Chapter 4

Polyurethane Adhesives

4.1 PREVIEW

In this chapter we present the formulation of a Polyurethane adhesive system using polyester polyol for wood to wood bonding as well as using acrylated polyol for metal to metal bonding. The effect of NCO/OH ratio, types of isocyanate adducts and chain length of glycols used in the polyols were studied by determining wood to wood adhesion in terms of lap shear strength. Also synthesized polyurethane adhesives from acrylated polyol having different isocyanate adduct, NCO/OH ratio and hydroxyl value of polyol were studied by determining metal to metal adhesion in terms of lap shear strength by standard procedure.

4.2 INTRODUCTION

Generally, several kinds of commercial polyurethane (PU) are used to prepare solvent-based adhesives but due to their unknown formulations, their performance can not be predicted and variation from batch to batch may produce significant differences in properties. A few studies dealing with the preparation of polyurethanes from raw materials and their application as adhesives have been carried out [1-5]. PU adhesives are widely used in different industries. Due to the versatility of polyurethane chemistry there are many different types of PU adhesives [6]. These normally consist of polyol (polyester or polyether type), isocyanate and other additives. Since the performance of an adhesive is related to its viscoelastic properties, in addition to its surface free energy and that of the adherend [7], the relationship between composition and properties are of great importance. The performance or behavior of a wood adhesive system is dependent on a wide range of variables, such as surface smoothness of wood substrate, presence of wood extractives, pH and amount of debris present, which are related to the environment, such as the level and rate of a change in both temperature and relative humidity [8]. The bonding mechanism of adhesives is due to complex chemistry of the cellulosic substrate i.e. hydrogen bonding with some adhesive and attractive weak vander waals forces with others [9]. Adhesives based on urea formaldehyde (UF) and phenol formaldehyde (PF), are the major adhesives used for bonding wood [10-12], but some of these adhesives are very sensitive to hydrolysis [13-14] and stress scission [15]. Polyacrylate type adhesives are also used as wood adhesives but it has some disadvantages such as shorter pot life, higher cost and limited durability. Literature studies reveal synthesis of different types of PU adhesives [16-17], made from synthetic chemicals. Extensive research work on synthesis of castor oil based PU is reported in literature [18-20], but very few study concerning use of castor oil based PU as adhesives are available. Hence, this is an effort to synthesize castor oil based polyol which is utilized in the PU adhesives. Chemical point of view castor oil has two reactive sites, the double bond of the unsaturated fatty acid and the carboxyl group, linking the acid to the glycerol. Castor oil is used in the synthesis of IPN's of polyurethane. It is a highly crosslinked polymeric structure and it acts as a very good adhesive for metal to metal bonding, Zhang Liuchang et al.[21] and Xie Hang-Quan et al [22] synthesized IPN's from castor oil based PUs. Rajalingam et.al [23] synthesized semi IPN's from polychloroprene and castor oil based PUs which are good adhesives for rubber to rubber bonding. In the present work we have made an attempt to synthesize castor oil based polyol for polyurethane to use as an adhesive. Most adhesives are polymeric adhesives and if made from renewable sources they will have low cost and biodegradability which are of importance. In view of these,- we synthesized polyurethane (PU) adhesives from three different polyester polyols, obtained by reacting a castor oil derivative and diols (glycols) with diisocyanate adducts, where different NCO/OH ratios were used to give various compositions. The effect of NCO/OH ratios, types of isocyanate adducts and chain length of glycols were studied, by determining wood-to- wood adhesion strength i.e. by lap shear strength measurement. The change in lap shear strength after being placed in cold water, hot water, acid solution and alkali solution was tested. Also we synthesized polyurethane adhesives form Acrylated polyol with different isocyanate adducts, where different NCO/OH ratio were used to give various different compositions. The types of NCO/OH ratio, different isocyanate adducts and hydroxyl value of acrylated polyols were studied, by determining metal to metal adhesion strength.

We used three different polyester polyol varying in chain length. They were reacted with different isocyanates for wood to wood bonding.

