Chapter 3

Polyurethane Coatings

3.1 PREVIEW:

This chapter we divide in two parts Part A, polyurethane coatings form polyester polyol and Part B, polyurethane coatings form castor oil and epoxy resin. In this chapter we present the formulation of the polyurethane coating systems and the determination of the various coatings properties by standards method and also a comparison with each other. At the end of chapter we also studied the thermal stability of all polyurethanes by thermogravimetric analysis.

[A] Polyurethane coatings from polyester polyols:

3.2 INTRODUCTION:

Over the last few years, reduction of organic solvents usage [1] has been a matter of great importance for paints and its applications technologies because of the restrictions imposed by environmental pollution agencies and users all over the world. This has caused a shift in attentions from conventional organic solvent based coating to water borne, powder coating, radiation cured coating and high solid coatings. In recent years, high solid coatings are gaining importance to comply well in keeping the environment clean. The polyurethanes have better mechanical and chemical properties. Castor oil based Polyurethanes have been extensively used as coatings and in network synthesis [2-5]. Varying a chain length of prepolymer with low viscosity and 100 percent solid content varies the crosslink density of network over a wide range. In general coating with 70% or above solids can be considered as high solid coatings [6]. Castor oil based polyols have great potential to be good reactive diluents.

Polyurethanes made from a variety of drying oils have been known for many years [7]. A low viscosity castor oil derivative was developed to improve flexibility and impact strength. Several authors have reported formulations of polyurethane coatings from modified oils. GüngÖr et al synthesized oil modified water borne polyurethane resin for high build coatings [8]. Pires et al formulated coating compositions for two pack polyurethane coatings [9]. Peshana et al synthesized oil modified polyurethane for cross-linkable, low VOC complainant and cost effective coatings [10]. In the present chapter, an attempt is made to report on the preparation of the high solid PU coatings from castor oil based polyols.

3.3 EXPERIMENTAL:

The various sets of polyurethane coatings were prepared from the polyester polyols (Polyol A , Polyol B and Polyol C) by adding required amount of aromatic isocyanate adducts, aliphatic isocyanate adducts with or without catalyst at room temperature. The NCO/OH ratio variations were taken into account, as shown in Table 1. Then PU resin was diluted with suitable solvents to have viscosity for appropriate application of coating with brush on cleaned mild steel and tin panels. These coatings were applied on test panels and the coating films were allowed to dry at room temperature for seven days to ensure complete curing.

3.4 CHARACTERIZATIONS OF POLYURETHANE COATINGS:

The polyurethane coatings were characterized for their various physical properties like viscosity, pot life, adhesion, flexibility, hardness, impact resistance, chemical resistance and solvent resistance by standard procedure. The coatings were also characterized by IR spectroscopy. Thermal properties of the polyurethane coatings were studied by TGA.

3.4.1 Thermal Analysis:

Thermogravimetry Analysis (TGA):

Thermal stability and activation energy of these synthesized polyurethanes were determined by Thermogravimetry analysis.

Thermogravimetry (TG) monitors the weight changes in a sample as a function of temperature. It is also considered to be one of the most important methods for studying polymer stability. It gives information concerning the thermal stability of intermediate compounds and the compositions of the residue.

Shimadzu model 3310 and Universal V3.OG TA thermogravimetry analyzer was used in the present study to record the thermogram of polymer samples. About 5 to 10 mg of the polymer sample was weighed in the boat of a thermo balance and was subjected to heating at a 10^0C/ min heating rate in air. The continuous trace of loss in weight of a sample as a function of temperature gave a TG themogram, which was used further for data analysis.

Broido's method for the analysis of TGA data:

When a polymeric substance is heated beyond some limit, it undergoes degradation. It is assumed that degradation products are volatile. The progress of the degradation can be observed by continuous weighing of the sample. The weight of the sample at time (t) is related to the fraction (y) of the number of initial molecules not yet decomposed by the following relation:

$$y = \frac{N}{N_0} = \frac{(W_t - W_\infty)}{(W_0 - W_\infty)} \qquad \text{..............................(i)}$$

where,

W_0 = initial weight of the sample

W_t = weight of the sample at temperature T ^{0}C

W_∞= weight of the resiude at completions of the reaction

If the degradation is carried out, isothermally, the rate of reaction is given by

$$\frac{dy}{dt} = -k.\ y^n \qquad \text{.................................(ii)}$$

where, n = order of the reaction

The rate constant 'k' changes with absolute temperature according to Arrhenious equations

$$k = A\ .\ e^{-E/RT} \qquad \text{..............................(iii)}$$

From equations (ii) and (iii), are can write

$$\frac{dy}{y^n} = -\ k\ .\ dt \ \text{.....................................(iv)}$$

$$= -A\ .\ e^{-E/RT}\ .\ dt \ \text{..........................(v)}$$

If, instead of operating the reaction isothermally, the reaction is operated at increasing temperature and if temperature and if temperature (T) is a linear function of a time (t) and if the rate of heating β, then

$$T = To + \beta t \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(vi)}$$

$$dT = \beta \, . \, dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(vii)}$$

From equations (v) and (vii), it follows:

$$\frac{dy}{y^n} = -\left(\frac{A}{\beta}\right) . \, e^{-E/RT} \, . \, dT \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(vii)}$$

The thermogravimertic curve of such a relation represents this rate equation integrated form a temperature To at which y = 1. Thus

$$\int_{y}^{1} \frac{dy}{y^n} = -\left(\frac{A}{\beta}\right) \int_{To}^{T} e^{-E/RT} \, . \, dT \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(ix)}$$

A large number of degradation processes are known to be first order reaction. As n = 1 , the integration of L.H.S. part is simple.

$$\int_{y}^{1} \frac{dy}{y^n} = \int_{y}^{1} \frac{dy}{y} = -\ln y = \ln\left(\frac{1}{y}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(x)}$$

Conversely, the integration of the R.H.S. part of equations of (ix) are not simple. Vallet [11] has reported the values of integrations of the terms like that involved in equations (ix.). From these data, the value of integrations of L.H.S. term was obtained by Broido [12]. van Krevelen and co-workers [13] revealed that the entire measurable reaction usually occur within ±10 % of the temperature of maximum reaction velocity (T_{max}). They applied a certain approximation and obtained the following relations.

