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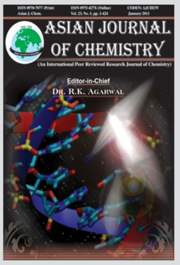

Synthesis and Characteristics of Two Component Polyurethane Coatings Based on Epoxy Polyol with Polyisocyanate

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Polyurethane coatings are formed from a chemical reaction between a polyol and a polyisocyanate hardener. Epoxy polyol resin was synthesized by reacting epoxy resin (diglicidyl ether of bisphenol A type), diethanolamine, cellosolve acetate and xylene at reflux temperature 60-70 ºC for 6 h. Two component polyurethane coatings were prepared by blending of epoxy polyol and hexamethylene diisocyanate (HDI) hardener. By keeping the ratio of epoxy polyol consistent and by changing the ratio of hexamethylene diisocyanate from 0.80-1.20, 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 isocyanate equivalent weight of hexamethylene diisocyanate. After the film coated with the prepared polyurethane coatings, various physical properties and mechanical properties were measured and compared. The electrochemical impedance spectroscopy (EIS) was used for the characterization of the coated film. The formation of the polyol was supported by FTIR spectral data.

Key Words: Epoxy polyol, Isocyanate hardener, FT IR, Properties, Electrochemical impedance spectroscopy.

INTRODUCTION

Coatings that have the properties to perform well in the given environment are generally known as performance or specialty coatings. Silicone, epoxy and polyurethane coatings are the examples for high performance coatings due to their chemical composition and its properties. For example epoxies consist of epoxy resin and its curing agent to form a very good physico-mechanical and corrosion properties[1]. 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 polyurethane 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 Wang *et al.*[6]. Yan *et al*[7]. prepared and compared the low infrared emissivity composite coatings based on epoxy polyurethane (EPU) and bronze. Dexter B Pattison prepared polyepoxides from polyalkylene ether glycols for obtaining Cured elastomers[8]. Motawie *et al*.[9] synthesized and characterized the epoxidized polyurethane form epoxidised linseed oil with toluene diisocyanate at a NCO to OH ratio equal to 5. Verborgt *et al.*[10] invented a formation of polyurethane from different diols and polyols monomer to react with polyisocyanate for thermo sets and volatile organic compound (VOC) free. The desirable system would have the chemical resistance of a polyepoxide and the curing mechanical properties of polyurethane. Schmidt *et al.*[11] invented a polymeric vehicle which comprises a reaction product of an epoxy polyol ester resin with unsaturated monomers which when neutralized with a base provides a water dispersible polymeric vehicle for use in coating compositions.

In the present work, we developed hydroxyl terminated epoxy systems as epoxy polyol resin in our laboratory. Two component polyurethane coatings were prepared by blending of epoxy polyol and hexamethylene diisocyanate (HDI) hardener. Seven types of experiments were conducted by keeping the ratio of epoxy polyol constantly and changing the ratio of hexamethylene diisocyanate from 0.80-1.20. All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of hexamethylene diisocyanate. 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[12-19]. Hence the optimized polyurethane coated film was analyzed by using the EIS tool. The formation of the polyol was supported by FTIR spectral data.

EXPERIMENTAL

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, hexa methylene diisocyanate (hexamethylene diisocyanate-desmodour N-75) from Bayer chemicals.

Preparation of polyol: A three necked 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-(266.67 g) 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 min. Gradually the temperature increases from 60-70 ºC to open up the oxirane ring of epoxy resin to generate secondary alcohol. The reaction mixture was refluxed for 6 h with stirring. The transparent secondary hydroxyl terminated epoxy polyol resin was transferred to air tight bottle. The samples were characterized for acid value (ASTM D-1639) hydroxyl value (ASTM D-1957) and isocyanate group content (ASTM D-2572) and per cent of volatile content. The reaction scheme of the epoxy polyol resin is given in the following Fig. 1.

Characteristics of epoxy polyol (EP): Solid content of epoxy polyol = 54.20 %. Hydroxy equivalent weight = 145.80 on solids 269.0 g/Eq. Hydroxyl content = 11.66 %.

