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Synthesis of New Polyurethane Coating Based On Rosin for Corrosion Protection of Petroleum Industries Equipment

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ABSTRACT

The coating polyurethane(PU) rosin are prepared by the reaction of maleopimaric acid with diethanol amine to give maleopimarate amide MPAD which cured with different ratio of toluene diisocyanate(TDI) 30,40, 50 ,60 and 70% to obtained the best optimum condation of polyurethane film which applied on steel specimen. The curing behaviors of cured PU resin with TDI were evaluated by DSC-TGA meaurements. The coated film are evaluated by measuring their mechanical properties , chemical resistance and salt spray resistance.

Keywords* –** *polyurethane coating, polyurethane rosin , polyurethane abietic acid , polyurethane, rosin paint.**

I. INTRODUCTION

Rosin has been developed as a feedstock for synthesis of various chemicals and intermediates for polymers. There have been some reports regarding the use of rosin maleic anhydride and acrylic acid in polymer synthesis [1–3], a mixture of rosin, maleic anhydride and acrylic acid along with some other chemicals were reacted together to obtain a polymer, or the acrylic acid modified rosin was used and not the pure adduct of rosin acrylic acid, In some patents these adducts were used for the production of alkyl and polyester resins or as a paper sizing agent [4–8].the modification of rosin with an appropriate reagent to convert it to di-, tetra-and hexa-glycidyl derivatives as epoxy binders and synthesis curing agents polyamides from rosin [9–12]. MDI (diphenylmethane-4,40-diisocyanate) and different mixtures of rosin acid and polyadipate of 1,4-butanediol equivalent % with respect to the equivalents of OH groups in the macroglycol) were reacted to produce a urethane prepolymer;. 1,4-butanediol was added as chain extender. The specific feature of this manufacturing procedure was the use of rosin acid as an internal tackifier in thermoplastic polyurethanes[13-16], However, there was no detailed report about the synthesis and characterization of the polyurethane obtained from the adducts of rosin . In this respect, we have designed both PU resins and hardeners based on TDI to produce cured PU resins that have good durability with excellent mechanical properties. The aim of this work was to use the rosin as potential raw materials for the production of PU resins as coatings due to its low price and ability to modify its chemical structures. In order to fulfill these goals, three steps were distinguished. We therefore report now the synthesis and characterization of polyurethane resins obtained by the reaction of rosin maleic anhydride adduct with diethanol amine . On the other hand, curing measurements and evaluation of the prepared PU resins using different weight ratios of TDI .and another gole for this work is applied the cured PU on steel as corrosion protection for petroleum equipments.

II. EXPERIMENTAL

2.1.Materials

All materials were used without further purification . commercial Rosin with acid number 183 mg KOH g^{-1}, Maleic anhydride (MA) , Diethanol amine (DEA) , toluene diisocyanate (TDI) and organic solvents were analytical grade products (Aldrich Chemical Co.)

2.2. Technique

2.2.1 Synthesis of Maleopimaric Acid (MPA)

A 0.5L reaction flask provided with stirrer, thermometer, condenser and nitrogen inlet was charged with Rosin (RO) (76g, 0.25 mol) and MA (24.5 g, 0.25 mol) were heated at 150°C under Nitrogen atmosphere for 0.5h and at 170°C for another 0.5 h. Finally the reaction temperature was raised up to 190°C for 3 h. Finally, the reaction mixture was cooled and precipitated with cyclohexane and purified by reprecipitation into petroleum ether.

2.2.2 Synthesis of Hydroxyl Derivatives of Maleopimaric Acid

A Three-necked flask (0.5L capacity) equipped with a thermometer, condenser, stirrer and Nitrogen atmosphere inlet was charged with maleopimaric acid (MPA) (80 g, 0.2 mol) and Diethanol amine (DEA)(54.6g , 0.6mol) in presence of 20 ml of xylene. The reaction mixture was heated with stirring under a slow N2 stream to 70°C. After stabilization of the system the temperature was corrected at 140°C and kept for a period depend on type of adducts. The end of the, period of heating at 140°C the quantity of condensed water rose so much that the reflux showed itself in the condenser after the ascendant condenser was substituted with a Dean stark separator . Finally the reaction mass run out cooled and the quantity of solvent was removed by evaporation under vacuum.