$$\ln \ln \left(\frac{1}{y}\right) = \left(\frac{E}{R} . T_m^2 + 1\right) \ln T + \text{constant} \ldots\ldots\ldots\ldots (xi)$$

According to equation (xi) a plot of ln ln(1/y) versus T yields a straight line whose slope is related to energy of activation. Horowitz and Metzer [21] introduced two alteranate approximations and developed relations (xii) and (xiii)

$$\ln \ln \left(\frac{1}{y}\right) = \left(\frac{E}{R\,T_m^2}\right) T + \text{constant} \ldots\ldots\ldots\ldots (xii)$$

$$\ln \ln \left(\frac{1}{y}\right) = - \left(\frac{E}{R}\right) \left(\frac{1}{T}\right) + \text{constant} \ldots\ldots\ldots\ldots (xiii)$$

the expression xiii, was found to be more accurate than equations (xi) and (xii). It was employed in the present work to calculate the activation energy (Ea) of thermal degradation of the polyurethanes from TG thermograms.

3.5 RESULTS AND DISCUSSION:

3.5.1 Viscosity and Pot life:

The viscosity data (Table 1) of the polyurethane coatings reveal that the viscosity of polyurethane coating compositions made from polyol A, B, and C respectively were quite low as compared to the conventional polyurethane coatings having similar solid contents. For a given NCO/OH ratio, the viscosity of the coating based on polyol A is lower than the remaining compositions based on polyols B and C. This could be attributed to the lower molecular weight of polyol A.

Polyurethane coating composition with polyol A as well as the composition with catalyst dibutyl tin dilaurate (DBTDL) showed lower pot lives compared to other compositions. This is a typical behavior of two pack system with more number of functional groups.

3.5.2 Drying properties.:

Times of surface dry, hard dry and tack free dry of various sets are reported in Table 1 as they give indications of drying time of the film after its application. The results show that polyol A dried faster than polyol C for a given isocyanate adduct and NCO/OH ratio. The coating compositions with aromatic isocyanate adduct as curing agent showed faster drying. This may be because of higher reactivity of their NCO groups with OH groups. The drying speeds of the coating films are also accelerated by catalyst.

3.5.3Mechanical properties:

- *Flexibility test and Adhesion test:*

Flexibility of all the systems were tested on tin panels by bending 1/8' mandrel. The results are shown in Table 2

Adhesion test of coated materials was observed by cross hatch. A crosshatch adhesion test was conducted according to standard method to determine unacceptable adhesion.

Results show that all panels have almost 100% adhesion in all the systems, i.e. film did not get removed from the coated panels. This indicates that system has good adhesion properties.

- *Impact Resistance and Scratch Hardness:*

A tabular impact tester tested impact resistance of dried film of all the systems on mild-steel panels. The results of this test are shown in Table 2.

The results show that when the indenter hits to panels from maximum height, systems having higher NCO/OH ratio, some sign of crack and film detachment are observed. Comparison of the system containing aliphatic and aromatic isocyanate adducts, particularly at higher NCO/OH ratio (1.3 and 1.7) shows low impact strength which may be due to the rigidity of aromatic structure of the adduct.

Scratch hardness of the dried film of all the systems were measured on ms panels with a mechanically operated "Sheen" scratch hardness. From the results it can be inferred that all the compositions were found to show good scratch resistance. This may be due to higher crosslink density in the coating resulted from the more number of functional group.

Table 1: Composition and Physical Properties of Polyurethane Coatings.

Designation of coating compositions code		Type of Isocyanate Adduct	Amount of polyol gms.	Amount of Isocyanate Adduct gms.	Ratio NCO/OH	Viscosity@ by FC B - IV secs. at 30 °C	Potlife at 30 °C hrs.	Drying properties		
								Surface Drying (min)	Tack free Drying h.	Hard Drying ~12h.
Polyol A	AAL1	ALI	41.8	58.2	1	21	4.5	25	3.0	O/N
	AAL2	ALI	35.6	64.4	1.3	27	4.5	35	3.0	O/N
	AAL3	ALI	29.7	70.3	1.7	34	4.5	35	2.5	O/N
	AAR1	ARO	35.2	64.8	1	31	4.0	20	2.0	O/N
	AAR2	ARO	29.5	70.5	1.3	42	3.5	15	2.0	O/N
	AAR3	ARO	24.3	75.7	1.7	57	3.0	15	2.0	O/N
	AAL1$_C$	ALI	41.8	58.2	1	21	4.0	15	1.5	O/N
	AAR1$_C$	ARO	35.2	64.8	1	31	2.0	8.0	1.0	O/N
Polyol B	BAL1	ALI	45.3	54.7	1	25	3.0	30	3.0	O/N
	BAL2	ALI	38.9	61.1	1.3	38	6.0	30	2.5	O/N
	BAL3	ALI	32.8	67.2	1.7	49	5.5	35	2.5	O/N
	BAR1	ARO	38.6	61.4	1	41	5.5	20	2.5	O/N
	BAR2	ARO	32.6	67.4	1.3	64	5.0	20	2	O/N
	BAR3	ARO	27.0	73.0	1.7	73	4.5	15	2	O/N
	BAL1$_C$	ALI	45.3	54.7	1	25	2.5	18	1.5	O/N
	BAR1$_C$	ARO	38.6	61.4	1	41	4.0	12	1.0	O/N
Polyol C	CAL1	ALI	46.9	53.1	1	38	4.5	40	4	O/N
	CAL2	ALI	40.5	59.5	1.3	50	7.0	45	4	O/N
	CAL3	ALI	34.2	65.8	1.7	62	6.5	50	5	O/N
	CAR1	ARO	46.9	53.1	1	42	6.0	15	2	O/N
	CAR2	ARO	40.5	59.5	1.3	65	6.0	15	2	O/N
	CAR3	ARO	34.2	65.8	1.7	79	5.5	10	2	O/N
	CAL1$_C$	ALI	46.9	53.1	1	38	3.5	15	2.5	O/N
	CAR1$_C$	ARO	46.9	53.1	1	42	4.5	13	1.5	O/N

ALI – Aliphatic Isocyanate adduct. ARO-Aromatic Isocyanate adduct.
A(AL1)c-The composition with 0.05% Dibutyl tin di laurate(DBTDL) catalyst.
@ 75% solids in xylene: MEK, 1:1 by weight. O/N over Night

Table 2: Adhesion, Scratch Resistance, Flexibility, Impact resistance and Pencil Hardness of the coating films.