Characteristics of hexamethylene diisocyanate: Solid content of hexamethylene diisocyanate = 74.28 %. Isocyanate equivalent weight = 192.48 on solids 259.13 g/Eq. Isocyanate content = 21.82 %.

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[20]. A 100 mL beaker containing epoxy polyol resin (39.80 g), hexamethylene diisocyanate hardener (38.30 g), butyl acetate (5.00 g), cellosolve acetate (3.00 g) and xylene (13.90 g) (xylene, butyl acetate and cellosolve acetate used as solvents for polyurethane coatings) at room temperature were stirred manually well for 10 min, 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 hexamethylene diisocyanate from 0.80-1.20, a total of seven types of experiments were conducted and tabulated in Table-1. All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of hexamethylene diisocyanate. 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 µ measured by using a magnetic thickness gauge meter. The films were allowed to cure at ambient conditions (room temperature of 30 ºC and relative humidity of *ca.* 50-60 %) for at least 48 h before the tests for mechanical and chemical properties were carried out. Compositions were tested for their pot life by checking the rise in 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[21], cross hatch adhesion (ASTM D 4752), impact resistance

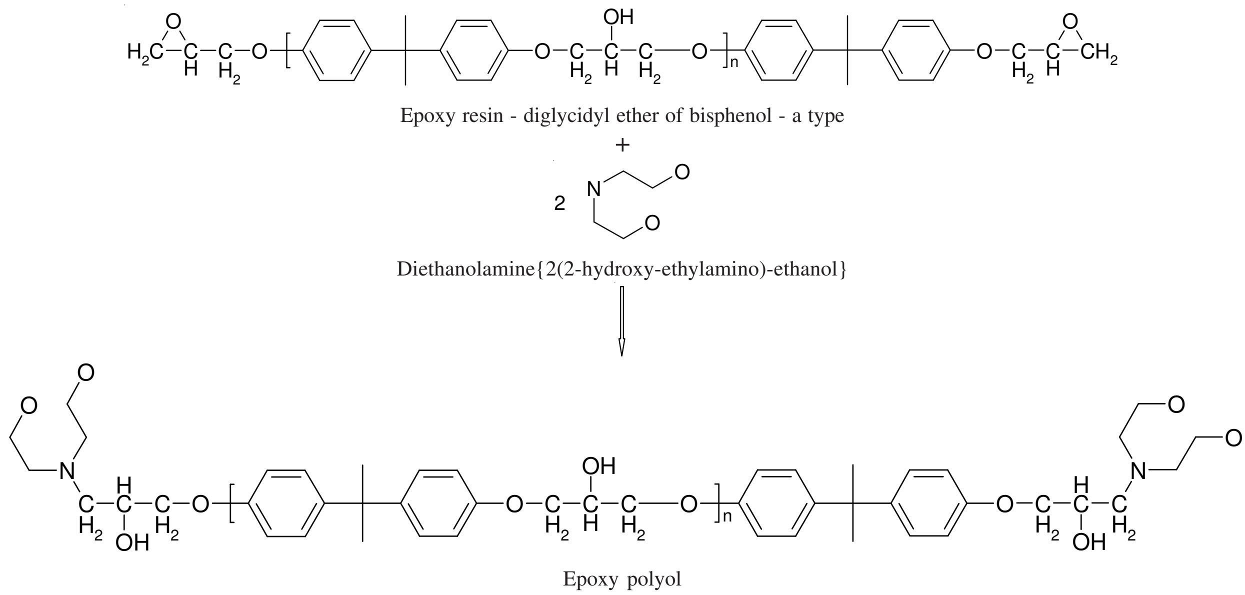

Fig. 1. Reaction scheme of epoxy polyol

TABLE-1
FORMULATION FOR THE EXPERIMENTS-TOTAL SOLIDS OF THE COMPOSITION IS 50.00 %

Ratio of EP	Ratio of HDI	Solid of EP	Solid of HDI	EP (%)	HDI (%)	Material EP in g for 50 %	Material HDI in g for 50 %	Xylene (g)
1.00	0.80	145.80	153.99	48.60	51.40	44.80	34.60	12.60
1.00	0.90	145.80	173.24	45.70	54.30	42.20	36.60	13.20
1.00	1.00	145.80	192.48	43.10	56.90	39.80	38.30	13.90
1.00	1.05	145.80	202.11	41.90	58.91	38.70	39.10	14.20
1.00	1.10	145.80	211.73	40.80	59.20	37.60	39.90	14.50
1.00	1.15	145.80	221.36	39.70	60.30	36.60	40.60	14.80
1.00	1.20	145.80	230.98	38.70	61.30	35.70	41.30	15.00

*Butyl acetate – 5 g and cellosolve acetate – 3 g commonly added in all experiments.

