxane was collected in clean glass stopper bottle. Hydroxyl value of the product was determined³⁴. The reaction scheme and characterization data of the polyols presented in Figure 3 and Table 2 respectively.

Note: All epoxy based polyols having zero epoxy equivalent value.

2.2.4. Polyurethane adhesive preparation

Preparation of adhesives were carried out by reacting polyols with different Isocyanate adducts having different NCO/OH ratio, along

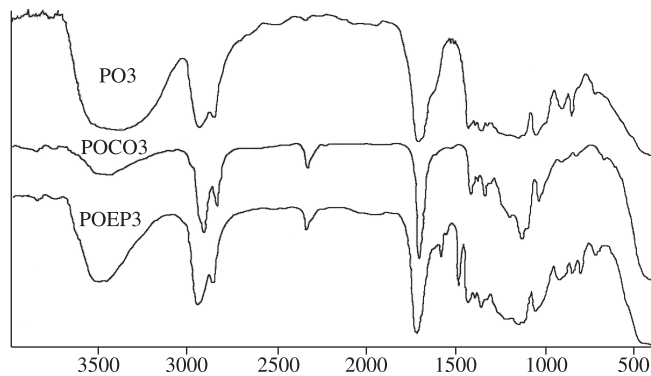


Figure 6. IR spectra of polyols.

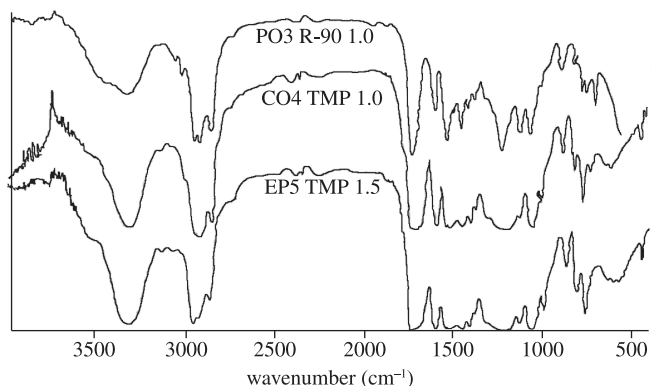


Figure 7. IR spectra of polyurethane.

with DBTDL (0.05% w.w⁻¹ of total composition). The compositions of different polyurethane adhesives studied in this work are shown in table 3. The adhesives were diluted by MEK to give an appropriate viscosity for effect application on wood and metal substrate.

2.2.5. Wood and metal specimen preparation

Teak wood has been relied upon and trusted for its uncommon strength. This wood is highly prized by lovers and collectors of furniture the world over. The reputation of Teak throughout the whole world in producing furniture of the highest quality has, however, never faltered. As per test sample requirement teak wood pieces (longitudinal) were cut into 300 × 25 × 3 mm³ strips and polished using sand paper grit number 60 (250 μm) the metal were cut into 203 × 25 × 1.62 mm³ strips and dried (at 100 °C for 15 minutes in oven) to make it moisture free and after drying they were polished using sandpaper grit number 60 (250 μm).

2.2.6. Bonding and testing (for wood and metal)

Using a brush the adhesive solution was applied on both the pieces of the substrate for a thickness of 0.1mm and lap joined giving 25 × 30 mm² for wood strips and 25 × 25 mm² for metal strips area of overlap. Load (2.5 kg) was placed over the contact points of wood and metal peaces and left overnight. After that the joints were kept at room temperature (30 °C) and at relative humidity of 50 ± 5% for seven days. Each joint specimen was tested for the lap-

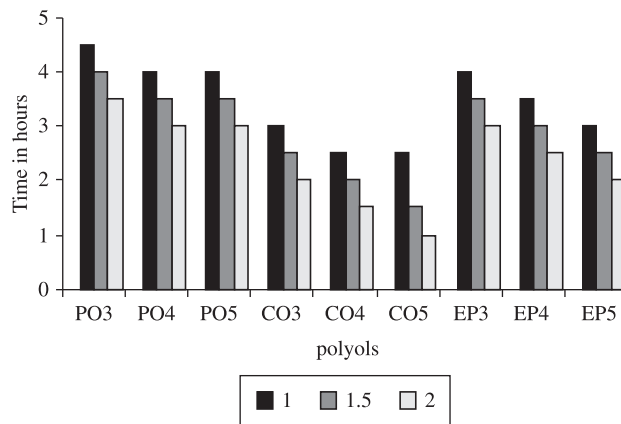


Figure 8. Gel times of PU'S at different NCO/OH ratio.

