Two component polyurethane coatings from Toluene Diisocyanate and epoxy polyol

J.TENNISANTHUVAN
Department of Science & Humanities,
Karur,Tamilnadu, India.

M.EASURAJA
Department of Science & Humanities,
Karur,Tamilnadu, India.

S.AUGUSTINRAJ
Department of Science & Humanities,
Karur,Tamilnadu, India.

Abstract : Polyurethane coatings are formed from a chemical reaction between a polyol and a polyisocyanate hardener. Two component solvent based polyurethane coatings were prepared by blending of epoxy polyol and Toluene Di Isocyanate hardener. By keeping the ratio of Epoxy Polyol consistent and by changing the ratio of TDI from 0.80 to 1.20, a total of seven types of experiments were conducted. All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of TDI. After the film coated with the prepared polyurethane coatings, the various physical properties and mechanical properties were measured and compared. The Electrochemical Impedance Spectroscopy was used for the characterization of the coated film. The formation of the polyol was supported by FTIR spectral data.

Keywords*: Epoxy polyol, Isocyanate hardener, FT IR, Properties, ElectrochemicalImpedanceSpectroscopy*

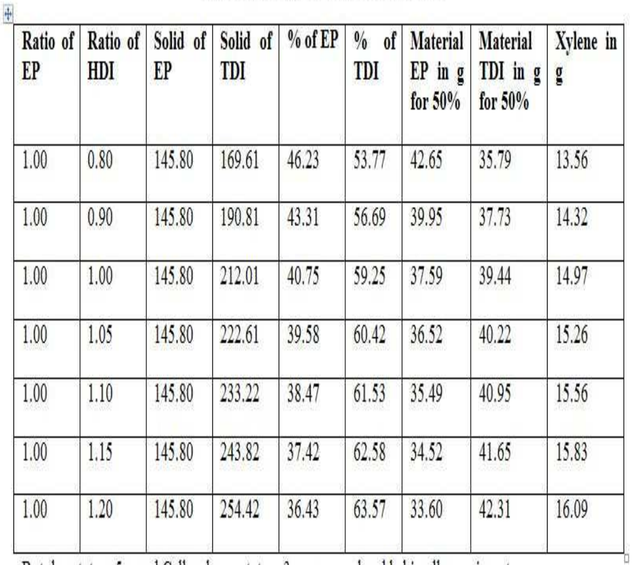
I. INTRODUCTION

The chemical structure of epoxy resins gives them high chemical resistance against a wide range of severe corrosive conditions [1]. These properties are derived from the aromatic nature of the backbone and good chemical stability of the phenolic ether linkage. Two component polyurethanes (PU) have found extensive applications in the coating industry mainly because they exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance and a wide range of mechanical strength[2-4]. Polyurethane coatings are formed from a chemical reaction between a polyol and a polyisocyanate hardener[5]. Among the common commercially available polyols for two components PU systems are hydroxyl functional polyester, acrylics, polyether and polyols. Hydroxyl-terminated polyurethane (HTPU) prepolymer and crystalline polymer particles were used to modify the toughness of diglicidyl ether of bisphenol-A (DGEBA)epoxy cured with diaminodiphenyl sulphone(DDS) having the improved toughness property as reported by Huei-Hsiung Wang et al[6]. Lizhi-hua et all study the structural characteristics and properties of polyurethane modified TDE85 (Diglycidyl-4,5-epoxy cyclohexane-1,2-dicarboxylate)/ MeTHPA (Methyl tetrahydrophalic anhydride) epoxy resin with interpenetrating networks[7]. Jong-Shin Park [8] prepared and investigates the mechanical properties PU films using starch as main polyol component with Toluene Diisocyanate (TDI) for various polyol starch content and NCO/OH molar ratio. Cardopolyester polyol has been synthesized by reacting epoxy resin of 1, 1 bis (3Methyl 4 Hydroxy phenyl) cyclohexane and recinoleic acid by PH Parsania[9]) for their industrial importance as coating and adhesive materials. In the present work, we developed in our laboratory hydroxyl terminated epoxy systems as epoxy polyol resin. Two component polyurethane coatings were prepared by blending of epoxy polyol and Toluene diisocyanate (TDI) hardener. Seven types of experiments were conducted by keeping the ratio of Epoxy polyol constantly and changing the ratio of TDI from 0.80 to 1.20. All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of TDI. After the film coated with the prepared polyurethane coatings, the various physical properties and mechanical properties were measured and compared. Electrochemical Impedance Spectroscopic (EIS) is a non-destructive technique useful for examining the corrosion performance of coated metals exposed to aqueous environments. Many researchers discussed corrosion performance of the polyurethane coating by using the EIS technique [10-17]. Hence the optimized polyurethane coated film is analyzed by using the EIS tool. The formation of the polyol was supported by FTIR spectral data.