2.2.3 Synthesis of Polyurethane by Using TDI (Toluene Diisocyanate).

TDI was added to prepared hydroxyl of maleopimaric acid at different ratio 5,10, 15,20 and 25% in beaker 250ml ,then stirring vigrassly about 5 minetes Then appyed the prepared polyurethane on steel panel by using air spray The obtained polyurethane are PU1(30%TDI), PU2(40%TDI), PU3 (50%TDI), PU4 (60%TDI) and PU5(70%TDI).

2.3 Measurements

Infrared spectra of the prepared compounds were recorded in polymer/KBr pellets using Mattson – Infinity series FTIR Bench Top 961. 1H NMR spectra of prepared resins were recorded on a 270 MHz spectrometer W-P-270 & Y Bruker. The solutions for1HNMR analysis were prepared by dissolving the prepared compounds in CDCl3. Transition temperature of cured polyurethane was measured with SDT Q600 V20.5 Build 15; differential scanning calorimeter at heating rate of 10 _C/min. Dynamic wdwuring was performed in DSC to observe the curing behavior of polyurethane binders. Dynamic curing was performed at a heating rate of 20 _C/min.

2.4. Testing of The Coatings

It is common to use mild steel panels (15 cm×l0 cm) to evaluate the different properties of coatings,. The other side of the panels is coated and protected against corrosion environments by using epoxy primer. the panels are subjected to different testing procedure to evaluate their mechanical properties and their durability. mechanical properties (pull of test ,pencil hardness, impact, T-bend tests), chemical resistances(hot water, acid and alkali resistance, and solvent resistance) were measured according to ASTM method as reported in our previous work (12) The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl and 5% of NaOH aqueous solutions using distilled water. The duration of the test was 90 days at 38°C.. The coated panels were evaluated for salt-spray resistance in accordance with ASTM B117. The test conditions were 35 (±1.5) ◦C, 95±5% relative humidity, and 5 wt.% of aqueous sodium chloride solution. The degree of adhesion and visual inspection of blister and cracks were evaluated for the coated panels.

III. RESULTS AND DISCUSSION

Using the rosin offers the possibility of a lower cost source for production of curable resins. The present study was intended to synthesis and characterization of polyurethane PU resins from rosin maleic anhydride adduct and evaluate the mechanical and chemical resistance of cured PU resin The synthesis of maleopimaric acid (MPA) from rosin has already been reported (9) The present work describes the condensation of DEA with MPA to produce hydroxymethylated derivatives. In this respect, the crude MPA were separated from diethyl ether solutions of the reaction mass by precipitation with petroleum ether. The Levopimaric adducts were subjected to react with diethanol amine DEA at 140°C to form amide of levopimaric acid MPAD which reacted with toluene diisocyanate to form polyurethane, the reaction scheme was represented in Figure (1). The structures of MPA and MPAD were confirmed by IR spectroscopy. IR spectra of these compounds were repersented in Figure 2(a, b) . The characteristic band in the IR spectra of MPA Figure (2a) are observed at 1700 Cm –1 (γ C= O in COOH group), 1470 Cm –1 (double bond in hydrophenanthrene moiety), 1780 and 1850 Cm –1 (γ C=O of cyclic anhydride group).In the IR spectrum of MPAD (Fig. 2b)the characteristic bands are observed at 1650. Cm –1 and 1530 Cm –1 (γ C= 0,sym and γ C= 0, asyn in amides) and at 3500 Cm –1 (γ O-H). The disappearance of the bands characteristic of cyclic anhydride group of MPA and