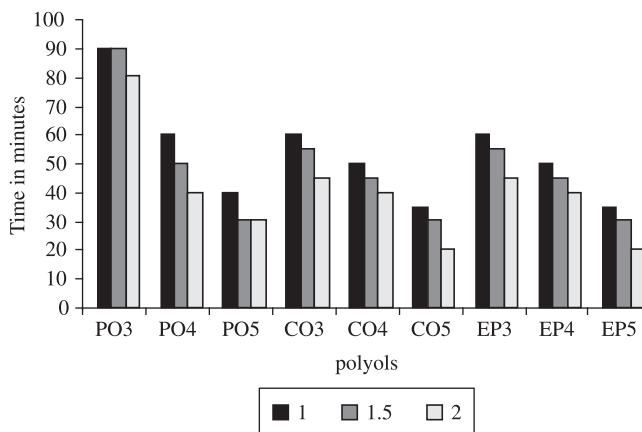


Figure 9. Surface drying of PU'S at different NCO/OH ratio.

shear strength using a Zwick UTM model 1445 according to ASTM D 906-82 (1987).

2.2.7. Thermogravimetry

Thermogravimetry analysis (TGA) was performed under air from 30 to 800 °C, at a heating rate of 10 °C/minute on Shimadzu Thermal (DT-30B) Analyzer.

3. Results and Discussion

3.1. Characterization through GPC (SEC), NMR and IR spectroscopy

Polyols were characterized by GPC, NMR and IR spectroscopy as shown in Figure 4, 5 and 6. The band at about 3400 cm^{-1} is due to -OH stretching of all the polyols. The strong and broad band indicates presence of the hydroxyl group associate to polymeric compound. The bands at about 1050 and 1350 cm^{-1} indicate the

O-H banding of primary alcohol and C-O stretching of ester group respectively. The very strong band in the range of 1750-1735 cm^{-1} shows C = O stretching of aliphatic ester. The bands are not observed in between 1770-1750 cm^{-1} clearly indicates the absence of aliphatic acid in PO3 i.e. polyester having zero acid value. The bands of C-H stretching and bending (deformation) in the -CH₂ group are observed at about 2962-2853 cm^{-1} and 1485-1445 cm^{-1} respectively.

The bands are not observed at about 920 cm^{-1} clearly indicates that there are no terminal epoxy group present in novel polyols EP3 but they are reacts with -OH group of polyester polyols and the oxirane ring of epoxy group is converted in the form of secondary alcoholic group of novel polyols which is conformed at about 1100 cm^{-1} of -OH banding in secondary alcohol. The band at about 1650-1500 and 1220-1020 cm^{-1} indicates N-H banding vibration and C-N vibration respectively of amine catalyst used in EP3 polyols synthesis.

IR spectra of Polyurethane showed in Figure 7. The bands at about 3330 cm^{-1} and about 1560-1650 cm^{-1} indicates that the N-H stretching and N-H bending of urethane group. The bands observed in between 2962-2853 cm^{-1} indicates the C-H stretching and C-H bending of alkane. The bands at 1220-1020 and 1410 cm^{-1} is the C-N vibration in urethane group. The band in between 1740-1690 cm^{-1} indicates clearly that the formation of urethane group. The frequency about the 870 cm^{-1} presents the substituted aromatic ring of TDI.

3.2. Gel and surface drying time

The gel and drying time measured for PU'S from the polyester polyols, castor oil based polyols, epoxy based polyols with R-90 based TDI adduct in different proportions to have different NCO/OH ratio.