Also a series of acrylated polyols were reacted with isocyanates for metal to metal (mild steel) adhesives

The present work describe the development of PU adhesives by reacting three different castor oil based polyester polyols of different chain length , with different isocyanate adduct and with different NCO/OH ratio. These PU adhesives were applied on to wood to wood substrates. Lap shear strength was measured using standard method and extent of crosslinking in adhesive was monitored by measuring the adhesives strength (green strength) as a function of time

The study has been continued to check the effect of hydroxyl value of acrylated polyols on bonding strength of adhesives for metal to metal substrates.

4.3 EXPERIMENTAL

Three different polyester polyol having varying chain length were selected for PU synthesis. These PU resin were applied on wood substrates.

Acrylated polyols differing in their hydroxyl value were selected for PU synthesis. These PU resins were applied on metal (mild steel) substrates.lap shear strength of these adhesives were measured by standard procedure.

For wood adherends to be held together with maximum strength, a liquid adhesive was spread freely to make an intimate contact with both surfaces, so that the molecules of adhesives must diffuse over and into surface to make contact with molecular structure of wood so that intermolecular forces of attraction between adhesives and wood can become effective.

Wetting of surface occurs when the contact angle approaches zero. The contact angle approaches zero when the adhesive has high affinity for wood adherends and surface tension is very low. When a drop of adhesive is spread over the surface to form a thin film, contact angle approached to zero. The adhesive spreads well and made intimate contact with the surface.

Polishing with sand paper as a pretreatment of wood has been used most commonly and effectively. The effectiveness increases the surface wettability and surface energy by polishing with sand paper, was studied with a sample test.

Three drops of PU resin were applied on the surface of wood at the same time using a micro syringe, and then photographs of wood strips were taken after 30 seconds. In the picture (Fig 1) the drop on the left has retained a large contact angle on the edge of unsanded surface, the drop in the centre has made smaller contact angle and improved wettability was obtained after surface was renewed by two passes on surface by 60 no. grit sand paper (250 μm). The drop on the right show a small contact angle and good wettability after four passes with same sand paper.

Fig 1

So this test proved the effectiveness of providing good adhesion by increase wettability of surface. Surface pretreatment of wood with sand paper grit no 60 showed quite effective to increase surface wettability.

4.3.1 Wood specimen prepartions

Teak wood was selected as bonding substrates. Teak wood is commonly used in furniture work and for other structural assembly in INDIA. As per test sample requirements, teak wood pieces (longitudinal) were cut into 300×25 ×3 mm^3 strips and dried (at 100^0C, for 15min in oven) to make it moisture free and after drying they were polished using sandpaper grit no. 60 (250 μm). The shape and dimensions of the test specimens used in this experiment are shown in Fig. 2.