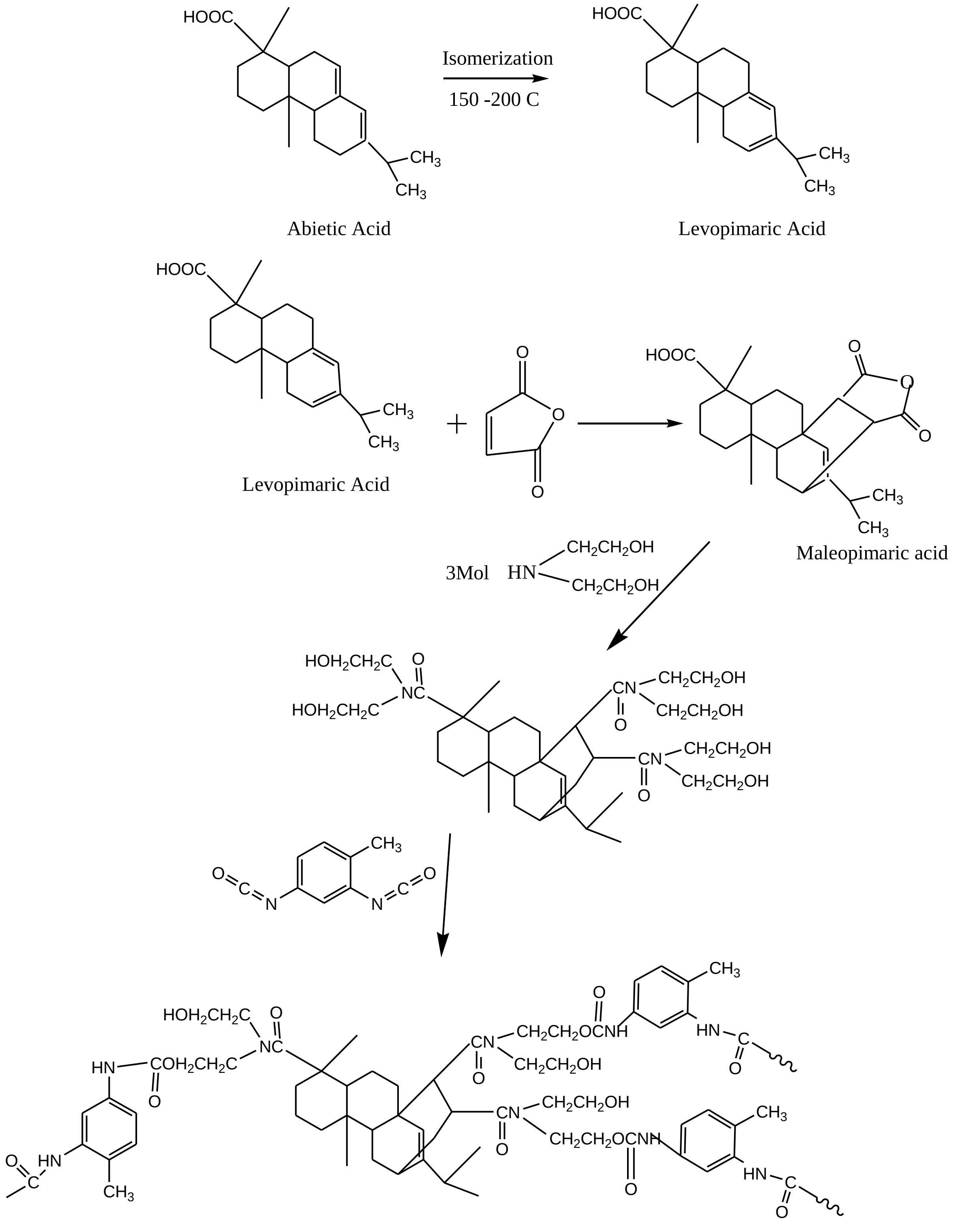
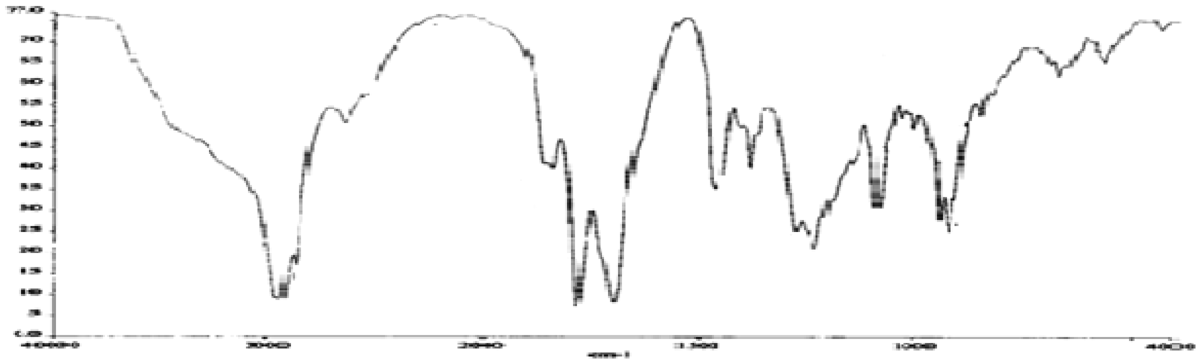
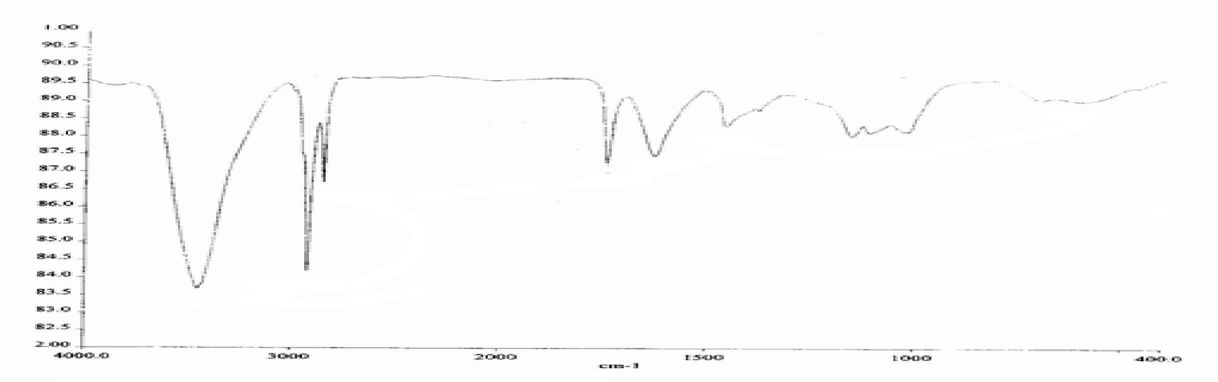