The results in Figure 8 clearly indicate that the gel time decreases as the NCO/OH ratio increases for all the sets. This is because of the higher reactivity of NCO group i.e. as the -NCO content increase reactivity towards -OH group required for cross linking increases. The increased reactivity with NCO content is highest with 2.0 NCO/OH in all the cases.

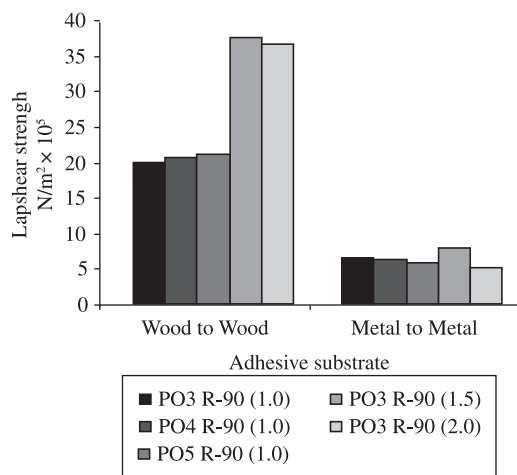


Figure 10. Effects of chain length of polyester polyols (PO3, PO4 and PO5) and cross linking density (NCO/OH) on PU's adhesion strength.

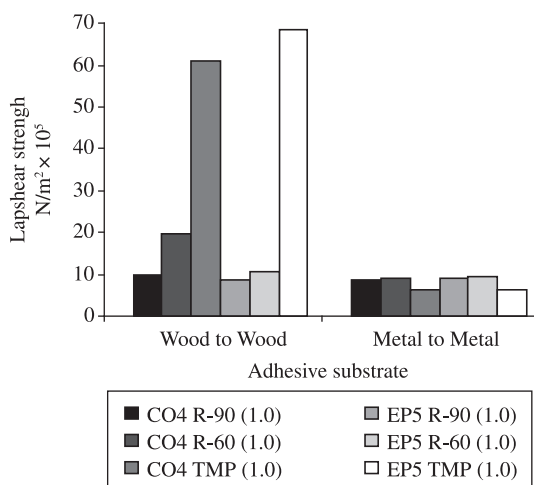


Figure 11. Effects of types of adducts (R-90, R-60 and TMP) on PU's adhesion strength.

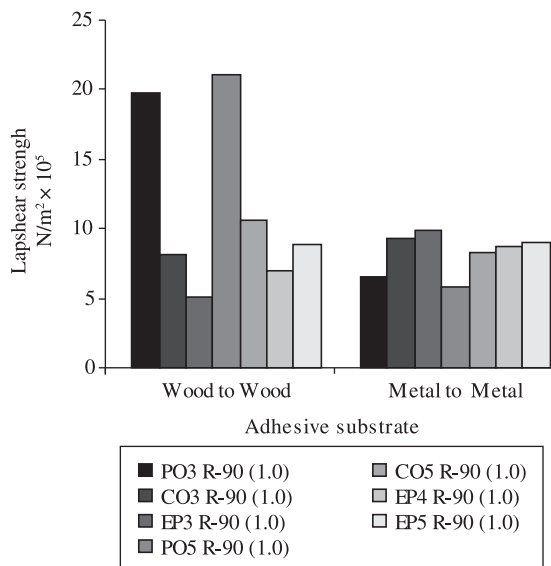


Figure 12. Effects of types of polyols (Polyester, castor oil and Epoxy based) on PU's adhesion strength.

Time of Surface drying for the same sets of polyurethane are also reported in the Figure 9. The observation of data indicates that:

- The castor oil polyols based and epoxy polyols based polyurethanes shows lower times for drying.
- Polyester polyols based polyurethanes took more time for drying.

In above trend the hydroxyl group of castor oil is activated by its combination with polyester polyols and as the hydroxyl functionality is more than two, the cross linking reaction is faster as a result of which polyurethanes based on these polyols shows faster drying.