Composition Code	Adhesion (cross-hatch)	Flexibility 1/8″ bending mendrel	Scratch Resistance g.	Impact resistance lb.in.	Pencil hardness[@]
AAL1	P	P	1500	300	2H
AAL2	P	P	2000	100	2H
AAL3	P	F	2000	100	1H
AAR1	P	P	2500	200	3H
AAR2	P	F	3000	50	3H
AAR3	F	F	3500	50	4H
BAL1	P	P	2000	300	1H
BAL2	P	P	2000	200	1H
BAL3	P	F	2500	200	1H
BAR1	P	P	2500	200	2H
BAR2	P	P	3500	50	4H
BAR3	F	F	3500	50	5H
CAL1	P	P	2500	300	1H
CAL2	P	P	3000	200	1H
CAL3	P	P	3000	200	1H
CAR1	P	P	2500	200	2H
CAR2	P	P	3500	50	4H
CAR3	P	F	3500	50	5H

[@] 6H>5H>4H>3H>2H>1H>H>HB>1HB>2HB>3HB>4HB>5HB>6HB.

- *Pencil Hardness:*

A coated panel was placed on a flat horizontal surface and pencil was held at an angle 45° to the film. The pencil was pushed away from the operator in a 1/4" stroke. The pencil, which did not cut the film, denotes its hardness. The coating of test formulations whose pencil hardness was measured at 27 °C is reported in Table 2.

Results indicate that irrespective of the type of glycol at given NCO/OH ratio, aromatic system show better pencil hardness compared to aliphatic system. This may be due to increase in the rigidity provided by more crosslinked structure.

3.5.4 Water and chemical resistance:

All of the experimental polyurethane coating compositions showed no effect on the films when immersed in water for specified time period. It clearly reflects the characterized water resistance property of the polyurethane coatings. The acid and alkali resistance of the polyurethane coatings was found to be good. However coating compositions with higher NCO/OH ratio (systems CAR 3, CAL 3, AAR 3, BAR 3) showed better acid and alkali resistance due to higher crosslink density. The results are shown in Table 3.

3.5.5 IR Spectra:

In the spectra of polymeric film (Fig.1), the characteristic carbonyl stretching of urethane linkage was observed at 1735 cm^{-1}, indicating the presence of a urethane linkage. The absorption resulting from N-H stretching and bending vibrations was observed at 3330 cm^{-1} and 1560 cm^{-1} respectively.

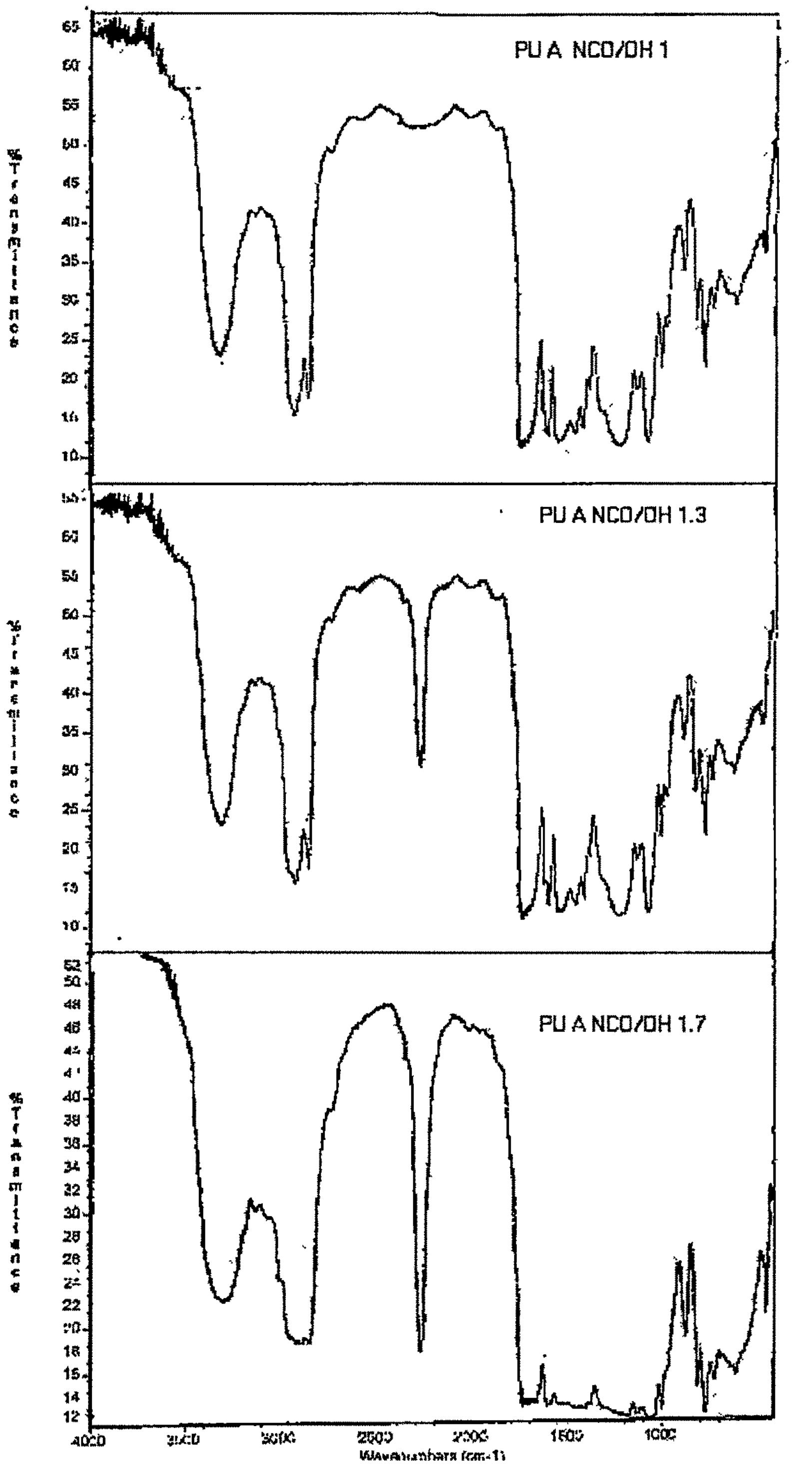
The band observed at 2273 cm^{-1} indicated the presence of unreacted NCO in the higher NCO/OH ratio samples (i.e. 1.3 and 1.7). The expected structures of the PU coating films were confirmed by FTIR spectroscopy. Fig 1 were FTIR spectra of PU A having NCO/OH ratio 1, 1.3 and 1.7 respectively. The formation of PU is clearly indicated, due to the absence of an -OH absorbance band associated with the polyol and the presence of a -NH band of PU.