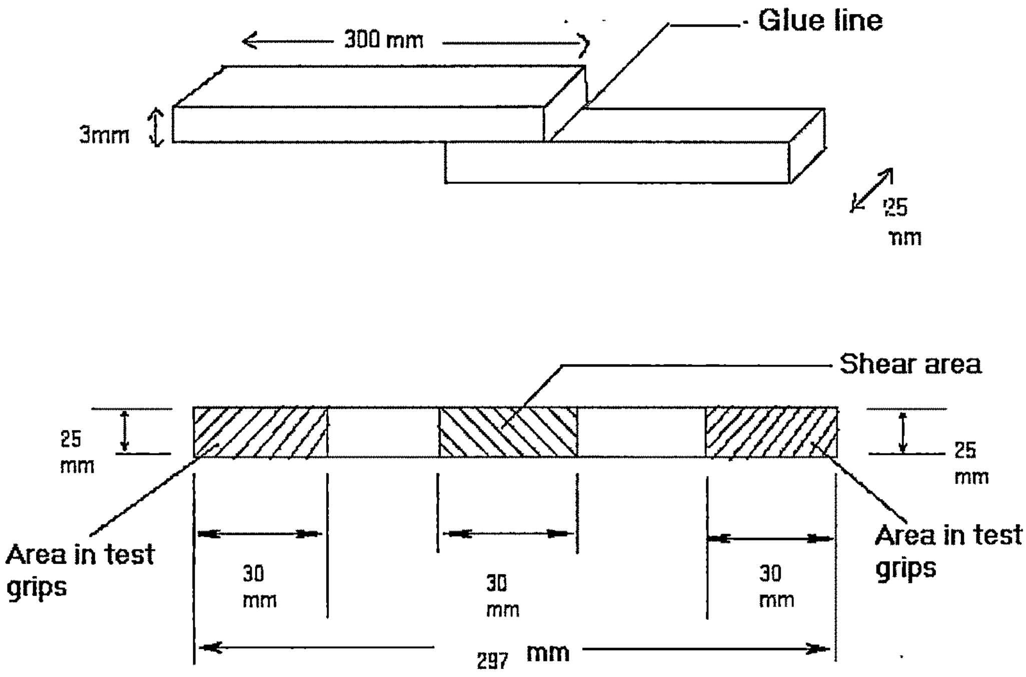

Figure 2 Schematic diagram of the lap-shear

4.3.2 Adhesive preparations:

Preparations of adhesives were carried out by reacting polyester polyol with either the aromatic isocyanate adduct or aliphatic isocyanate adduct, along with the dibutyltindilaurate, (0.05% w/w of total composition). The compositions were of various NCO/OH ratios. The composition and designation codes of the adhesive systems are shown in Table 1. The adhesives were diluted by methyl ethyl ketone, to give an appropriate viscosity for effective application on to the wood strips.

4.3.3 Wood to wood bonding:

Using a brush, the adhesive solution was applied on both pieces of the wood strips for a thickness of 0.1mm and a lap joined giving 25 ×30 mm^2 area of overlap. A load (2.5 kg) was placed over the contact points of wood pieces and left overnight. After that, the wood joints were kept at room temperature (30 ^{0}C) and at a relative humidity of 50 ± 5 % for seven days.

Testing of bond strength (Lap shear strength):

Each wood joint specimen was tested for lap shear strength using a Zwick UTM model 1445 with the crosshead speed 0.1m/mm according ASTM D 906-82 (1987). At least five replicate specimens were used for each test and averages of five were reported followed by indicating of variance amongst different test samples.

4.4 RESULTS AND DISCUSSION:

4.4.1 Gel Time

The gel time or pot life is an important property of adhesive systems, with respect to their application, as this indicates the maximum time during which the system remains in a fluid state for use. The results, shown in Table 1 indicate that the adhesives containing an aromatic isocyanate adduct gelled (cured) faster than the aliphatic isocyanate adduct. Also as the NCO/OH ratio in each formulation increased, curing time decreased. The adhesive composition A -Aro 3 cured faster compared to all other compositions synthesized in this study. This was because of the presence of higher NCO/OH ratio (1.7), as well as the higher hydroxyl value of polyol A in A -Aro 3.

4.4.2 Effect of presence of different polyols in Polyurethane adhesives and NCO/OH ratio on adhesion:

The lap shear strengths of all the systems were determined and the results are shown in Table 2 It was found that the lap shear strengths of the systems initially increases with increase in NCO/OH ratio, but then decreased at much higher NCO/OH ratios. As the NCO/OH ratio increased (i.e. greater cross-link density), the rigidity and strength of the adhesive bond increases. However, beyond a critical value, increase in NCO/OH ratio increased the stiffness, which is responsible for decrease in adhesion strength. Among all the systems for a particular NCO/OH ratio in PU adhesive, the chain length of the polyol increased from polyol A to polyol C. Polyols A, B, C were synthesized from ethylene glycol, diethylene glycol and triethylene glycol, respectively. The presence of the shorter chain length in polyol A resulted in a decrease in molecular weight between two crosslink points and increase in crosslink density, whereas the presence of ethylene oxide linkages in polyol B and C increased the flexibility and distance between two crosslink points. Both these factors were responsible for higher lap shear strength of polyol A, compared to polyols B and C. The system A-Aro2 having a NCO/OH ratio of 1.3 was found to exhibit the best adhesive performance.