II. EXPERIMENTAL ANALYSIS

Materials - Epoxy resin GT 6071-X75(Diglycidyl ether of Bisphenol-A Type, Epoxy equivalent weight 501 g/Eq and solids 75% in Xylene) from M/S Ciba Gaey – Mumbai, Diethanol amine from Spectrum Baroda, Xylene, cellosolve acetate and butyl acetate from E-Merck, Toluene diisocyanate (TDI) Desmodur L75% from M/S Bayer chemicals. A three neck flask (500 ml), equipped with a mechanical stirrer, condenser and a Thermometer was placed in a water bath. One mole of di-epoxy resin GT 6071-X75-(266.67g), and two moles of Diethanolamine (42 g) were placed in a three neck flask. Then Cellosolve acetate (40 g) and Xylene (93.33 g) was added as solvents to carry out the reaction and stirred well at room temperature for 5 minutes. Gradually the temperature increases from 60°C to 70°C to open up the oxirane ring of epoxy resin to generate secondary alcohol. The reaction mixture was refluxed for 6 Hrs with stirring. The transparent secondary hydroxyl terminated epoxy polyol resin was transferred to air tight bottle.

Table 1. Formulation for the experiments

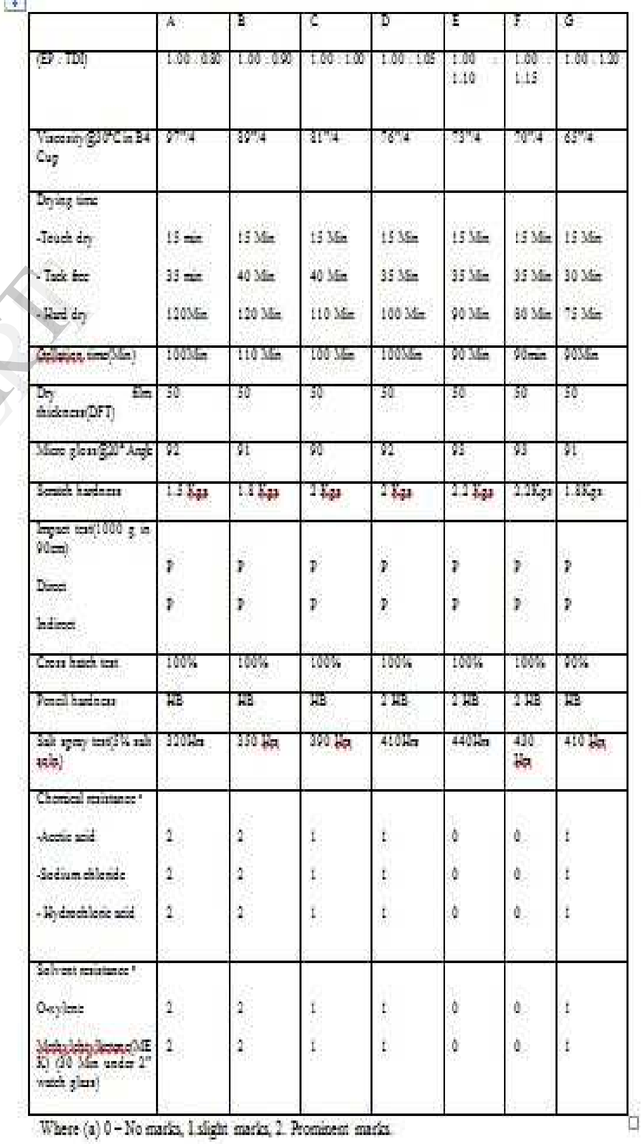


Ratio of EP	Ratio of HDI	Solid of EP	Solid of TDI	% of EP	% of TDI	Material EP in g for 50%	Material TDI in g for 50%	Xylene in g
1.00	0.80	145.80	169.61	46.23	53.77	42.65	35.79	13.56
1.00	0.90	145.80	190.81	43.31	56.69	39.95	37.73	14.32
1.00	1.00	145.80	212.01	40.75	59.25	37.59	39.44	14.97
1.00	1.05	145.80	222.61	39.58	60.42	36.52	40.22	15.26
1.00	1.10	145.80	233.22	38.47	61.53	35.49	40.95	15.56
1.00	1.15	145.80	243.82	37.42	62.58	34.52	41.65	15.83
1.00	1.20	145.80	254.42	36.43	63.57	33.60	42.31	16.09

- Butyl acetate – 5 g and Cellosolve acetate – 3 g commonly added in all experiments.