In the case of epoxy based polyester polyols is having higher hydroxyl functionality increases its reactivity while a bulky bis-phenol group hindered mobility and hence decreases reactivity. These two opposite effects ultimately balance the reactivity of hydroxyl groups towards Isocyanate and hence drying time of polyurethane is in the range of castor oil based polyols.

Low reactivity of polyester polyols is known and hence shows highest drying time.

3.3. Adhesive strength

Lap shear strength of different polyurethanes on wood-wood and metal-metal substrate (10 pcs.) analysed under the effects of chain length of polyols, cross linking density, types of polyols and Isocyanate adducts shown in Figure 10, 11 and 12.

3.3.1. Effects of chain length and cross linking density (NCO/OH)

The adhesive strength in PU prepared from shorter polyols (PO5) shows higher degree of adhesion than PU prepared from higher chain length polyols (PO3) on wood substrate. As length between two-cross linking point's decreases, flexibility decrease, the possibility of orientation of ester group towards substrate decreases. This in turn decreases the possibility of interaction between hydrogen group of substrate and ester linkage of polyurethane.

There fore actually for polyol of higher length should show higher adhesion. But on other hand the concentration of urethane linkage is more with PO5 polyurethanes (shorter chain), which increases the possibility of hydrogen-bond formation between adhesive and substrate, and it is predominant. Thus the adhesion is more in PO5 polyurethanes compare to PO4 and PO3 polyurethanes.

In case of metals interaction is through polarity and not through hydrogen bonding, therefore the ester linkage interaction is much more important in metal compare to wood. The interaction of ester group of polyurethane with metal substrate will be more in PO3 due to more number of ester groups and higher flexibility, provides higher orientation of ester group towards substrate in PO3. Therefore the adhesion tends of polyurethane metal system is exactly reverse then that of polyurethane wood systems.

With increasing in NCO/OH ratio strength of adhesive also increases. This is responsible for higher cross-linking density to improve adhesion property. But after certain limit (NCO/OH = 1.5) much more cross-linking hindered the orientation of ester groups decreases the flexibility. Therefore adhesion properties decrease after critical value. After critical value the rigidity increases, imposed by higher concentration of NCO hindered orientation possibility required for optimum interaction between substrate and adhesive decreases, therefore beyond critical value of NCO/OH ratio adhesion decreases rather than increases.

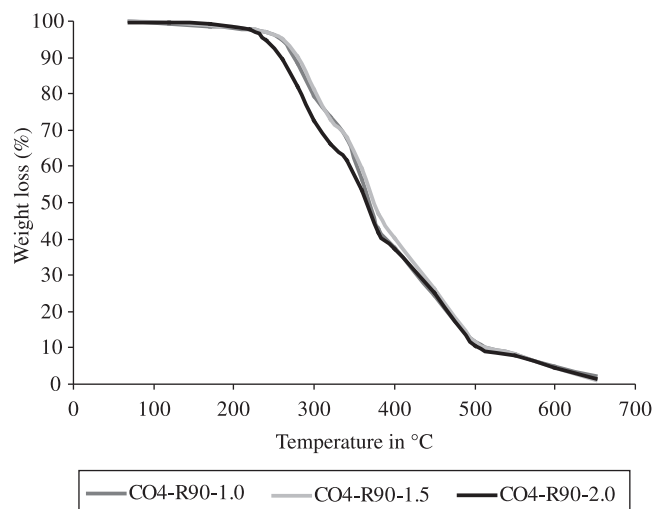


Figure 13. Thermogram of polyurethane adhesives

Table 4. Activation energy of polyurethane adhesives:

Polyurethanes	IDT	Ea (kJ/mol)
CO4 R-90 1.0	354	39.54
CO4 R-90 1.5	362	40.64
CO4 R-90 2.0	346	38.95

3.3.2. An effect of isocyanate adducts

The results of wood-wood polyurethane adhesive elaborate that the Isocyanate adducts are also play an important role for adhesive strength.