Figure. 1-Scheme of synthesis of polyurethane rosin



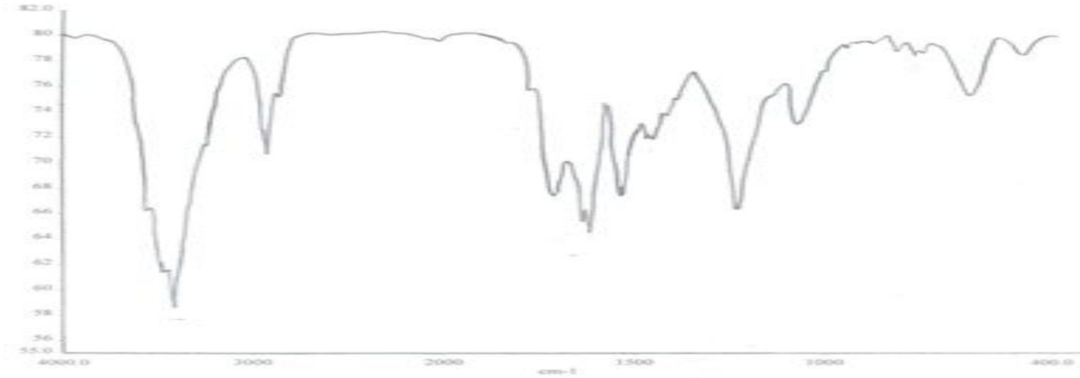
Wave Number, cm-1

a)



Wave Number, cm-1

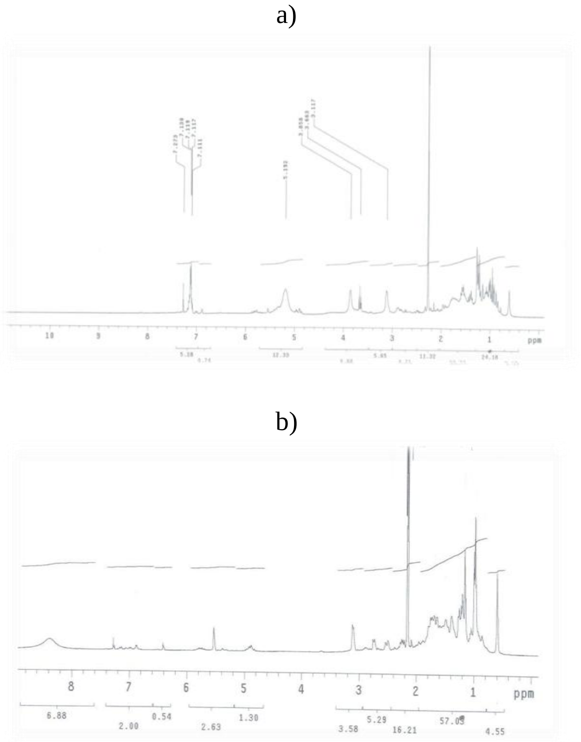
b)