Table 3: Chemical resistance and corrosion resistance of the coating films.

Coating compositions code	Acid Resistance 5% H_2SO_4 solution	Alkali Resistance 5% NaOH solution	Corrosion resistance 10% NaCl solution
AAL1	2	4	P
AAL2	3	5	P
AAL3	5	3	P
AAR1	4	5	P
AAR2	5	2	P
AAR3	5	3	P
BAL1	1	2	P
BAL2	2	5	P
BAL3	3	5	P
BAR1	4	2	P
BAR2	4	3	P
BAR3	5	4	P
CAL1	1	4	P
CAL2	4	5	P
CAL3	4	5	P
CAR1	2	4	P
CAR2	4	5	P
CAR3	5	5	P

0-film completely removed
1-film cracked and partially removed
2-film partially cracked
3-loss of gloss
4-slight loss of gloss
5-practically film unaffected .P-Pass, F-Fail

Fig 1: FTIR spectra of PU A having NCO/OH ratio 1, 1.3 and 1.7



3.5.6 Thermogravimetry:

Thermal studies of PUs were carried out in air up to 700^{0}C to observe the effect of

i) different polyol used in PU

ii) different isocyanates adduct used in PU

iii) crosslink density of PU

iv) Chain length of polyol used in PUs ,

on their thermal stability. Initial decompositions temperature (IDT) and other analysis of thermograms are given in Tables 4. Thermogram of PUs show degradation takes place in two stages. However they are not well distinct. Stage one may correspond to the urethane bond breaking which starts at 250^{0}C (lower NCO/OH ratio 1) leading to formations of carbon dioxide, alcohols, amines, aldehydes, carbon monoxide etc. [15,16] and stage two may be due to the polyol decompositions which occurred at ~ 375 ^{0}C to ~ 400 ^{0}C . Since polyols used in this study are based on castor oil, the main chain scission may occur with the formations of 10 undecanoic acid and heptanal as evidenced by the thermal degradations of ricinoleic acid [17].

In case of different polyols, chain length of polyol increases than activations energy is increases, while using different isocyanates adduct, aromatic isocyanate adduct used in PUs shows more activation energy compared to aliphatic isocyanate adduct used for the synthesis of PUs. Even though thermal stability of PUs made from aromatic isocyanate adduct more stable up to 400 ^{0}C compared to aliphatic isocyanate adduct. 50% weight loss of all PUs are show above 350 ^{0}C, so that PU is thermally stable.

The initial decompositions temperature and the % weight loss at different temperature, maximum decompositions temperature (T_{max}), temperature at which 50% weight loss occurred (T_{50}) and integral procedural temperature (IPDT) are presented in Table 1. Integral procedural decompositions temperature of this polyurethane was calculated by well-known Doyle's method [18]. Thermogram of PUs from polyols (A, B, C) with aromatic isocyanate adduct having NCO/OH ratio 1 shown in Fig 2. Thermogram of Polyol A and B with aliphatic isocyanate adduct having NCO/OH ratio 1 are shown in Fig.3and4.respectively.

Table 4 : Activation Energy(Ea) , IDT, IPDT, T_{max} , T_{50} of Polyurethanes.

Sr. No.	Sample code	IDT [a] (°C)	% weight loss at different Temperature			T_{max} [b] (°C)	T_{50} [c] (°C)	IPDT [d] (°C)	Ea (kJ/mole)
			250	350	400 °C				
1	A-Aro -1	310	1.5	2.5	12.0	542	575	399	71.3
2	A-Ali –1	278	5.0	18.0	50.9	463	390	448	48.9
3	B-Aro -1	290	2.0	4.0	8.5	520	-	406	79.8
4	B- Ali- 1	296	4.5	25.0	56.2	446	398	473	58.4
5	C-Aro -1	300	1.5	3.0	9.0	528	512	411	94.6
6	C-Ali –1	285	5.3	28.0	54.2	453	390	494	67.4

a = Initial Decomposition Temperature ^{0}C
b = Temperature at which maximum decompositions
c = Temperature at which 50% weight loss occurred
d = Integral procedural decompositions temperature

This castor oil based PUs showed two stage degradations; this can be shown in plots of derivatives weight (%) vs. temperature of the PU. The plot (Fig 5) of derivative weight (%) vs Temperature of PU from polyol A with aliphatic isocyanate adduct having NCO/OH ratio 1. This clearly indicates that castor oil based Polyurethane showed two stage decompositions on heating.

