Available online at www.elixirpublishers.com (Elixir International Journal)

Computational Chemistry

Elixir Comp. Chem. 81 (2015) 31801-31806

ISSN: 2229-712X

Physicochemical Properties of Epoxy Polyol with Isophorne Diisocyanate based two Component Polyurethane Coatings

J. Tennis Anthuvan[1], G. Paruthimal Kalaignan[2] and L. Guru Prasad[1]

[1]Department of Science & Humanities, M. Kumarasamy College of Engineering College, Karur-639113, Tamilnadu, India.

[2]Advanced Materials Research Lab, Department of Industrial Chemistry, Alagappa University, Karaikudi 630003,Tamilnadu, India.

ARTICLE INFO

Article history:

Received: 20 February 2015;

Received in revised form:

28 March 2015;

Accepted: 10 April 2015;

Keywords

Epoxy polyol,
Isocyanate hardener,
FT IR, Properties,
Electrochemical Impedance
Spectroscopy.

ABSTRACT

Polyurethane coatings are formed from the chemical reaction between polyol and polyisocyanate hardener. By varying the concentration of isophorne diisocyanate, two component polyurethane coatings have been prepared with the blending of epoxy polyol and isophorne diisocyanate (IPDI). Totally seven types of experiments were conducted with the prepared blend mixtures. All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of IPDI. Films were coated on the mild steel using the clear polyurethane solution. The Electrochemical Impedance Spectroscopy (EIS) was used to characterize the coated film. The formation of the polyurethane was confirmed FTIR spectral data.

Introduction

Two component polyurethanes (PU) are used in the coating industry mainly because it exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical & corrosion resistance and a wide range of mechanical strength [1-3]. Polyurethane coatings are formed from a chemical reaction between the polyol and the polyisocyanate hardener [4]. Hydroxyl functional polyester, acrylics and polyether are used in the commercially available polyols for two components PU systems [5]. 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]. Synthesis, thermal properties and morphology of blocked polyurethane/epoxy full-interpenetrating polymer network have been investigated by chin-hsing Chen [7]. Dexter B Pattison prepared polyepoxides from polyalkylene ether glycols for obtaining Cured elastomers [8]. 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. Verborgt et al [10] invented a formation of polyurethane from different diols and polyols monomer to react with polyisocyanate for thermo sets and VOC (Volatile organic compound) free. The desirable system would have the chemical resistance of a polyepoxide and the curing mechanical properties of polyurethane. Schmidt et al 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 [11]. V.V.Gite et al recently reported the preparation and properties of polyurethane coatings based on acrylic polyols and IPDI [12].

In our laboratory, we developed hydroxyl terminated epoxy systems as epoxy polyol resin [13]. In the present work, two component polyurethane coatings were prepared by blending of epoxy polyol and Isophorne diisocyanate (IPDI) hardener. Seven types of experiments were conducted by keeping the same concentration of epoxy polyol and by varying concentration of IPDI with epoxy polyol 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 IPDI. In order to prepare a film, polyurethane clear applied on the mild steel and the prepared film were subjected to various characterization techniques to study the physical and mechanical properties of the film. Electrochemical Impedance Spectroscopic (EIS) is a non-destructive technique useful for examining the corrosion performance of coated metals exposed to aqueous environments [14-20]. Hence the optimized polyurethane coated film is analyzed by using the EIS tool. The formation of the polyol was supported by FTIR spectral data.

Objective and Importance of the work

Epoxy systems are particularly suitable for the preparation of primer and intermediate coatings because of their good adhesion and water resistance properties. Whereas, polyurethanes offer very good color stability and gloss retention and therefore they tend to be used for top coats where a cosmetic finish is required. Where there is a requirement for good adhesion and water resistance as well as high gloss and color stability (i.e. non-yellowing), epoxy and polyurethane systems can be used in combination of the same substrate. In this work, we are mainly concentrating on the combination of the epoxy and polyurethane for metal finishing.

Experimental

Materials

Epoxy polyol resin, Xylene, cellosolve acetate and butyl acetate from E-Merck, Isophorne diisocyanate(IPDI 75% in Xylene) from M/S Perstrop chemicals, Mumbai. Epoxy resin GT 6071-X75-(266.67G), Cellosolve acetate(40 G), Xylene (93.33 G), Diethanolamine(42 G) were placed in a three necked flask and stir well at room temperature for 5 min.