c) Wave Number , cm -1

Figure. 2 a). IR spectrum of MPA, b). IR spectrum of MPAD C). IR spectrum of PU

the appearance of bands at 1670 Cm –1 (γC =0 sym in amides), 1710 Cm –1 (γ C = 0, sym of COOH) indicate that the amidation of MPA was completed by reaction of carboxylic group of rosin with NH group of DEA. The structure of the cured polyurethane were confirmed at 3420 Cm –1 (N-H stretching), 1740 Cm–1 (C=O Non-bonded urethane stretching), 1690 Cm –1 (C=O Associated urethane and isocyanurate ring stretch) and 1510 Cm –1 (H-N-C=O Amide II Combined motion)which was represented in Figure(2c). The chemical structures of MPA and MPAD were confirmed by 1HNMR Figure (3). In (Fig. 3a), the peak at 5.49 ppm was attributed to the proton on the unsaturated carbon formed after Diels–Alder reaction. In (Fig. 3b) the structure of MPAD was confirmed by disappearance of signal at 5.49ppm and appearance of signal at 7.2ppm attributed to OH of MPAD.


a)

b)

**FIGURE 3 . a) H1NMR spectrum of MPA
b) H1NMR spectrum of MPAD**

TGA and DSC data as shown in Table 1, exhibited relative thermal stability till 197°C where the weight loss was just 5% at PU1and DSC measurements recorded Tg value as 105 °C while at PU5 thermal stability reached to 242°C by weight loss 5%, and DSC measurements recorded Tg value as 130 °C that observed high thermal stability of the prepared PU modified rosin with different of TDI ratios exhibit high thermal stability which would increased with the TDI ratios increase. This means that the incorporation of rosin amide in to PU coatings offer a stabilizing effect against decomposition. DSC-TGA of PU4 were selected and represented in Figure (4).

Table (1): Thermal analysis (TGA & DSc) of cured PU resins.

PU Resin	TDI ratio	DSC measurements (Tg ˚C)	TGA measurements At 5 % Wt. loss (˚C)
PU1	30%	105	157
PU2	40%	110	194
PU3	50%	120	215
PU4	60%	122	225
PU5	70%	130	242

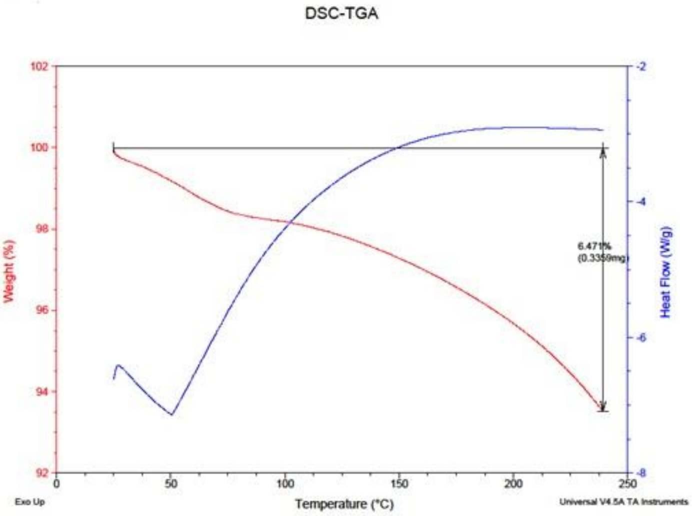


Figure (4). DSC-TGA thermal characteristics of cured polyurethane PU5

3.1 Mechanical Properties of the Cured polyurethane Resin

Among the different resinous materials utilized in polymeric applications, rosin exhibit to improve their appearance, lifespan, scratch and corrosion resistance. In general PUs are segmented block copolymers composed of soft polyester or polyether segments and hard segments, formed by diisocyanates and low molar mass diols The use of rosin polymers as precursors with a compact architecture instead of linear polyether or polyester polyols results in rosin polyurethane with different material properties [6]. In fact, new PU systems with rosin polymers, incorporated in a PU matrix as blends or introduced in the network as a cross linker, so in our present work the amide of maleopimaric acid MPAD was prepared using maleopimaric adduct MPA with diethanol amine . These MPAD are cured with TDI by different ratios forming a hyprebranched polyurethane net work. The cured products have good physical strength, excellent moisture, solvent and chemical resistance. Their main problem is relatively salt spray and alkaline resistances. The development of new polyurethane rosin has been carried out on two aspects of the polyurethane resins namely, development and modifications of newer polyurethane from rosin which is low price materials and their applications in manufacturing composites, coatings, adhesives, paints, varnishes, construction materials and some other advanced fields. The present work aims to synthesis of rosin amide with toluene diisocyanate to produce cured polyurethane film having good durability with excellent mechanical properties. The mechanical properties of cured resins have been evaluated through impact, adhesion and hardness tests. These samples were sprayed (by using an air spray gun) with wet film thickness, WFT, 140 µm on blasted steel panels. The tests for measuring the mechanical properties were evaluated after 48 h at ambient temperature. The data reported on mechanical properties are listed in Table 2. The data indicate that all cured polyurethane resins PU5 based on TDI 70% have superior adhesion properties with steel. This can be attributed to the high cross linked of the cured film due to increase the number of OH at rosin amide which meets the suitable quantity with TDI. Where PU5 give the best results with impact and T-bend tests. These characteristics indicate that the ratios between rosin amide resins and cross-linking agents ,(TDI) affect the mechanical properties of the coatings. These characteristics lead one to speculate that the high crosslink density networks possess good mechanical properties. The mechanical properties of the resin systems can also be used to estimate the degree of cure. This was observed by the variation of hardness results from softer (minimum cross links) to hardener coatings (maximum cross-link-density)