Fig 2: Thermogram of PUs from polyols (A, B, C) with aromatic isocyanate adduct having NCO/OH ratio 1

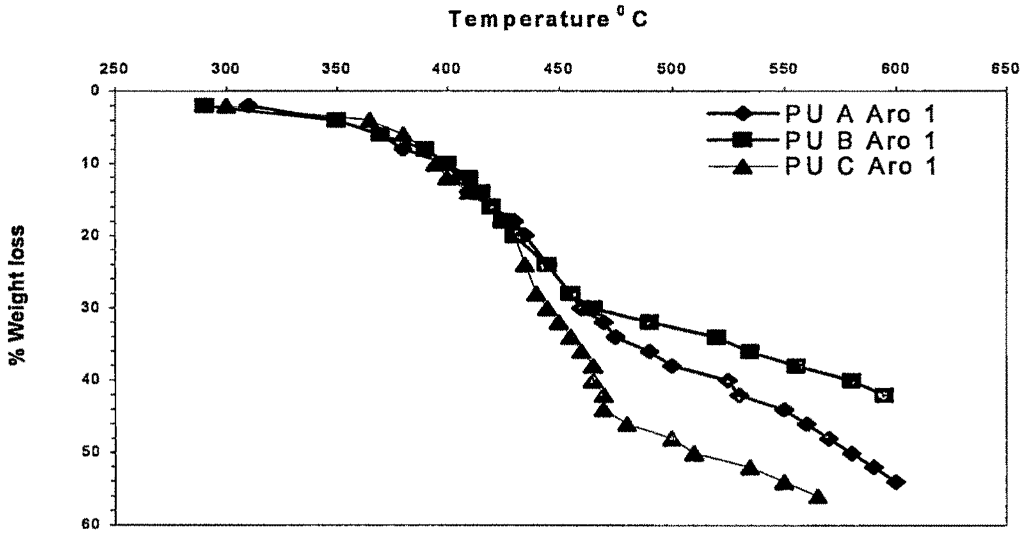


Fig 3 : Thermogram of Polyol A with aliphatic isocyanate adduct having NCO/OH ratio 1

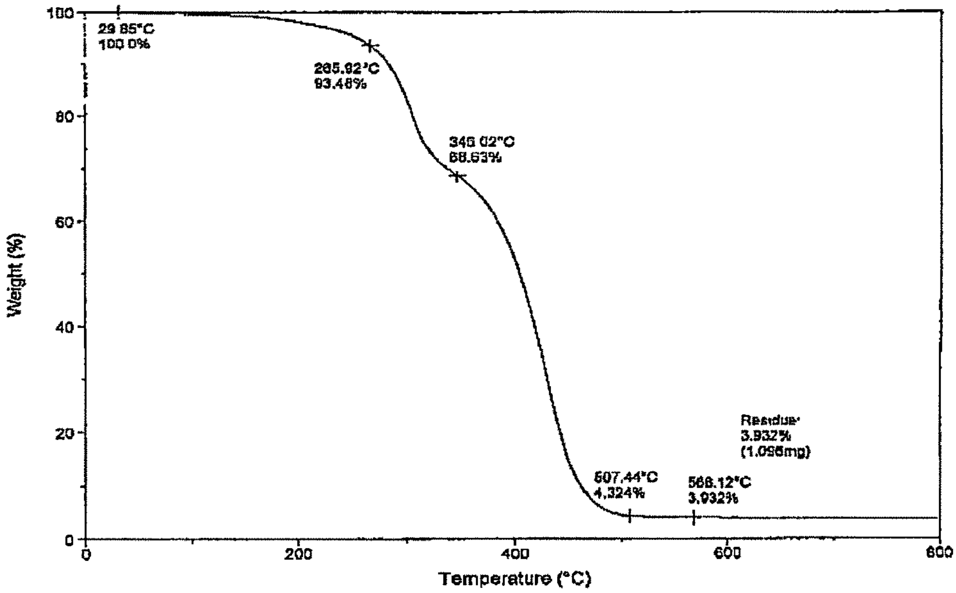


Fig 4 : Thermogram of Polyol B with aliphatic isocyanate adduct having NCO/OH ratio 1

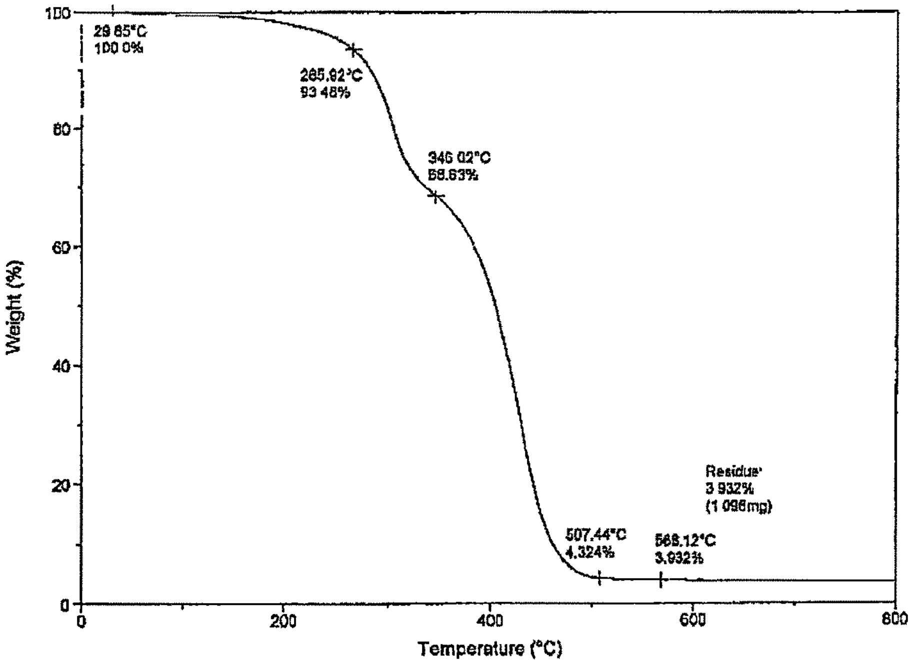
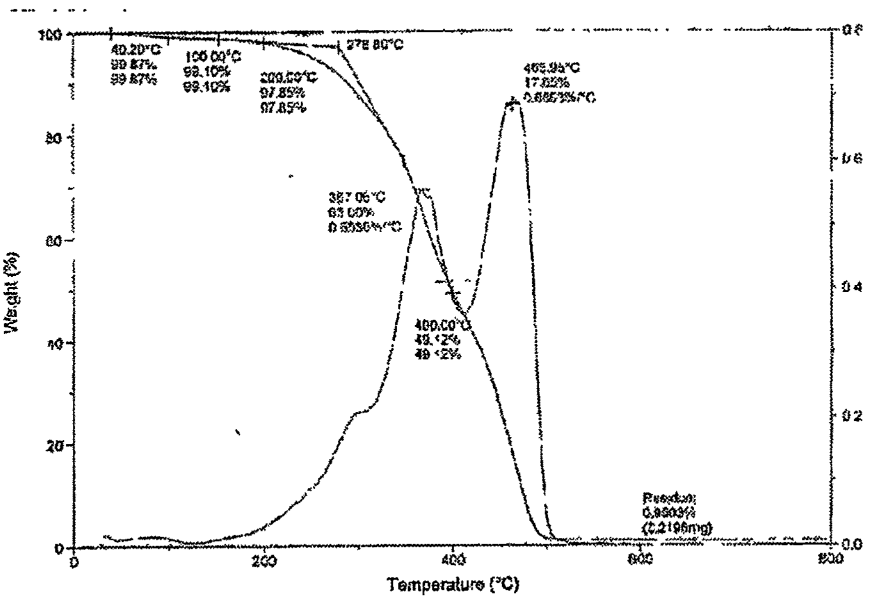