(ASTM D 2794-92) and salt spray test (ASTM B 117). Solvent resistant and chemical resistances of the films were studied by the spot test for 0.5 h under 2 inch watch glass. After the film coated with the prepared polyurethane coatings, the various physical properties and mechanical properties were measured and presented in Table-2. The FT IR spectra were taken and interpreted for epoxy polyol resin on KBr pellets and recorded using BomemMichelson series spectrophotometer.

RESULTS AND DISCUSSION

FT IR spectra of epoxy polyol: IR spectrum (Fig. 2) of epoxy polyol showed the following bands, 3389 cm^{-1}-OH-stretching, 3036 cm^{-1}-C-H bonding for aromatic carbon, 1475 cm^{-1}-tertiary-C-C-stretching due to the presence of the above absorption bands in the spectra[22,23], it was conformed that the formation of the epoxy polyol resin shown in the reaction scheme of epoxy polyol resin in Fig. 1.

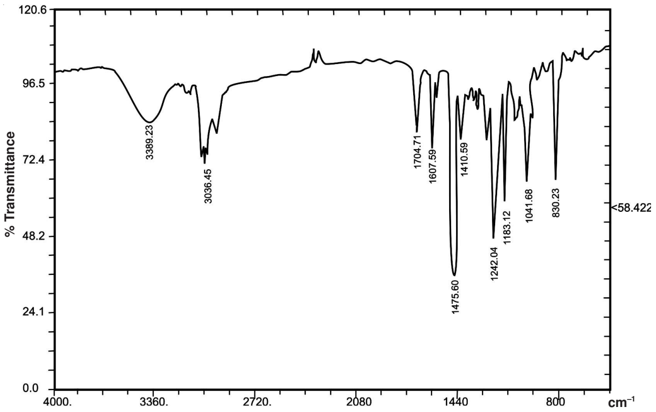

Fig. 2. FT IR spectra for epoxypolyol resin

From the Table-2, column A to G the NCO ratio is varied from 0.80-1.20. The experiment conducted without the catalyst dibutyltin dilaurate (DBTL). Hatada *et al.*[24] have experimentally determined the 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, the 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 of 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) and experiment (B) due to 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 compared, how resistant the film for the transfer of sodium and chloride ions through it. From the Table-2, 1: 1.1 and 1: 1.15 epoxy polyol and hexamethylene diisocyanate ratio have given a comparatively more resistant film to the corrosive environment. Reisch *et al.*[25] have optimized the coating performances of polyurethane coatings prepared with the blends of polyisocyanates. The physical, mechanical and chemical resistance properties were used for the optimization. Electro chemical impedance spectroscopy (EIS) were used 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 and G instruments AC 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. 3, consists of solution resistance (Rs), charge transfer resistance (Rt), coating capacitance (Cc) and double layer capacitance (Cdl) 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. Charge transfer resistance (Rt) and the double layer capacitance (Cdl) values were obtained from bode plots of both coatings for different duration and reported the same in Table-3.

From Table-3, it can be seen that, charge transfer resistance 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[26]. The initial decrease in charge transfer resistance values can be ascribed to the uptake of the electrolyte through the micro pores and capillaries in the coating. The increase in charge transfer resistance 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 charge transfer resistance values of 10^6 ohms cm^2 and more can be rated as protective to mild steel substrate from aggressive ions[27]. Although both the experi-