Table 1: *Designation code and composition of Adhesive and Gel time of adhesives.*

Type of Polyol	Type of Isocyanate Adduct	Designation of Adhesive composition code	NCO/OH ratio	*Amount of polyol (g.)	*Amount of Isocyanate Adduct (g.)	Gel time at 30 ^{0}C (min.)
Polyol A	Aromatic	A-Aro 1	1	3.52	6.48	115
	Aromatic	A-Aro 2	1.3	2.95	7.05	110
	Aromatic	A-Aro 3	1.7	2.43	7.57	100
	Aliphatic	A-Ali 1	1	4.18	5.82	235
	Aliphatic	A-Ali 2	1.3	3.56	6.44	210
	Aliphatic	A-Ali 3	1.7	2.97	7.03	203
Polyol B	Aromatic	B-Aro 1	1	3.86	6.14	130
	Aromatic	B-Aro 2	1.3	3.26	6.74	120
	Aromatic	B-Aro 3	1.7	2.70	7.30	110
	Aliphatic	B-Ali 1	1	4.53	5.47	235
	Aliphatic	B-Ali 2	1.3	3.89	6.11	230
	Aliphatic	B-Ali 3	1.7	3.28	6.72	195
Polyol C	Aromatic	C-Aro 1	1	4.69	7.00	135
	Aromatic	C-Aro 2	1.3	4.05	7.84	120
	Aromatic	C-Aro 3	1.7	3.42	8.67	115
	Aliphatic	C-Ali 1	1	4.22	4.78	240
	Aliphatic	C-Ali 2	1.3	4.01	5.89	200
	Aliphatic	C-Ali 3	1.7	3.89	7.48	180

*In all system the composition with 0.05% dibutyltindilautrate added as a catalyst.

However, in the PU adhesive systems containing the aliphatic isocyanate adducts, as the NCO/OH ratio increased, the lap shear strength showed a little decrease. Comparative studies of PU adhesives containing aliphatic isocyanate adducts and different polyols indicate, that the PU system containing A Ali 1 showed a better lap shear strength compared to all other systems under investigation. Lap shear strength of these castor oil based adhesives was found to be ten times greater than that for the commercially available wood adhesives.

4.4.3 Comparison with commercial adhesives:

Synthesized PU adhesives were also compared with some of the commercially available wood adhesives in INDIAN market

Adhesives	**Supplier Name**
A	Dunlop Adhesives
B	Superbond adhesive
C	Dentrite adhesives
D	Fevibond adhesive

The lap shear strengths of these adhesives were compared to our synthesized PU adhesives in Table 3. The lap shear strength of these commercial adhesives was mentioned in other reference [24]

The resulting data are shown in Table 3. The synthesized adhesives were found to have better adhesive strength then the adhesive most commonly used for wood bonding in India.

Table 2 : *Lap shear strength of Adhesives.*

systems	Polyol with aromatic isocyanate adduct having NCO/OH ratio	Lap shear strength (N/m^2 X10 $^{5)}$		Lap shear strength (N/m^2 X 10 $^{5)}$	Polyol with aliphatic isocyanate adduct having NCO/OH ratio	systems
A-Aro 1	1	93.0		13.1	1	A-Ali 1
A-Aro 2	1.3	96.7		12.3	1.3	A-Ali 2
A-Aro 3	1.7	94.3		13.8	1.7	A-Ali 3
B-Aro 1	1	70.7		6.5	1	B-Ali 1
B-Aro 2	1.3	90.4		7.5	1.3	B-Ali 2
B-Aro 3	1.7	77.3		8.6	1.7	B-Ali 3
C-Aro 1	1	56.3		<5.2	1	C-Ali 1
C-Aro 2	1.3	82.5		6.3	1.3	C-Ali 2
C-Aro 3	1.7	73.3		7.2	1.7	C-Ali 3