Tele:

E-mail addresses: guruphysics@gmail.com

Gradually the temperature increases from 60°C to 70°C, active hydrogen of diethanolamine to open up the oxirane ring of epoxy resin to generate secondary alcohol. The reaction mixture was heated upto 120°C and refluxed for 6 Hrs with stirring and secondary hydroxyl terminated epoxy polyol are prepared.

Characteristics of epoxy polyol (EP)

Solid content of Epoxy polyol = 54.20%

Hydroxy equivalent weight = 145.80 on solids 269.0 g/Eq

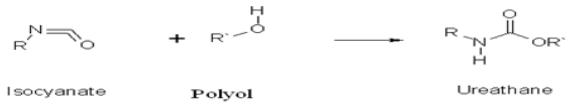
Hydroxyl content = 11.66 %.

Characteristics of IPDI

Solid content of IPDI = 74.85%.

Isocyanate equivalent weight =212.66 on solids 284.13 g/Eq.

Isocyanate content = 19.75%. The reaction scheme is as follows,



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 [21]. To a 100 ml beaker containing Epoxy polyol resin (37.52g), IPDI hardener (39.63 g), Butyl acetate (5.00g),Cello solve acetate(3.00g) and Xylene (14.85g) (Xylene, Butyl acetate and Cello solve acetate used as solvents for PU coatings) at room temperature and stirred manually for ten minutes as 1 : 1 ratio of polyureathane solution(OH/NCO ratio). By keeping the ratio of Epoxy Polyol as constant and by changing the ratio of IPDI from 0.80 to 1.20, a total of seven types of experiments were conducted (Table.1). All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of IPDI. Total solids of all experiments were taken as 50% solids.

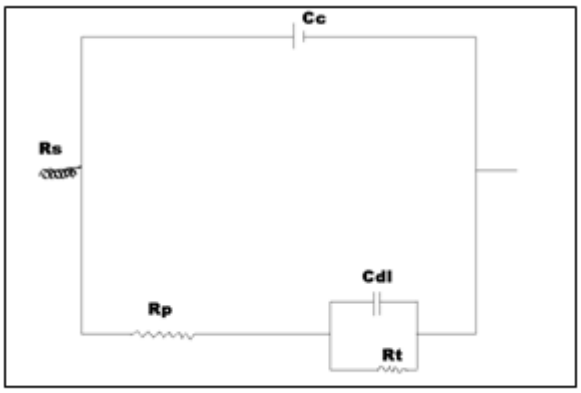


Fig 1. Schematic Diagrams of the Equivalent Circuit for Coated Panels

Preparation of polyol

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.

The test solution was thoroughly mixed just before the application of their films on to mild steel panels. Films were applied using bar applicator 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 [(22)], 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 Table. 2. The FTIR spectra were taken and interpreted for Epoxy polyol resin on KBr pellets and recorded using BomemMichelson series Spectrophotometer.

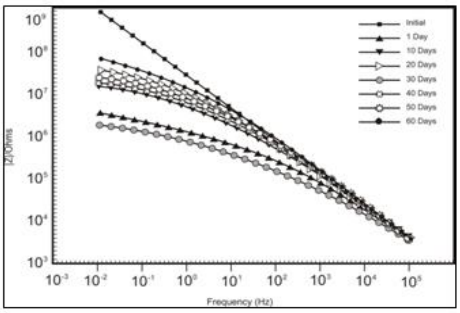


Fig 2. Bode plot for Experiment 1(Epoxy polyol with IPDI at 1: 1.10)

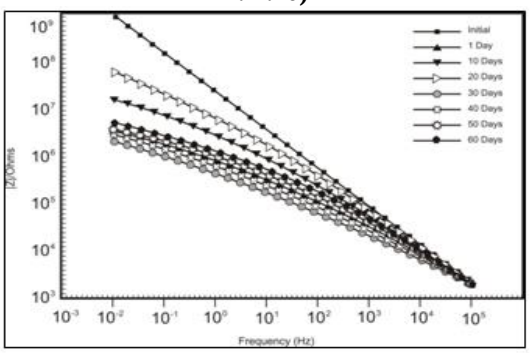


Fig 3. Bode plot for Experiment 2(Epoxy polyol with IPDI at 1: 1.15)