Fig 5 : Thermogram of derivatives weight (%) vs. temperature of the PU from polyol A with aliphatic isocyanate adduct having NCO/OH ratio 1.



3.6 CONCLUSIONS:

The high solids two pack polyurethane coatings were made successfully from the castor oil based polyols. The various polyurethane coating compositions with different ratio of NCO/OH, type of polyol, type and amount of isocyanate adduct were studied for their physical and film performance properties. The study reveals the findings like, (i) the presence of catalyst accelerates the drying properties of polyurethane coatings, (ii) lower amount of curing agent gives better flexibility and impact resistance, higher amount of curing agents gives better scratch hardness, chemical and water resistance, (iii) the aliphatic isocyanate curing agents containing coating films gave better flexibility and impact resistance than the coating containing aromatic adduct.

From the overall study we can conclude that the high solids polyurethane coating with castor oil based polyols and aliphatic isocyanate adduct (NCO/OH 1.3) and aromatic isocyanate adduct (NCO/OH 1) gave optimum film performance.

[B] Polyurethane coatings from Novel polyol (EpxR) :

3.7 INTRODUCTION

Majority of coating films exists in the form of three-dimensional polymer network produced by crosslinking of resins. Polyurethane is one of the most versatile resins. Literature survey indicates extensive use of polyols such as polyether polyol and polyester polyol along with diisocyanate for polyurethane. However the demand of biodegradability stresses the use of renewable sources. Castor oil based polyurethane have been extensively studied as coatings and in network synthesis [19,20]. Because of low reactivity of castor oil, focus has been directed to its derivatives. In view of this, a main constituent of castor oil i.e. ricinoleic acid which posses secondary hydroxyl functionality is frequently utilized in the synthesis of polyurethanes [21]. Ricinoleic acid having free carboxyl group, which is highly reactive, was selected in combination with epoxy resin to overcome disadvantages of epoxy coatings like brittleness, poor scratch resistance at higher temperature [22]. The venture of synthesizing novel polyol for polyurethane coating was carried out with the aim to have polyurethane of better mechanical and chemical properties compared to polyurethane of polyester polyol derived from different glycol's and ricinoleic acid as was done earlier in part A.

3.8 EXPERIMENTAL

3.8.1 Preparation of Polyurethane Coating

Synthesis of polyurethane for coatings was carried out by reacting novel polyol with respective isocyanates (aromatic isocyanate, aliphatic isocyanate, R-60 isocyanate adducts) with or without catalyst at room temperature. The NCO/OH ratio variations were taken into account, as shown in Table 5. Then PU resin was diluted with suitable solvents to have viscosity for appropriate application of coating with brush on cleaned mild steel and tin panels. The coated panels were examined for impact resistance, scratch hardness, and pencil hardness, flexibility test, chemical resistance and adhesion test as per standard procedure.

3.9 RESULTS AND DISCUSSION

3.9.1 Drying Characteristics

After application of polyurethane films the panels were kept in a vertical position for air-drying. Drying times were observed of all coated panel systems. Results indicates (Table 4) that catalyst increases the rate of cross-linking in all the cases as expected.

3.9.2 Flexibility

Flexibility test of all the system panels was done on tin panels by bending mendrel 1/8″ as per standard method. Results are shown in Table 6, which indicates that system B of coated panels have good flexibility compared to coated panels with systems A and C. Because of more aliphatic nature of isocyanate adduct in system B, it provides flexible nature to the film. On the other hand system A coatings are more rigid due to aromatic nature of diisocyanate adduct. The results also indicate that the increase in NCO/OH ratios in systems A and C along with aromatic nature of isocyanate adduct increase the cross-linking density resulting into increase in rigidity as expected and hence flexibility decreases. Thus higher NCO/OH ratio gives poor results in flexibility test in all the systems.

3.9.3 Adhesion

Adhesion test of coated materials was by cross hatch adhesion conducted according to standard method to determine unacceptable adhesion. All systems show almost 100 % adhesion. This extra ordinary adhesion can be attributed to strong dipole-dipole interaction as well as H-bond formation possibility between substrate and adhesive coating which arises due to the presence of –NH, -CO and O groups in the systems. However in case of relative increase of NCO/OH ratio where there is high cross linking, it becomes progressively more difficult for adhesive to interact with the substrates.

3.9.4 Scratch hardness

From the results in the Table 6 it can be inferred that compare to system A and B, system C has good hardness because of the combination of aromatic and aliphatic moieties in adduct, which provides higher degree of cross linking and uniformity of network.

Table 5: Composition and coding of coating system.