*Chemical compositions***:**The coatings industry needs analytical methods that allow the assessment of coating characteristics before and after their exposure to a wide variety of service conditions. This assessment may help to predict the service life time of a coating material or to verify when it meets requirements for a particular application and/or commercialization [18]. To a 100 ml beaker containing Epoxy polyol resin (37.59g), TDI hardener (39.44 g), Butyl acetate (5.00g),Cellosolve acetate(3.00g) and Xylene(14.97g) (Xylene, Butyl acetate and Cellosolve acetate used as solvents for PU coatings) at room temperature and stirred manually for ten minutes as 1 : 1 ratio (OH/NCO ratio). The outcome of the result, the Polyurethane solution, was taken for the rest of our experiments**.** By keeping the ratio of Epoxy Polyol consistent and by changing the ratio of TDI from 0.80 to 1.20, a total of seven types of experiments were conducted and tabulated at Tab.1**.** All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of TDI. Total solids of all experiments were taken as 50% solids. The test solution was thoroughly mixed just before the application of their films on to mild steel panels. Films were applied with varying wet film thickness, such that the dried films of all the compositions had a thickness of approximately 50 microns measured by using a magnetic thickness gauge. The films were allowed to cure at ambient conditions (Room temperatue30 °C and relative humidity of approximately 50-60%) for at least 48 Hrs before tests for mechanical and chemical properties were carried out. Compositions were tested for their pot life by checking for the rise in their viscosity after mixing the two components at an interval of 20 min until the value approximately double the initial value at ambient temperature. Films were tested for drying time (ASTM D 5895), Micro Gloss (IS 101- Testing of paints – Part 4 – Optical test Section 4-Gloss), Scratch hardness (IS 101 – Testing of paints – Part 5-Mechanical test on paint films Section 1 – Hardness test, Pencil hardness [19], Cross hatch adhesion (ASTM D 4752), impact resistance (ASTM D 2794-92) and salt spray test (ASTM B 117). Solvent resistant and Chemical resistance of the films was studied by the spot test for 30min under 2" watch glass. After the film coated with the prepared polyurethane coatings, the various physical properties and mechanical properties were measured and tabulated in Tab.2. The FT IR spectra were taken and interpreted for Epoxy polyol resin on KBr pellets and recorded using BomemMichelson series Spectrophotometer.

Table 2 : Characteristics of the formulated experiments.



	A	B	C	D	E	F	G
(EP : TDI)	1.00 : 0.80	1.00 : 0.90	1.00 : 1.00	1.00 : 1.05	1.00 : 1.10	1.00 : 1.15	1.00 : 1.20
Viscosity@30°C in B4 Cup	97"/4	89"/4	81"/4	76"/4	73"/4	70"/4	65"/4
Drying time							
-Touch dry	15 min	15 Min	15 Min	15 Min	15 Min	15 Min	15 Min
- Tack free	35 min	40 Min	40 Min	35 Min	35 Min	35 Min	30 Min
- Hard dry	120Min	120 Min	110 Min	100 Min	90 Min	80 Min	75 Min
Gellation time(Min)	100Min	110 Min	100 Min	100Min	90 Min	90min	90Min
Dry film thickness(DFT)	50	50	50	50	50	50	50
Micro gloss@20° Angle	92	91	90	92	93	93	91
Scratch hardness	1.5 Kgs	1.8 Kgs	2 Kgs	2 Kgs	2.2 Kgs	2.2Kgs	1.8Kgs
Impact test(1000 g in 90cm)							
Direct	P	P	P	P	P	P	P
Indirect	P	P	P	P	P	P	P
Cross hatch test	100%	100%	100%	100%	100%	100%	90%
Pencil hardness	HB	HB	HB	2 HB	2 HB	2 HB	HB
Salt spray test(5% salt soln)	320Hrs	350 Hrs	390 Hrs	410Hrs	440Hrs	430 Hrs	410 Hrs
Chemical resistance ᵃ							
-Acetic acid	2	2	1	1	0	0	1
-Sodium chloride	2	2	1	1	0	0	1
- Hydrochloric acid	2	2	1	1	0	0	1
Solvent resistance ᵃ							
O-xylene	2	2	1	1	0	0	1
Methylethylketone(MEK) (30 Min under 2" watch glass)	2	2	1	1	0	0	1

Where (a) 0 – No marks, 1.slight marks, 2. Prominent marks.