Results and Discussion

From the Table.2, column A to G the NCO ratio is varied from 0.80 to 1.20. Seven experiments conducted, with reference to J.W.Reisch et al (Surface coating international, Vol 9, 1995, PP 380) was taken the OH/NCO ratio at 1.0: 1.10, for urethane coatings formulated with blends of polyisophorne diisocynate and polyhexamethylene diisocynate. Hence in our experiments we have taken in the following ratio's 1.0: 0.80, 1.0: 0.90, 1.0: 1.0, 1.0: 1.05, 1.0:1.10, 1.0: 1.15, and 1.0: 1.20. i.e. between 1.0:

1.0 to 1.0: 1.20 we have studied in detailed. According to that data we have optimized the best two sets of experiments for studying the EIS studies. The FTIR studies indicate the formation of cross-linked bond between the polyol and the isocyanate. If the formation of the bond is strong and uniform, then the resistant exerted from the Bode plot is very high. If the bond formation is incomplete, then the resistant obtained from the EIS study is below the protective line. Thus this study leads a good relation between the FTIR and EIS study. The experiment conducted without the catalyst DBTL (Dibutyltin dilaurate), Hatada et al [23] 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.

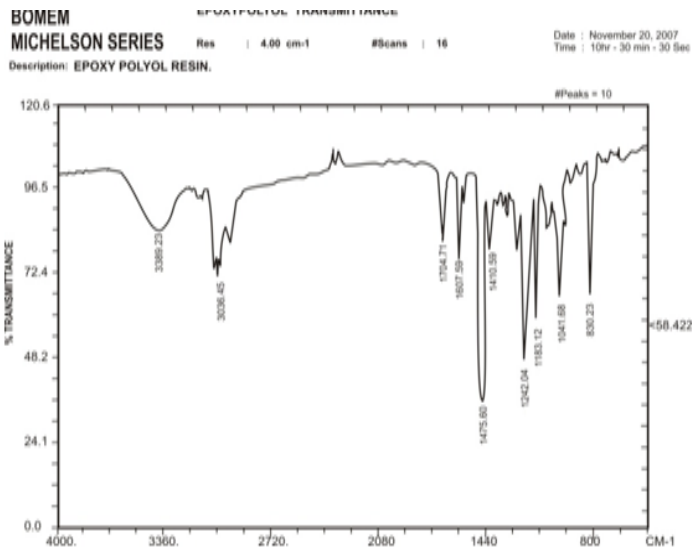


Fig 4. FT IR Spectra for Polyol

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 IPDI ratio gave a comparatively more resistant film to the corrosive environment. J.W.Reisch et al [24] 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):

Impedance measurements were carried out with the help of a PAR model 6310 EG & G instruments A.C. impedance analyzer at a frequency range 10^{-2} to 10^{5} Hz