TABLE-2
CHARACTERISTICS OF THE FORMULATED EXPERIMENTS

	A	B	C	D	E	F	G
(EP : HDI)	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@30ºC IN B4 CUP	81"/4	86"/4	71"/4	79"/4	81"/4	79"/4	63"/4
Drying time							
-Touch dry	5 min	5 min	5 min	5 min	5 min	5 min	5 min
- Tack free	55 min	45 min	45 min	45 min	45 min	45 min	45 min
- Hard dry	90 min	90 min	90 min	90 min	90 min	90 min	90 min
Gellation time (min)	105 min	105 min	100 min	105 min	90 min	100 min	110 min
Dry film thickness (DFT)	50	50	50	50	50	50	50
Micro gloss@20º angle	92	90	91	93	94	94	92
Scratch hardness	1.5 Kgs	1.8 Kgs	2 Kgs	2 Kgs	2.2 Kgs	2.2Kgs	1.8 Kgs
Impact test (1000 g in 90 cm)							
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)	350 h	390 h	420 h	450 h	510 h	500 h	405 h
Chemical resistance[a]							
-Acetic acid	2	2	1	1	0	0	1
-Sodium chloride	3	3	1	1	0	0	1
- Hydrochloric acid (10% in water 8 Hrs)	3	3	1	1	0	0	1
Solvent resistance[a]							
o-xylene	3	2	1	1	0	0	1
Methylethylketone (MEK) (30 min under 2" watch glass)	3	3	1	1	0	0	1

Where (a) 0: No marks, 1: Slight marks, 2: Prominent marks, 3: Partial paint film detachment.

TABLE-3
CHARGE TRANSFER RESISTANCE (Rt) AND THE DOUBLE LAYER CAPACITANCE (Cdl) VALUES OBTAINED FROM ELECTROCHEMICAL IMPEDANCE SPECTRA AT 1:1.10 AND 1:1.15 RATIOS

S.No.	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	3.84×10^{8}	4.65×10^{-10}	9.88×10^{8}	8.33×10^{-10}
2	1 day	9.60×10^{7}	1.96×10^{-10}	6.28×10^{7}	3.92×10^{-10}
3	10 days	2.64×10^{8}	4.90×10^{-11}	1.09×10^{9}	4.50×10^{-11}
4	20 days	1.59×10^{9}	4.90×10^{-11}	3.48×10^{8}	4.92×10^{-11}
5	30 days	2.00×10^{9}	4.90×10^{-11}	5.51×10^{8}	3.67×10^{-11}
6	40 days	2.41×10^{9}	1.07×10^{-10}	5.88×10^{8}	7.55×10^{-11}
7	50 days	1.20×10^{9}	6.89×10^{-11}	4.83×10^{8}	4.33×10^{-11}
8	60 days	2.00×10^{9}	5.20×10^{-11}	5.20×10^{8}	5.80×10^{-11}

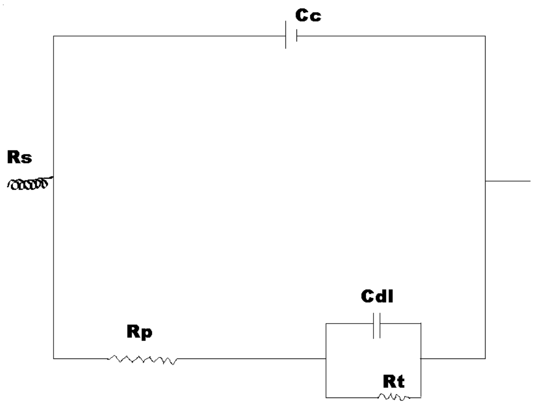

Fig. 3. Schematic diagram of the equivalent circuit for coated panels

ments had charge transfer resistance values more than 10^6 ohm, the coating in experiment-1 has showed much better value than the coating in experiment-2, hence the outcome of experiment-1 was better than experiment-2[28]. Hence, it is concluded that the stoichiometry of an OH-NCO ratio will be 1:1.10 much better than 1:1.15 in epoxy polyol and hexamethylene diisocyanate reactivity product.

Conclusion

Epoxy polyol can be synthesized by the reaction between epoxy resin and diethanolamine. The two component polyurethane coatings were prepared by blending with polyisocyanate, hexamethylene diisocyanate with these epoxy polyol resin. Thus 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 stoichiometry of 1: 1.10 of OH:NCO ratio was much better than 1:1.15 ratio of mixing in epoxy polyol and hexamethylene diisocyanate reaction products based on the electrochemical impedance spectroscopy results.

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