Table (2) Coating Tests of Polyurethane Resin Cured by TDI

PU Resin	Impact (Jole)	Pull of resistance (MP)	T-bend	Hardeness
PU1	8	5	+	H
PU2	9	7	+	H
PU3	11	8	+	HB
PU4	12	10	+	2H
PU5	15	12		3H

3.2 Evaluation of Chemical Resistance for Cured Resins

There are two test methods used to evaluate the durability of coatings including chemical resistance and mechanical tests. In this respect the coated panels have been subjected to chemical environments (alkali, acid, solvent and salt spray) to study the durability of the coats. The failure of the test indicates that the coating films lose their adhesion to the panels and show cracking and flaking of the film. The reasons for coating failure are legion. Nevertheless some reasons for failure are readily identifiable, and attempts can be made to compile them. Architectural coatings based on autoxidizable binders have the seeds of degradation. The oxidation process does not stop when the film has dried. The adequacy of the durability of modern exterior coating depends on a careful choice of binder. It will be clear that the requirements include both chemical resistance and optimum mechanical properties. The failure of coating systems will be due to either of these factors or a combination of them. We shall now discuss an extensive range of tests and the data of tests that have been devised to give an indication of the probable performance of coating films conducive to their durability. Solvent resistance may be tested for very different causes. The use of polar solvents such as ketones is often undertaken to assess the degree of cure of a cross linked composition for solvent resistance; methyl isobutyl ketone or acetone is recommended. In addition to immersion testing, solvent resistance may be assessed by a solvent rub test. In this respect, acetone is used to determine the degree of curing of the present coating systems by both immersion and rub methods. Failing the tests was determined either by the disruption or the dissolution of the coating films from the panels. Generally, solvent resistance depends primarily on the polarity of the cured network resins. Non-polar polymers show the solvent resistance to water, acetone and other polar solvents, whereas polymers containing sites for hydrogen bonding are most affected by moisture humidity and polar solvent. Moreover, the molecular weight and crosslink density of polymer networks are directly related to theirresistance to solvent attack. This is due to the thermodynamic relation between polymer network structures and solvent . Cross linking is the ultimate structural factor in preventing a polymer from dissolving in a solvent. Although this cannot completely eliminate the effects of polarity and hydrogen bonding, it raises molecular weight to the size of an infinite network, preventing individual polymer chains from dissolving in the solvent The higher degree of cross linking indicates less free volume; and segmental mobility remains available in the polymer. So the solvent molecules can hardly penetrate the cross linked network at all. The crosslink density can be controlled by the ratio of curing agent and functionality of the of rosin amine. In this respect, the chemical resistance data of the cured polyurethane resins were listed in Table 3. It was found that all the prepared PU resins based rosin. have good solvent resistance. This can be attributed to the increasing of the crosslink density by the increment of hydroxyl functional groups which increase the cross link net work of polyurethane by increase the ratio of TDI to rosin amide forming polyurethane resin from PU1 to PU5. we observed failure the chemical resistivity of the system which low TDI ratio(30%) to MPAD This can be attributed to the decreasing the crosslink density of the network and increasing the attack on hydroxyl groups of the network by acidic and alkaline solutions, but PU5 is the most chemical resistivity where TDI is 70% and at increasing TDI more than 70% the chemical resistivity decrease because the 70% TDI to is most efficient ratio. The data relating to acid and alkali chemical resistance for cured polyurethane rosin indicate that these networks possess high resistance to alkaline and acidic aqueous solutions, although they have polyurethane groups. The high crosslink density of the networks decreases their exposure to the environment.