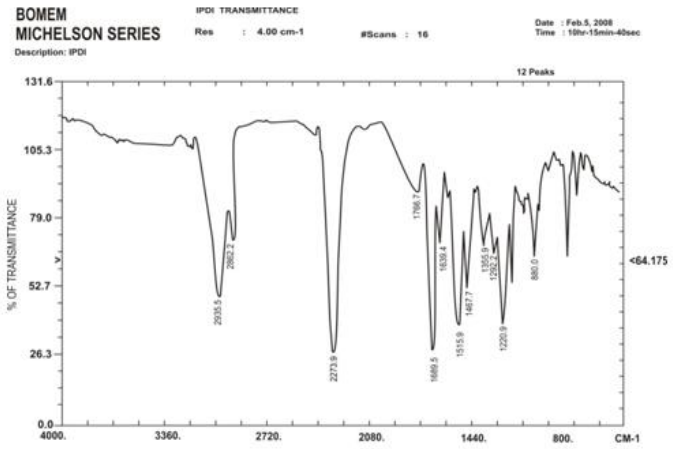


Fig 5. FT IR Spectra for IPDI

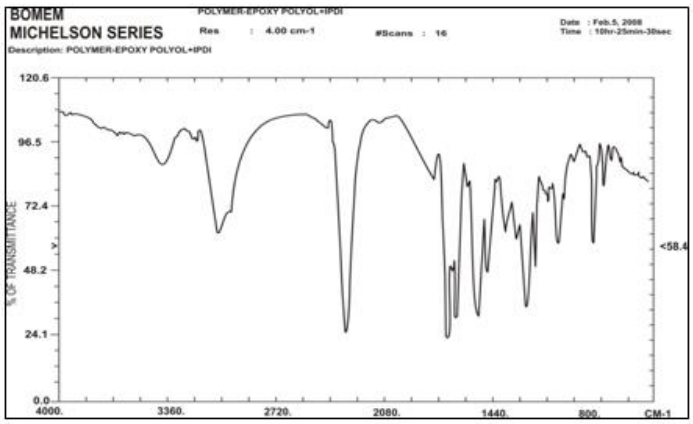


Fig 6. FT IR Spectra for Polyureathane

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. 1, 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 (Fig.2 & Fig.3) for different duration for both coatings reported in Table 3.

From Table. 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 [25]. The initial decrease in Rt values can be ascribed to the uptake of the electrolyte through the micro pores and capillaries in the coating. The increase in Rt 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 Rt values of 10^6 ohms cm^2 and more can be rated as protective to mild steel substrate from aggressive ions [26]. Although both experiments had R_t values more than 10^6 ohm, the coating in Expt 1 showed much better value than the coating in Expt 2, hence the outcome of Expt 1 was better than Expt 2 [27]. Hence we confirm that the stokiometry of an OH-NCO ratio will be 1: 1.10 much better than 1:1.15 in epoxy polyol and Isophorne diisocyanate reactivity product.

Table 1. Formulation for the experiments - Total solids of the composition is 50.00%

Ratio of EP	Ratio of IPDI	Solid of EP	Solid of IPDI	% of EP	% of IPDI	Material EP in g for 50%	Material IPDI in g for 50%	Xylene in g
1.00	0.80	145.80	170.13	46.15	53.85	42.57	35.97	13.46
1.00	0.90	145.80	191.39	43.24	56.76	39.89	37.91	14.20
1.00	1.00	145.80	212.66	40.67	59.33	37.52	39.63	14.85
1.00	1.05	145.80	223.29	39.50	60.50	36.44	40.41	15.15
1.00	1.10	145.80	233.92	38.40	61.60	35.43	41.15	15.42
1.00	1.15	145.80	244.56	37.35	62.65	34.42	41.85	15.73
1.00	1.20	145.80	255.19	36.36	63.64	33.54	42.51	15.95

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

Table 2. Characteristics of the formulated experiments

	A	B	C	D	E	F	G
(EP : IPDI)	**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	**77"/4**	**75"/4**	**70"/4**	**68"/4**	**65"/4**	**63"/4**	**58"/4**
Drying time							
-Touch dry	10 min	10 Min	10Min	10 Min	10 Min	10 Min	10 Min
- Tack free	55 min	50 Min	45 Min	45 Min	45 Min	45 Min	40 Min
- Hard dry	90Min	80 Min	75 Min	75 Min	75 Min	75 Min	70 Min
Gellation time(Min)	105 Min	105 Min	100 Min	105 min	90 Min	100min	110Min
DFT (Microns)	50	50	50	50	50	50	50
Micro gloss@20° 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	1.8Kgs
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)	360Hrs	390 Hrs	425 Hrs	490Hrs	540Hrs	560 Hrs	510 Hrs
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
Methylehtylketone(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. 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

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	6.40×10^{9}	4.11×10^{-11}	9.88×10^{9}	3.33×10^{-11}
2	1 day	5.14×10^{6}	2.67×10^{-9}	6.28×10^{6}	5.71×10^{-9}
3	10 days	2.14×10^{7}	8.73×10^{-10}	1.28×10^{7}	6.37×10^{-10}
4	20 days	6.44×10^{7}	5.37×10^{-10}	8.44×10^{7}	3.10×10^{-10}
5	30 days	3.60×10^{6}	6.61×10^{-9}	3.84×10^{6}	5.51×10^{-9}
6	40 days	2.60×10^{7}	5.71×10^{-9}	5.10×10^{6}	3.55×10^{-9}
7	50 days	4.40×10^{7}	4.31×10^{-9}	6.40×10^{6}	1.33×10^{-9}
8	60 days	8.60×10^{7}	1.16×10^{-9}	7.40×10^{6}	9.8×10^{-8}