Table 3 : *Comparison with commercial available adhesive.*

Adhesives	Lap shear strength (N/m^2 X 10$^{5)}$
A	*7.5*
B	*3.4*
B	*13.4*
D	*7.5*
A-Aro 2	96.7
B-Aro 2	90.4
C-Aro 2	82.5

4.4.4 Effect on Chemical Resistance

Wood pieces bonded with the adhesives, prepared from different polyols with aromatic isocyanate adducts, were kept in cold water (30 ^{0}C) for 24 h and then dried at room temperature for 24 h. Lap shear strength was determined as mentioned earlier. Similarly, bonded pieces were immersed in hot water (100 ^{0}C) and in acid solution (pH 2) and alkali solution (pH 10) both at 80 ^{0}C for one h and then dried at room temperature for 24h. After immersion, lap shear strength was determined. The results are shown in Table 4. The results indicate good resistance to both cold and hot water. The acid solution (pH 2) had a negative effect on adhesion, because polyester is easily hydrolyzed in the presence of acid, resulting in deterioration in adhesive strength. In the alkali solution (pH 10) the adhesion decreased to some extent in terms of lap shear strength, probably because of alkaline hydrolysis.

Table 4: *Lap shear strength of different Adhesive after soaking in chemicals.*

System	NCO/OH	Lap shear strength (N/m^2 X10 $^{5)}$ (Before)	After treatment Lap shear strength (N/m^2 X10 $^{5)}$			
			Cold water	Hot water	Acid Solution pH 2	Alkali solution pH 10
A-Aro 1	1	92.9	91.7	904	39.3	68.1
A-Aro 2	1.3	96.9	96.9	95.6	49.8	78.6
A-Aro 3	1.7	94.3	93.0	91.0	44.5	65.5
B-Aro 1	1	70.7	70.7	68.1	13.9	44.5
B-Aro 2	1.3	90.4	90.4	86.4	26.2	65.5
B-Aro 3	1.7	77.3	77.4	72.0	20.9	52.4
C-Aro 1	1	56.3	56.3	52.4	11.8	26.2
C-Aro 2	1.3	82.5	82.3	74.6	18.4	52.4
C-Aro 3	1.7	73.3	73.3	65.5	13.1	39.3

4.4.5 Study of green strength and curing time

Green strength is one of the important properties of the adhesives. It shows the ability of an adhesive to hold the substrates together when brought into contact and before the adhesive develops ultimate stronger properties with full cure. It is the strength measured before complete curing of adhesive i.e. before achievement of ultimate strength. For these purposes, different polyols with aromatic isocyanate adduct having a NCO/OH ratio of 1.3 was selected. The curing properties of these PU adhesives were monitored using lap shear strength tests for a number of days. The results (shown in Table 5), indicate that over a period of time, the lap shear strength increased up to seven days and beyond which, it leveled off. This may be due to the ongoing cross-linking processes during storage.

Table 5 : *Green Strength of Adhesives*

No of Days	Lap shear strength (N/m^2 X10 $^{5)}$		
	A-Aro 2	B-Aro 2	C-Aro 2
1.	6.5	5.2	5.2
2.	13.1	15.7	18.3
3.	26.2	36.7	39.3
4.	44.5	51.1	55.0
5.	68.1	76.0	78.6
6.	78.6	87.7	81.2
7.	94.7	90.4	82.5
10.	97.0	90.4	82.5
15.	98.2	89.1	82.5
30.	96.9	90.4	82.5

Polyurethane Adhesives for metal to metal Bonding:

4.5. EXPERIMENTAL:

A series of acrylated polyol differing in their hydroxyl value were selected for PU synthesis. Polyurethane was synthesized by reacting different acrylated polyol with aromatic isocyanate and R60 isocyanate with different NCO/OH ratio. Designation codes of Adhesive were shown in Table 6.