Table (3) Chemical resistance tests of cured polyurethane resin .

PU Resin	Alkali resistance (days)	Acid resistance (days	Solvent resistance	Hot water resistance 38°C
PU1	50	60	+	+
PU2	60	75	+	+
PU3	90	90	+	+
PU4	90	90	+	+
PU5	90	90	+	+

3.3 Testing Corrosion Resistance of Coating.

Salt spray tests are probably the most common tests applicable to corrosion resistance and the most controversial. It is well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrates, and it is useful to have information on the behavior of a particular system in protecting such substrate from corrosion both with intact and damaged coating films. However, they are well established, and despite the problem of reproducibility, are quite useful guides to performance in the absence of longer term corrosion data. They are this unlikely to be discarded. They are considered to be unrealistic by some workers because of the degree of acceleration of the corrosion process that they achieve and the variability of the extent of damage that is inflicted in some of the tests. There are two tests: the continuous salt spray test and the intermittent. The continuous salt spray test was used to study the effect of salts on the properties of coating films. The duration times of tests were determined for all cured polyurethane systems based on rosin amide and TDI which listed in Table 4. Photos of the coated panels of PU5 and PU1 after exposure to salt spray Were selected and represented in Figure (5) .The test was stopped when the films show poor adhesion. The results of salt spray indicate the strong adhesion of coatings by increase of cross linked density. Coating performance was consistently improved for each exposure time for both coatings. This can be attributed to relationships between coating properties and performance. In this respect the adhesion of substrate with coat is the main problem for coating failure. Cracking, flaking scaling or blistering due to under rusting (the latter often being accompanied by brown discoloration of the film) is due to mechanical action by the products of corrosion. In our polyurethane systems it was observed that increasing of terminated hydroxyl groups increases the adhesion of coat with steel. This can be referred to the curing of hydroxyl groups with TDI hardener produce polyurethane groups. It has been shown that the concentration of resultant hydroxyl group has a deleterious effect on the adhesion of the polyurethane coating to the steel metal.

Table (4) Salt spray resistance of cured PU resins.

PU Resin	Expoure time (hours)	Disbonded area		ASTM Rating
		Cm^2	**%**	
PU1	500	8.3	5.5	7
PU2	500	6.2	4	7
PU3	600	5.4	3.5	8
PU4	600	4.6	3	8
PU5	690	1.5	1	9

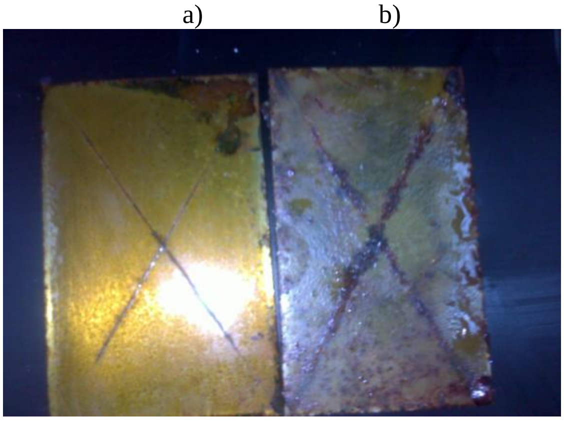


Figure (3). a). salt spray resistance of PU5 after 690 hours. b). salt spray resistance of PU1 after 500 hours

It was also observed that the increment of TDI ratio to hydroxyl groups of rosin amide until reach to 70% TDI (PU5) by comparing the salt resistance of cured PU1 30% TDI, increases the salt resistance of polyurethane systems. This can be attributed to the completely cure of PU5 which is high cross linked net work which increases their resistance to chemicals and salt solutions and consequently increases their corrosion resistance but in case of PU1 the net work is not completely cure enough so the cross linked film is weak and also if TDI ratio to rosin amide more than 70% the cross linked is week due to excess of isocyanate on the film which affect the properties of the cured film. In the present system of cured rosin polyurethane have excellent alkali, acid and solvent resistance and provide a dense hard coating with good adhesion. So from these points it can be used in linings for petroleum equipments.