Trimethylol propane based isocyanate adducts, castor oil based R-90 and R-60 adducts reacts with polyol in which Trimethylol propane adducts have higher strength compare to R-90 and R-60 adducts on wood. Higher reactivity and rigidity of TMP compare to castor oil based R-90 and R-60 which is responsible to improve the strength of adhesion.

3.3.3. Effects of types of polyols

In case of metal-to-metal bonding the excellent adhesion strength is obtained in epoxy based polyol compare to polyester and castor oil based polyols. Aromatic nature of epoxy based polyol shows higher adhesive strength due to Electronic resonating cloud of Bisphenol-A moiety, Higher cross linking density compare to polyesterpolyol and Higher strength of adhesive film compare to castor oil based polyol.

The reverse phenomenon observed in wood to wood adhesive because of decreasing in cross linking density as well as increasing in flexibility to provide the orientation of groups for H-bonding formation with substrate.

Compare to polyester-polyol, castor oil based polyol are more flexible. Orientation of ester groups as well as higher cross-linking density in castor oil based polyol compare to linear polyester polyol, which is responsible for formation of hydrogen bonding with substrate as well as increase in adhesive strength. The sufficient functionality in epoxy based polyols to cross linking but the aromaticity of bis'phenol A moiety to hindered the orientation of the group towards substrate so the polyurethanes based on epoxy polyols having lower adhesion strength compare to castor oil polyols as well as polyester polyols on wood substrate.

4. Thermal Analysis

The effects of cross-linking density on thermal stability of castor oil based polyurethane adhesives were studied. Thermograms indicate that the negligible weight loss up to 240 °C i.e. the polyurethanes are stable up to 240 °C with irrespective of cross-linking density (NCO/OH ratio) which shown in Figure 13.

The polyurethanes degraded not well-distinguished two stages. The degradation in the first stage of polyurethanes may correspond to the breaking of urethane bond and leading the formation of carbon dioxide, alcohols, amines carbon monoxide etc.³⁵⁻³⁶. In the second stage at about 350 °C may be due to the decomposition of ether and ester links. Castor oil based polyols and castor oil based adduct, the main chain degradation may occur with the formation of 10 undecanoic acid and heptenal as evidenced by the thermal degradation of recenoleic acid³⁷.

The decomposition activation energy of these polymers was evacuated using the well-known Broido's method (Table 4)³⁸.

The activation energy of the polyurethanes having 1.5 NCO/OH shows higher value. It indicates that the thermal stability increases with increasing NCO/OH ratio up to certain limit. Above the certain limit a high cross-linked structure of polyurethanes having more number of urethane linkages provides less energy to degradation.

5. Conclusion

Adhesives were prepared from different polyols with different isocyanate adducts. The NCO/OH ratio (1.5) was optimized for adhesives as the higher NCO/OH ratio (2.0) increasing cross-linking density and decreases adhesion. Lower NCO/OH ratio (1.0) provides low cross-linking density and low strength of adhesives.

- Gel time decreases as the NCO/OH ratio increases in all the cases;
- Low reactivity of polyester polyols shows highest surface drying time;
- Adhesion on wood through hydrogen bonds and on metal substrate through polarity showed reverse trends for polyurethane adhesives for wood and polyurethane adhesives for metal;
- Adhesive strength of shorter chain length polyols (PO5) has higher value for wood and lower for metal substrate;
- The adhesive based on TMP adducts gave the higher value of adhesion for wood compare castor oil based R-90 and R-60 adducts;
- The Castor oil polyol with TMP adduct based adhesive provided good adhesive strength compare to epoxy polyols with TMP adduct based adhesive, as flexibility of long chain presence in castor oil polyols;
- Polyester polyols with R-90 based adhesives shown higher adhesive strength for wood compare to castor oil polyols and epoxy polyols with R-90 adducts; and
- Adhesive based on castor oil polyol and epoxy polyols with R-90 adducts shown lower adhesive strength due to high cross-linking density and rigidity respectively.

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