III. RESULTS AND DISCUSSION

FT IR Spectral analysis: IR spectrum of Epoxy polyol in Fig.1 showed the following bands,

3389.23 cm^{-1} – OH - Stretching, 3036.45 cm^{-1} – C-H bonding for aromatic carbon, 1475.60 cm^{-1} – Tertiary –C-C- stretching due to the presence of the above absorption bands in the spectra[20,21]it was conformed that the formation of the epoxy polyol resin.

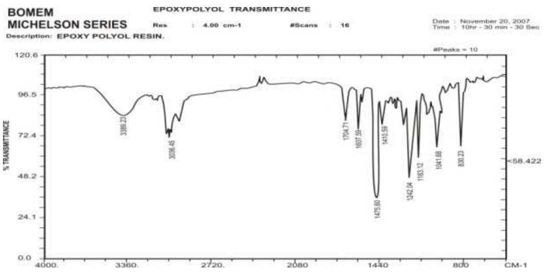


Fig-1. FT IR Spectra for Epoxypolyol Resin.

From the Tab.2, column A to G the NCO ratio is varied from 0.80 to 1.20. The experiment conducted without the catalyst DBTL (Dibutyltin dilaurate), Hatada et al[22] experimentally determined NCO group reactivity changes with catalyst and experimental conditions. The coatings prepared from epoxy polyol resin and isocyanate hardener showed a rapid drying character, pot life and good gloss. By practically, the viscosity parameter showed that experiment (G) gave a low viscosity due to the higher ratio of NCO. In hardness test experiment (G) fails to pass the test due to higher amounts of NCO in the composition are more brittle. More brittle coatings do not have the balance of hardness /flexibility desired from 'high performance coatings'. Hence experiment (G) is not to be considered due to low viscosity and fails to pass the hardness test. Experiment A fails in hardness test due to insufficient degree curing of the two components. Solvent and chemical resistance test, the lesser amounts of NCO are soluble in chemicals and solvents and the film fails to pass the test in experiment (A) & experiment (B) insufficient degree of curing. Salt spray test is the most popular laboratory accelerated test that has been used and accepted by many to compare the corrosion resistance of coatings. The test can also compare how resistant the film is to the transfer of sodium and chloride ions through it. As per the result in the table, 1: 1.1 and 1: 1.15 epoxy polyol and TDI ratio gave a comparatively more resistant film to the corrosive environment. J.W.Reisch et al[23] optimize the coating performance of polyurethane coatings prepared with the blends of polyisocyanates. The physical, mechanical and chemical resistance properties were used for the optimization. We took an Electro chemical impedance spectroscopy (EIS) tool for the above optimized ratios. *Electro chemical impedance spectroscopy (EIS):*An impedance measurements were carried out with the help of a PAR model 6310 EG & G instruments A.C. impedance analyzer at a frequency range from 10 MHz to 100 KHz. The Electrochemical cell used for the study consisted of a coated mild steel panel as the working electrode, a platinum foil as the counter electrode, a saturated calomel electrode as the reference electrode and a 3% NaCl solution as the electrolyte. The circuit as shown in Fig .2, consists of solution resistance (R_s), charge transfer resistance (R_t), coating capacitance (C_c) and double layer capacitance (C_{dl}) elements by fitting the EIS data to the circuit. Impedance measurements were carried out at different duration ranging from initial, one day, 10, 20,30,40,50 and 60 days. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) evaluated from bode plots for different duration for both coatings reported in Tab.3.