IV. CONCLUSION

New polyurethane resins based on rosin were prepared by the preparation of amide resins from MPA adducts which was cured with toluene diisocyanate by different mixing ratios 30,40, 50 ,60 and 70% to obtained the best optimum condation of polyurethane film which applied on steel specimen.TGA data observed that temperature corresponding to 5% decomposition of the prepared PU modified rosin amide with70% TDI ratio exhibit high thermal Stability. This means that the incorporation of rosin amide in to PU coatings offer a stabilizing effect against decomposition and the mechanical properties of the cured polyurethane resins are dependent on the degree of cross linking densities of the networks. The high chemical and solvent resistance of the prepared resins can refer to the percentage of70% TDI which give high cross linked .The cured polyurethane based on rosin can be used as having high coating application on steel .

REFERENCES

[1] K.H. Bulai, I.YA. Slonim, YA.G. Urman, O.S. Tsvetkova and Z.V.Mikhailova, Polym Sci. USSR vol. 27(2), 1985, 2173.

[2] N.H .Sahu, P.M Mandaogade, A.M. Deshmukh, V.S. Meghre, .K. Dorle, "Biodegradation studies of rosin-glycerol ester derivative ,J Bioact Compat Polymer, 14,1999, 344-360.

[3] L.T.N. Hoa, J.P. Pascault, L.T. My, C.P.N. Son, Unsaturated polyester prepolymer from] rosin, Euro Polym Jnl , 29 (4),1993, 491-495.

[4] I. Bicu, F. Mustata, Polymers from a. levopimaric acid–acrylonitrile Diels– Alder adduct: synthesis and characterization, J Polym Sci Part A; Polym Chem, 43,2005, 6308-6322.

[5] S.V. Fulzele, P.M.Satturwar, A.K.Dorle, Study of novel rosin-based biomaterials for pharmaceutical coating , AAPS Pharm Sci Tech, ,3(31)2202, 4

[6] U.V. Barabde, S.V. Fulzele, P.M .Satturwar, A.K. Dorle, S.B .Joshi," Film coating and biodegradation studies of new rosin derivative", React Funct Polymer, 62,2005, 241-248.

[7] P.M Mandaogade, P.M .Satturwar, S.V. Fulzele, B.B .Gogte, A.K. Dorle. Rosin derivatives: novel film forming materials for controlled drug delivery. React Funct Polym , 50,2002, 233-242.

[8] I. Bicu ,F. Mustata , Polymers from a levopimaric acid–acrylic acid Diels– Alder adduct: Synthesis and characterization. J Polym Sci Part A; Polym Chem,vol. 45, 2207, 5979- 5790.

[9] A.M. Atta, R. Mansour, M.I. Abdou, and. A.M. Sayed, Epoxy resins from rosin acids: Synthesis and characterization , Polym. For Advanced Technol., 15(9),2004, 514.

[10] A. M. Atta , A. M. Elsaeed, R. K. Farag, S.M. El-Saeed, Synthesis of unsaturated polyester resins based on rosin, acrylic acid adduct for coating applications , Reactive & Functional Polymers , 67,2007, 549–563.

[11] A. M. Atta and A. M. Elsaeed, Preparation and Evaluation of Epoxy Binders Based on Rosin as Organic Coating for Steel , Recent Patents on Corrosion Science , 1,2012, 132-143.

[12] M.H. Reich , K .Nelson, Hydrophilic polyether polyurethane containing carboxylic acid , Patent WO 98/11854, 1998.

[13] A.A.Francisca , A. M. T.Palaua , A. B. oa, J.M.Martın-Martınezb, Addition of rosin acid during thermoplastic polyurethane synthesis to improve its immediate adhesion to PVC", International Journal of Adhesion & Adhesives ,25, 2005,31-38.

[14] Li.He, S. Cui, S. Shang, D. Wang, J.Song, Properties of rosin-based waterborne polyurethanes/cellulose nanocrystals composites", Carbohydrate Polymers, 96(2), 2013,510-515 ..

[15] P. C.Blasco, J. M. Martín-Martínez, I. V Antoniac , Synthesis and characterization of polyurethane sealants containing rosin intended for sealing defect in annulus for disc regeneration International Journal of Adhesion and Adhesives, 42,2013, 11-20.

[16] Ashraf M. Elsaid, Magd M. Badr, and Mohamed S. Selim, Environmental Friendly Polyurethane Coatings Based On Hyperbranched Resin, International Journal of Materials Science and Engineering Vol:7 (8), 2013, 224-230.

[17] X.Yan, G. Xu, Corrosion and mechanical properties of epoxy- polyurethane/bronze composite coatings with low infrared emissivity, Surface and Coatings Technology, VoL. 205(7) , 2010, 2307-2312. .