FTIR Analysis of PU based on Epoxy polyol with IPDI

FTIR analysis of epoxy polyol:

IR spectrum of Epoxy polyol is shown in Fig. 4 A peak observed at 3389 cm^{-1} is attributed to OH – Stretching. Vibration of C-H bonding give raises an absorption peak at 3036 cm^{-1}. Due to the presence Tertiary –C-C- stretching a band traced at 1475 cm^{-1} in the FTIR Spectrum.

FIIR spectrum of IPDI is shown in Fig. 5. Presence of methyl group vibration is confirmed by observing a peak at 3381cm^{-1} in the recorded FTIR spectrum. Stretching of CH group in IDPI is observed at 2935 cm^{-1}.

2273.90 cm^{-1}– N-C Stretching and 1689.50 cm^{-1} –C=O Stretching,1515.90 cm^{-1} – Tertiary – C-C- Stretching. From the above peaks, it is confirmed that the tested sample contain the NCO group.

FTIR Spectra of polyurethane

The test solution was prepared as per the procedure given above in the chemical composition. Epoxy polyol and IPDI are taken in the ratio of 1: 1.10 as a test solution. The broad peak appeared at 3380 $^{-1}$ (in Fig.4) is resulting from the formation of NH of the urethane linkage [12]. A peak observed at 3000cm^{-1} is attributed to C-H Stretching vibrations [28] and at 2280 cm^{-1} is assigned to N-C Stretching vibrations. Because of the formation of urethane linkage, the C=O stretching vibration is observed at 1700 cm^{-1}. From the above bands the formation of polyurethane product has been confirmed.

Conclusions

The two component polyurethane coatings were prepared by blending with polyisocyanate, Isophornediisocyanate 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 Isophornediisocyanate reaction products by using the electrochemical impedance spectroscopy method.

References

[1]. R.R.Roestler, P.R.Hergenrother, "Two component polyurethane coatings" Journal of protective coatings and lining, vol 13, pp 83-85, 1996.

[2]. C.H.Hare, "Protective coatings: fundamentals of chemistry and composites", SSPC, 1994, PP 239.

[3]. Wicks. Z.W, Jones. F.N and Pappas .S.P., Organic coatings science and technology, 2nd ed., , Wiley Interscience, 1999, pp 180.

[4]. V.C.Malshe, Basics of paint technology – part 1, Colour publications Pvt Ltd, 2002, Page 465.

[5]. S.S.Yadav, F.Zafar, A.Hasnat, S.Ahmad, "Poly(urethane fattyamide) resin from linseed oil –A renewable resin source" Progress in organic coatings, vol 64, pp 27-32, 2009.

[6]. Huei-Hisung Wang and Jung-Chieh Chen, "Polyurethane modified epoxy resin and their polymer particlefiled epoxies" Journal of Polymer Research, vol 3, pp 133-138, 1996.

[7]. Chin-Hsing Chen, Meng-Hueichen, "Synthesis, thermal properties and morphology of blocked polyurethane epoxy full interpenetrating network" Journal of Applied Polymer Science, vol 100, pp 323-328, 2006.

[8]. Dexter B. Pattison, "Poly(alkylene ether urethane polymers containing terminal epoxide groups" US Patent –No.2830038,

[9]. S.I.Mavani, N.M.Mehta and P.H.Parsania, "Synthesis and physico-chemical study of polyester polyol of epoxy resin of 1, 1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane and ricinoleic acid and its polyurethanes with polyethylene glycol" Journal of Scientific & Industrial Research, vol 66, pp 377, 2007.

[10]. Jozef Verborgt, Arthur A Webb, "Polyurethane coating" 2009 US Patent –US 7622541B2.

[11]. Roger Schmidt, Bryan R.Swenson, **"**Vehicle binders for enamels; gloss; adhesion; nonhydrolyzing; hardness" 1991 US Patent –US 5066690.