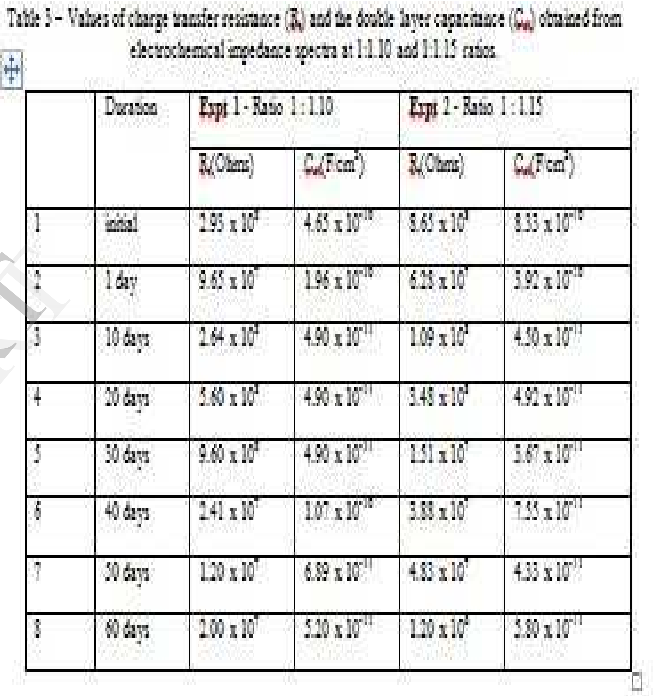


Table 3 – Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) obtained from electrochemical impedance spectra at 1:1.10 and 1:1.15 ratios.

	Duration	Expt 1 - Ratio 1 : 1.10		Expt 2 - Ratio 1 : 1.15	
		R_t(Ohms)	C_{dl}(F/cm^2)	R_t(Ohms)	C_{dl}(F/cm^2)
1	initial	2.95×10^{8}	4.65×10^{-10}	8.65×10^{8}	8.33×10^{-10}
2	1 day	9.65×10^{7}	1.96×10^{-10}	6.25×10^{7}	3.92×10^{-10}
3	10 days	2.64×10^{8}	4.90×10^{-11}	1.09×10^{8}	4.50×10^{-11}
4	20 days	5.60×10^{8}	4.90×10^{-11}	3.48×10^{8}	4.92×10^{-11}
5	30 days	9.60×10^{8}	4.90×10^{-11}	1.51×10^{7}	3.67×10^{-11}
6	40 days	2.41×10^{7}	1.07×10^{-10}	3.88×10^{7}	7.55×10^{-11}
7	50 days	1.20×10^{7}	6.89×10^{-11}	4.83×10^{7}	4.33×10^{-11}
8	60 days	2.00×10^{7}	5.20×10^{-11}	1.20×10^{8}	5.80×10^{-11}

From Tab.3, it can be seen the R_t values for the two experiments decreased from their initial value one day then they increased and attained almost a steady value after duration of 10 days [24]. The initial decrease in R_t values can be ascribed to the uptake of the electrolyte through the micro pores and capillaries in the coating. The increase in R_t values can be ascribed to the formation of a passive layer at the interface between the metal substrate and the coating. It has been proved that only coatings which show R_t values of 10^6 ohms cm^2 and more can be rated as protective to mild steel substrate from aggressive ions[25]. Although both experiments had R_t values more than 10^6 ohm, the coating in Expt1 showed much better value than the coating in Expt2, hence the outcome of Expt 1 was better than Expt 2[26]. Hence we have concluded that, the stokiometry of an OH-NCO ratio will be 1: 1.10 much better than 1:1.15 in epoxy polyol and Toluene diisocyanate reactivity product.

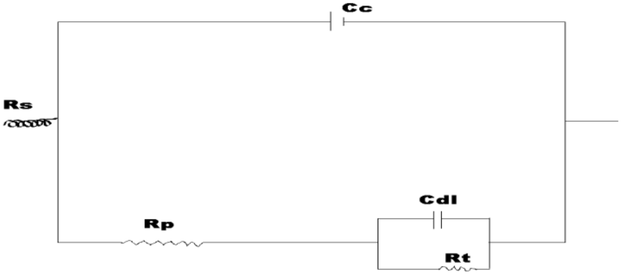


Fig. 2 – Schematic Diagrams of the Equivalent Circuit for Coated Panels

IV..CONCLUSIONS

Epoxy polyol can be synthesized by the reaction of epoxy resin and diethanolamine. The two component polyurethane coatings were prepared by blending with polyisocyanate, Toluene diisocyanate with these epoxy polyol resin. The prepared coatings showed a rapid drying character with 90-120 Min of pot life and good gloss level. The hydroxyl group and isocyanate group (OH / NCO) ratio of 1:1.10 and 1: 1.15 were optimized by comparing the other physical properties of polyurethane coatings such as Scratch hardness, Impact resistance, cross hatch test, chemical resistance and corrosion resistance. The optimized two combinations were analyzed and concluded that the stokiometry of 1: 1.10 of OH: NCO ratio was much better than 1: 1.15 ratio of mixing in epoxy polyol and Toluene diisocyanate reaction products by using the electrochemical impedance spectroscopy method.

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