Designation of Coating system	Type of Isocyanate Adduct	Ratio NCO/OH	Potlife at 30 ^{0}C (min.)	Amount of Polyol g.	Amount of Isocyanate Adduct g.
A1	Aromatic	1.0	240	24.3	33.6
A2	Aromatic	1.3	205	24.3	43.5
A3	Aromatic	1.7	150	24.3	57.12
B1	Aliphatic	1	360	24.3	25.5
B2	Aliphatic	1.3	390	24.3	33.15
B3	Aliphatic	1.7	420	24.3	43.35
C1	R-60	1.0	300	24.3	42.5
C2	R-60	1.3	255	24.3	55.25
C3	R-60	1.7	180	24.3	72.25
A1C	Aromatic	1.0	105	24.3	33.6
A2C	Aliphatic	1.0	210	24.3	25.5
A3C	R-60	1.0	135	24.3	42.5

Note: A1C, A2C, and A3C are catalyst system (DBTDL were added 0.05% w/w with their total composition.)

Table 6: Performance of coating properties.

Composition Code	Adhesion Crosshatch	Flexibility 1/8"bending mendrel	Impact Resistance lb.inch	Scratch Hardness g.	Pencil Hardness
A1	P	P	200	3500	3H
A2	P	F	100	4000	3H
A3	F	F	150	4500	4H
B1	P	P	300	2000	1H
B2	P	P	350	2500	1H
B3	P	P	350	3500	1H
C1	P	P	350	4000	3H
C2	P	P	300	3500	3H
C3	F	F	200	3000	2H
A1C	P	P	200	3500	3H
A2C	P	P	300	2000	1H
A3C	P	P	350	4000	4H

P = Pass

F = Fail

3.9.5 Pencil hardness

The results (Table 6) show that system A coated panel has good pencil hardness compared to systems B and C coated panels. As the NCO/OH ratio increases the pencil hardness also increases in system A, B and C of coated panels. Systems of coated panels with catalyst show maximum hardness, because the catalyst increases the crosslink density compared to systems without using catalyst.

3.9.6 Water and Chemical Resistance

All the system panels were immersed in distilled water, 5% NaOH, 5% H_2SO_4 and 10% NaCl solution at room temperature. Results, shown in Table 7, indicate that all compositions of systems of dipped coated panels show no effect of water and also show good overall chemical resistance. However at higher NCO/OH ratio it shows better resistance even for acids, because it provides higher cross linking density and allowing low permeation and diffusion of chemicals.

3.9.7. IR Spectra:

In the spectra of polymeric film (Fig 6), the characteristic carbonyl stretching of urethane linkage was observed at 1735 cm^{-1}, indicating the presence of a urethane linkage. The absorption resulting from N-H stretching and bending vibrations was observed at 3330 cm^{-1} and 1560 cm^{-1} respectively.

The formation of PU is clearly indicated, due to the absence of a -OH absorbance band associated with the polyol and the presence of a -NH band of PU.

3.9.8 Thermogravimetry:

Thermal studies of PUs were carried out in air up to 700^{0}C to observe the effect of

i) different isocyanates adduct used in PU ii) crosslink density of PU on their thermal stability. Initial decompositions temperature (IDT) and other analysis of thermograms are given in Tables 8.

PUs synthesized from EpxR show more stability compared to other polyester polyols discussed earlier .This polyol (EpxR) with different isocyanate adduct shows activation energy above 70 kJ/mole. While in case of using R 60 isocyanate adduct shows good thermal stability. If NCO/OH ratio increases then crosslink density increases so more and more crosslinkd structure formed, hence activation energy decreases. Results show that activation energy decreases with increase in NCO/OH ratio.

Thermograms PU from Polyol (EpxR) with different isocyanate adduct having NCO/OH ratio 1 shown in Fig 7 and polyol (EpxR) with R60 isocyanate adduct having different NCO /OH ratio shown in Fig 8.

Fig 6: FTIR spectrum of PU film (EpxR polyol with R60 isocyanate adduct having NCO/OH ratio 1).

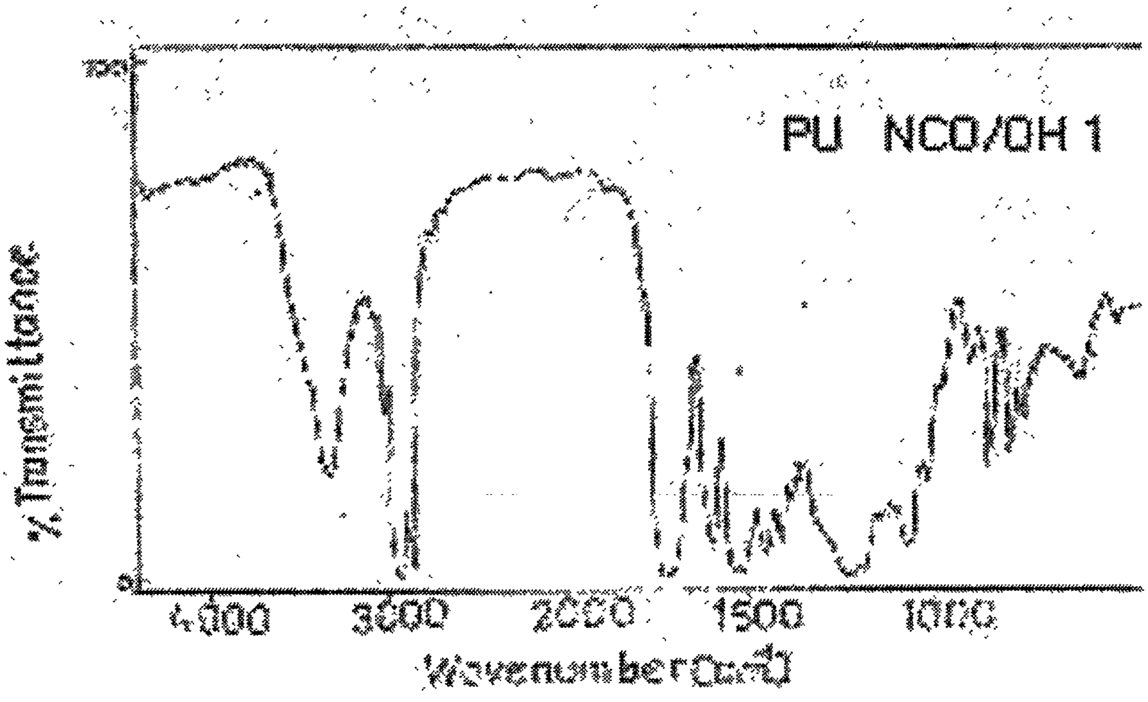


Table 7: Chemical Resistance of coated panels.