4.5.1. Adhesive power measurements

The lap shear strength of adhesion for metals was measured according to standard method using tensile tester. The shape and dimensions of the test specimens used in this experiment are shown in Fig. 3 The dimensions of the test specimen were as per ASTM D 1002. Metal surface (mild steel) was cleaned with a detergent. The recommended area of overlap is (12.7 mm ± 0.5 mm) X (25.4 mm ±0.5 mm) and thickness 1.62mm ± 0.1mm [25]. The resin was applied as thin layer (nearly 0.03 mm thickness) over required area on the surfaces of both pieces to be joined for comparison of the adhesives strength, the flow times of all the resins were kept the same. The surfaces were joined and cured at room temperature and 2.5 kg pressure and left overnight. Then the shear force was applied by a tensile testing machine (Shimadzu AG 100KGN) and the adhesive strength was measured as the breaking load/shear area.

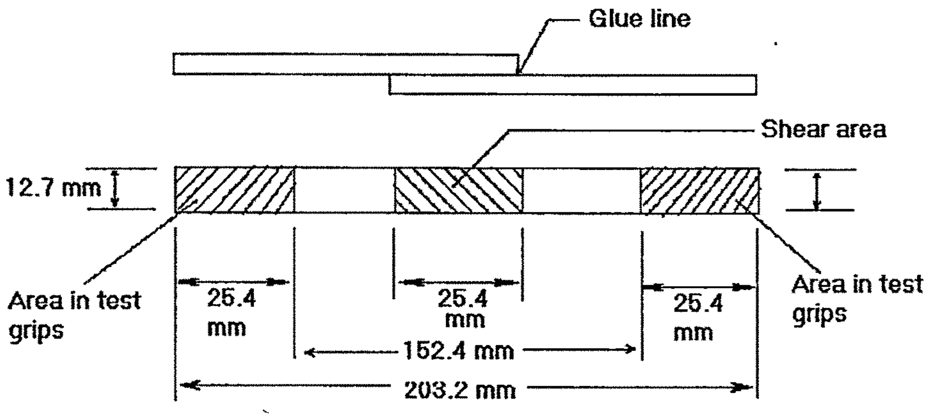

Figure 3 Schematic diagram of the lap-shear test

4.6. RESULTS AND DISCUSSION:

4.6.1 Gel Time

The gel time or pot life is an important property of adhesive systems, with respect to their application, as this indicates the maximum time during which the system remains in a fluid state for use. The results, shown in Table 6 indicate that the adhesive containing an aromatic isocyanate adducts gelled (cured) faster than the R 60 isocyanate adduct. Also as the NCO/OH ratio in each formulation increased, curing time decreased. Increase in the percentage of acrylated polyol also decreased the gel time. The adhesive composition E18 -Aro 3 cured faster compared to all other compositions synthesized in this study. This was because of the presence of higher NCO/OH ratio (1.7), as well as the higher hydroxyl value of acrylated polyol.

Table 6 : *Composition code of acrylated polyol and Gel time of adhesive system.*

Type of Polyol	Type of Isocyanate Adduct	Designation of Adhesive composition code	NCO/OH ratio	Gel time at 30 ^{0}C (min.)
EpxR Polyol (0% acrylated) (0%)	Aromatic	E-Aro 1	1	105
	Aromatic	E-Aro 2	1.3	99
	Aromatic	E-Aro 3	1.7	94
	R 60	E-R 60- 1	1	135
	R 60	E-R 60- 2	1.3	125
	R 60	E-R 60- 3	1.7	112
5% Acrylatyed polyol (5%)	Aromatic	E5-Aro 1	1	86
	Aromatic	E5-Aro 2	1.3	78
	Aromatic	E5-Aro 3	1.7	70
	R 60	E5-R 60- 1	1	130
	R 60	E5-R 60- 2	1.3	112
	R 60	E5-R 60- 3	1.7	89
10% Acrylatyed polyol (10%)	Aromatic	E10-Aro 1	1	85
	Aromatic	E10-Aro 2	1.3	72
	Aromatic	E10-Aro 3	1.7	68
	R 60	E10-R 60-1	1	109
	R 60	E10-R 60-2	1.3	99
	R 60	E10-R 60-3	1.7	80
15% Acrylatyed polyol (15%)	Aromatic	E15-Aro 1	1	75
	Aromatic	E15-Aro 2	1.3	68
	Aromatic	E15-Aro 3	1.7	58
	R 60	E15-R 60-1	1	97
	R 60	E15-R 60-2	1.3	86
	R 60	E15-R 60-3	1.7	70
18% Acrylatyed polyol (18%)	Aromatic	E18-Aro 1	1	58
	Aromatic	E18-Aro 2	1.3	48
	Aromatic	E18-Aro 3	1.7	35
	R 60	E18--R 60-1	1	89
	R 60	E18-R 60-2	1.3	60
	R 60	E18-R 60-3	1.7	48