[12]. V.V.Gite, P.P.Mahulikar, D.G.Hundiwale, "Preparation and properties of polyurethane coatings based on acrylic polyols and trimer of isophorone diiscyanate" Progress in Organic Coatings, vol 68, pp 307-312, 2010

[13]. J. Tennis Anthuvan, G.Paruthimal Kalaignan, B.Joseph Vincent, "Synthesis and characteristics of two component polyurethane coatings based on epoxy polyol with polyisocyanate" Asian Journal of Chemistry, vol.23, pp 4130-4134, 2011.

[14]. A Al-Hasem, J A Carew and A Hasan, "The use of electrochemical impedance spectroscopy (EIS) for the determination of the protective properties of solvent and water based paints systems" Surface coatings international Part B, Coating transaction, vol 82, pp 26 - 30, 1999.

[15]. D.Ramesh, T.Vasudevan, "Evaluation of Corrosion Stability of Water Soluble Epoxy-Ester Primer through Electrochemical Studies" Materials Sciences and applications, vol.3, pp 333-347, 2012.

[16]. F.Masfeld, "Recording and Analysis of AC Impedance Data for Corrosion Studies" Corrosion, vol 37, pp 301-307, 1981.

[17]. F.Gui and R.G.Kelly, "Performance Assessment and Prediction of Corrosion Prevention Compounds with Electrochemical Impedance Spectroscopy" Corrosion, vol 61, pp119-129, 2005.

[18]. E.Spengler,F.L.Fragata, I.C.P.Margarit and O.R.Mallos, "Corrosion protection of low toxicity paints" Progress in Organic Coatings, vol.30, pp 51-57, 1997.

[19]. R.Selvaraj, M.Selvaraj and S.V.K.Iyer, "Studies on the evaluation of the performance of the two types of the polyurethane coatings on steel rebar's for the prevention of corrosion in concrete structures" Portugaliae Electrochemical Acta, vol 26, pp 407-416, 2008.

[20]. Xiaoxing Yan and Guoyue Xu "Corrosion and mechanical properties of Epoxy-Polyurethane / Bronze composite coatings with low Infrared emissivity" Surface and Coating Technology, vol 205, pp 2307-2312, 2010.

[21]. S.G.Croll, "Quantitative evaluation of photo degradation in coatings" Progress in Organic Coatings, vol 15, pp 223-247, 1987.

[22]. Shreekant Patil, Testing of Paints, Pencil hardness, Colour Publications Pvt Ltd 1993, pp 157,

[23]. Hatada K, Ute K and Oka K, "Unambiquous C^{13} NMR assignments for isocyanate carbons of Isophorne diisocyanate and reactivity of isocyanate groups in Z and E Stereoisomers" Journal of Polymer Science: Polymer Chemistry vol 28, pp 3019-3027, 1990.

[24]. J.W.Reisch, R.S.Blackwell, R.T.Wojcik, J.M.O'Connor and K.B.Chandalia, "Urethane coatings formulated blends of polyisophorne diisocyanate and polyhexa methylene diisocyanate" Surface Coatings International, 9 pp 380-387, 1995

[25]. L.Mathivanan and S.Radhakrishna, "Heat –resistant anti-corrosive paint from epoxy silicone vehicles" Anticorrosion Methods & Materials, vol 44, pp 400 – 406, 1997.
[26]. B.S.Skerry and D.A.Edew, "Electrochemical testing of assess corrosion protective coatings" Progress in Organic Coatings, Vol15, pp 269-285, 1987.
[27]. R.Selvaraj, B.Bhuvaneshwari, "Characterization and development of organic coatings for steel rebars in concrete" Portugaliae Electrochemical Acta, vol 27, pp 657-670, 2009.
[28]. J.I.Iribarren, E.Armelin, F.Liessa, J.Casanovas and C.Aleman, "On the use of conducting polymers to improve the resistance against corrosion of paints based on polyurethane resins" Materials and Corrosion, vol 57, pp 683-688, 2006.
[29]. Dilek Kincal, Saim Ozkar, "Kinetic study of the reaction between hydroxy terminated polybutadiene and Isopohorne diisocyanate in bulk by quantitative FT IR Spectroscopy" Journal of Applied Polymer Science, Vol 66, pp 1979-1983, 1997.