Coating Composition	Acid Resistance 5% H_2SO_4 soluton	Alkali Resistance 5% NaOH soluton	Corrosion Resistance 10% NaCl soluton
A1	3	4	P
A2	4	5	P
A3	5	5	P
B1	2	3	P
B2	3	4	P
B3	4	5	P
C1	5	5	P
C2	5	6	P
C3	6	6	P
A1C	4	5	P
A2C	3	4	P
A3C	5	6	P

2 film partially cracked

3 loss of gloss

4 slight loss of gloss

5 practically film unaffected

6 no effect

P-Pass

Table 8 : Activation Energy(Ea) , IDT, IPDT, T_{max} , T_{50} of Polyurethanes.

Sr. No.	Sample code	IDT [a] (°C)	% weight loss at different Temperature			T_{max} [b] (°C)	T_{50} [c] (°C)	IPDT [d] (°C)	Ea (kJ/mole)
			250	350	400 °C				
1	Epx Aro 1	345	1.25	2.0	3.0	580	560	549	76.6
2	Epx Ali 1	345	1.25	2.0	3.5	570	545	499	78.9
3	Epx R60 1	350	0.75	2.0	12.0	480	530	436	72.6
4	Epx R60 2	360	1.25	1.8	4.0	505	590	377	67.1
5	Epx R60 3	375	2.75	5.0	5.0	-	398	368	51.2

a = Initial Decomposition Temperature ^{0}C
b = Temperature at which maximum decompositions
c = Temperature at which 50% weight loss occurred
d = Integral procedural decompositions temperature

Fig 7 : Thermograms PU from Polyol (EpxR) with different isocyanate adduct having NCO/OH ratio 1

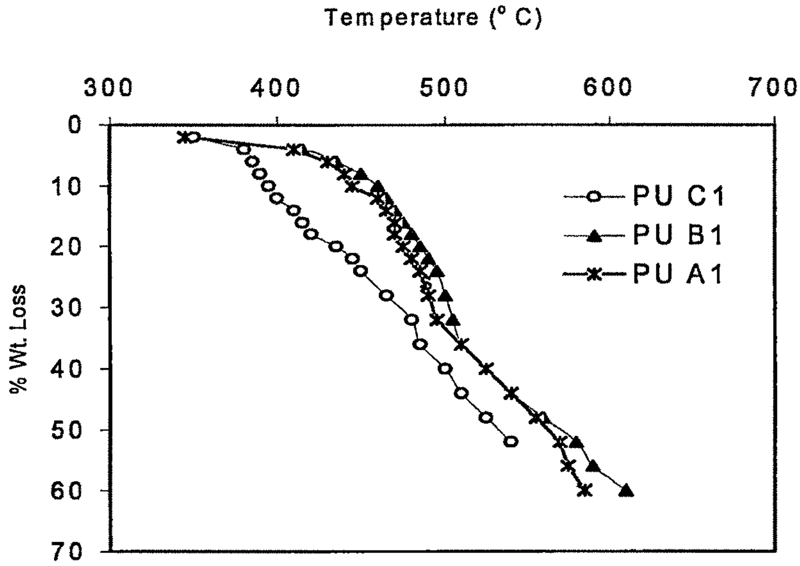
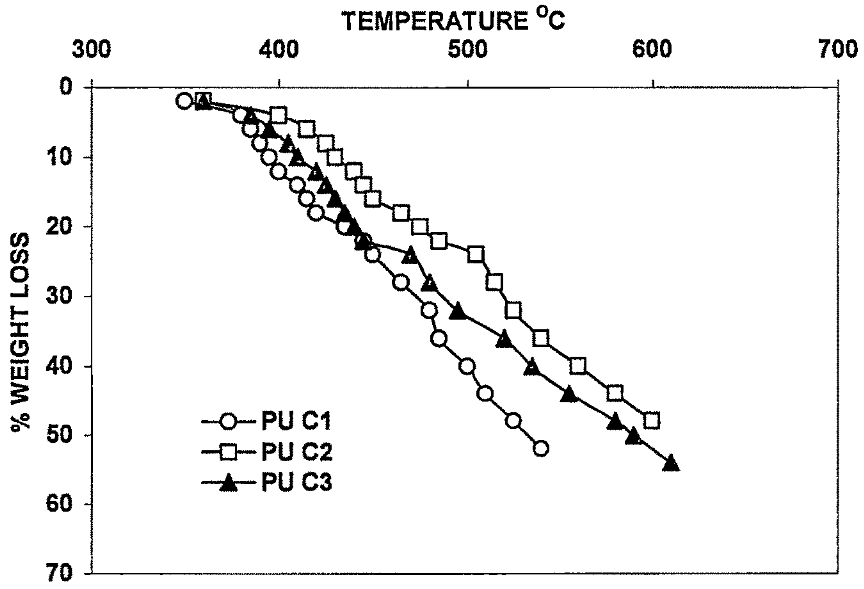


Fig 8: Thermogram of polyol (EpxR) with R60 isocyanate adduct having different NCO /OH ratio



3.10 CONCLUSIONS

All coating composition systems reported show good scratch resistance and good adhesion on substrate. Use of catalyst enhances the mechanical properties of coating systems at the cost of adhesion. The polyurethane systems containing aromatic isocyanate adduct show more brittleness and less impact strength than their aliphatic isocyante adduct.

System containing castor oil based adduct (R-60 isocyanate adduct) have good impact strength, good scratch resistance and excellent chemical and water resistance, compared to aromatic isocyanate adduct. Drying time of catalyst containing coating system is lower than one without catalyst. PUs synthesized from EpxR show more stability

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