4.6.2 Effect of presence of different acrylated polyols in Polyurethane adhesives and NCO/OH ratio on adhesion

From the Table 7a and 7b, we can conclude that acrylated polyol with R 60 isocyanate adduct show good results compared to using aromatic isocyanate adduct. In both cases, the EpxR polyol contents of 2-hydroxy ethyl methacrylates (HEMA) were increased (from 0 to 18%) then the lap shear strength increased as NCO/OH ratio was increased. But at higher content of acrylated (>15% of HEMA) homogeneous cleavages of adhesives were seen which showed cohesive failure of adhesives.

In case of R 60 isocyanate adduct, NCO/OH increase in ratio increased the adhesive strength. If higher percentage of HEMA and higher NCO/OH ratio were taken a brittle layer of adhesive was formed hence the bond cleavage easily with applied load. The result of adhesives is at NCO/OH ratio equals to 1.3.

In case of aromatic isocyanate adduct, NCO/OH ratio was increased then lap shear strength was found to decrease because of more and more compact structure of adhesive was formed in networks. It formed a very brittle structure hence it caused deterioration of its the strength. The best results of adhesives is at NCO/OH ratio equal to 1.

Table 7a: *Adhesives power measurements for metal to metal bonding Acry lated polyol with Aromatic isocyanate adduct having different NCO/OH ratio.*

Acrylated polyol (%)	With Aromatic Isocyanate Adduct Lap Shear strength (MPa)		
	NCO/OH ratio		
	1	1.3	1.7
0	1.05	0.75	0.65
5	1.4	1.1	0.9
10	1.6	1.55	1.3
15	1.9	1.30	0.89

Table 7b: *Acrylated polyol with aromatic isocyanate adduct having different NCO/OH ratio.*

Acrylated polyol (0%)	With R 60 Isocyanate adduct Lap shear strength (MPa)		
	NCO/OH ratio		
	1	1.3	1.7
0	0.40	0.60	0.70
5	1.15	1.95	0.90
10	2.15	2.80	1.56
15	5.12	5.80	5.15

4.7 CONCLUSIONS

Adhesives were prepared from three different polyols with different isocyanate adducts. Adhesives made from the polyol and aromatic isocyanate adduct, gave superior bonding strength for wood-to-wood specimens. The adhesives made from polyol A of higher hydroxyl value with an aromatic isocyanate adduct having a NCO/OH ratio 1.3 gave excellent lap shear strength compared to other homologous adhesive systems and was found ten times higher than with commercially available wood adhesives. PU adhesives synthesized from polyol A and aromatic isocyanate adduct showed good adhesion strength and chemical resistance as there is no ether linkages in the networks, while ether linkages in polyol B and C, is some what responsible for lower adhesion strength value and chemical resistance.

The adhesive strength of acrylated polyol with different isocyanate adduct were measured. Adhesive strength was found to increase by increasing the percentage of HEMA in polyol. Also NCO/OH ratio was responsible for increasing adhesive strength of metal to metal bonding. Comparison between adhesive strength of metal to metal bonding, using R 60 isocyanate adduct and Aromatic isocyanate adduct, the former showed better results, while aromatic isocyanate adduct show poor results because it formed a brittle layer of adhesive film in between metal substrates. Cohesive failure of adhesive was observed, which decreased the adhesive strength for metal to metal bonding.

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