

Environmental Friendly Polyurethane Coatings Based On Hyperbranched Resin

Ashraf M. Elsaid, Magd M. Badr, and Mohamed S. Selim

Abstract—Water borne polyurethane (PU) based on newly prepared hyperbranched poly (amine-ester) (HBPAE) was applied and evaluated as organic coating material. HBPAE was prepared through one-pot synthesis between trimethylol propane as a core and AB2 branched monomer which was obtained via Michael addition of methyl methacrylate (MMA) and diethanol amine (DEA). PU was prepared from HBPAE using different ratios of toluene diisocyanate (TDI) to form cured coating film. The prepared HBPAE was characterized using; GPC, FT-IR and ¹H-NMR. The mechanical properties (impact, hardness, adhesion, and flexibility), thermal properties (DSC and TGA) and chemical resistance of the applied film were estimated. The results indicated 50% of TDI is the selected ratio. This formulation represents a promising candidate to be used as coating material.

Keywords—Curing, Hyperbranched polymer, Polyurethane, Urethane-acrylates, water borne Coatings.

I. INTRODUCTION

IN the last decades dendritic polymers have attracted special scientific interest due to their desirable extraordinary characteristics. Dendritic polymers can be either dendrimers or hyperbranched polymers. Dendrimers are characteristic by their perfect monodisperse structure and molar mass. In contrast, hyperbranched polymers, HPs, have a less defined structure with incorporated linear units and are therefore polydisperse in structure and molar mass [1], [2].

The properties of dendritic polymers differ from their linear equivalents of the same molar mass, e.g. dendritic polymers exhibit low viscosity, high solubility and low entanglement degree [2]–[5]. Beside the nature and structure of the backbone, their physical and chemical properties are to a large extent dependent on the nature of their end-groups, so the chemical number modification end groups gives the possibility of designing the macromolecules with enhanced characteristics.

The applications of HBPs in various coating systems, such as high solids alkyds, powder coatings, UV-curable coatings have been already presented [6], [7]. One of the most

promising fields of applications of HBP's in coating technologies is waterborne polyurethane dispersions (WPUDs), it has received much attention in recent years and are expected to substitute the solvent-based coatings to save the environment. However, the properties of cured WPUD films such as surface gloss, chemical resistance, hardness, and abrasion resistance need to be improved [8], [9]. UV curing systems provide the coatings with high solvent and scratch resistance but lack of flexibility due to high crosslink density [10]. Therefore, UV curable waterborne polyurethane dispersions (UV-WPUDs) are supposed to combine the advantages of WPUD and UV curing system. The conventional UV-WPUDs are usually prepared by end capping the linear polyurethane prepolymer with single-hydroxyl (meth) acrylate, resulting in low unsaturation density, and thus crosslink density. As a result, the mechanical properties, solvent and water resistance of cured films are not good enough [11]–[13]. Using pentaerythritol diacrylate as an extension agent, a novel UV-WPUD through incorporating acrylate double bonds as side chains of polyurethane has been reported to give the excellent solvent resistance and mechanical properties of UV cured films [14]–[16]. Recently, the UV-WPUDs with different functionality were prepared using various chain extension agents, and showed that the mechanical properties and solvent resistance increased with increasing the functionality of modified polyurethane [17]–[20].

Hence, Hyperbranched polymers represent a promising candidate to prepare the UV-WPUDs with high functionality due to their desirable characteristics. The modifications of UV-WPUDs with hyperbranched poly (amine-ester) HBPAE were synthesized in our group. In this study, The prepared HBPAE was carried out using couple monomer methodology where "AA'+B'B2" monomers undergo Michael addition at mild conditions to form the AB2 prepolymerized monomer followed by polycondensation reaction with trimethylolpropane which was used as a core at 120°C [21]. Water borne polyurethane was prepared throw the reaction of toluene diisocyanate with the prepared hydroxyl terminated HBPAE. The cured polyurethane-HBPAE showed enhanced characteristics such as high thermal stability and good mechanical properties which were applied on steel.

II. EXPERIMENTAL

A. Materials

Methyl methacrylate (MMA), diethanol amine (DEA), trimethylol propane (TMP), p-toluene sulphonic acid (pTSA),

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toluene diisocyanate (TDI), were purchased from Sigma-Aldrich chemical Co. methanol, ethyl methyl ketone, sodium hydroxide and hydrochloric acid from Merck A. G. chemical company.

B. Synthesis of Hyperbranched Poly (Amine-Ester)

Hyperbranched poly (amine-ester) (HPAE) had trimethylolpropane as a core and N, N-diethylol-3-amine methyl propionate as the AB₂ branched monomer followed the literature [21]. It was synthesized by a pseudo-one-step process. The N,N-diethylol-3-amine methyl propionate (1) synthesized via Michael addition of (0.1 mol) methyl methacrylate and (0.1mol) diethanolamine in methanol solvent were stirred at 40 °C for 2h, followed by removing solvent through vacuum distillation, obtained faint yellow oily liquid (1). In another reaction, (0.1 mol) trimethylolpropane (0.3 mol) (1) and 0.5 wt% catalyst of p-toluene sulfonic acid were stirred at 130 °C for 4 h. The residual unreacted monomers were removed by vacuum distillation. HPAE was yellow oily liquid and yield was 92%.

C. Cured of Hyper Branched Polyurethane Film

Polyurethane hyperbranched film was prepared from mixing HBPAE using different ratios of toluene diisocyanate (TDI) to form cured film as in Table I.

TABLE I
COMPOSITION OF THE DIFFERENT HYPER BRANCHED POLYURETHANE RESINS

POLYURETHANE RESIN	HBPAE: TDI	PERCENTAGE OF TDI
PU1	90:10	10
PU2	80:20	20
PU3	70:30	30
PU4	60:40	40
PU5	50:50	50
PU6	40:60	60

D. Measurements & Instrumentation

The prepared polymer and coatings were characterized via different investigation techniques such as Fourier Transform Infrared spectra (FT-IR), gel permeation chromatography (GPC), nuclear magnetic resonance (1H-NMR) and thermal analyses such as thermal gravimetric analyses (TGA) and differential scanning calorimeter (DSC).

FT-IR was recorded by using an infrared Bruker IFS 66 FT-IR Spectrometer with 1 Cm-1 resolution and in range from 4000-500 cm⁻¹. The samples were cast on potassium bromide (KBr) pellets. While, the molecular weight was measured by GPC (Waters model 510) using THF (HPLC grade) as eluent and Ultrastaygel 500; 1000; 10,000; 100,000 Å as column. GPC measurements were completed using polystyrene molecular weight standards. on the other hand; 1HNMR Spectra were recorded on a Varian EM 360 spectrometer in deuterated chloroform (CDCl₃) with 1% tetramethylsilane (TMS) as internal solvent.

TGA was carried out by using TGA-50 shimadzu instrument, in the range 0 – 400 °C; the heating rate was 20 K/min. The DSC measurement was carried out by using differential scanning calorimeter DSC-60 shimadzu in the

range from -20 -140 °C, with a scanning rate of 10 c/min, working with 8-10 mg sample in aluminum pans and under nitrogen atmosphere. The heat evolved during the reaction of the mixture has been directly determined by integration of the exothermic peaks. The glass transition temperature, T_g was taken in a second scan as the beginning point of the endothermic shift in the DSC scan. Viscosity measurement was carried out using a standard D 1545-89 method ASTM.

E. Testing of the Coatings

It is common to use mild steel panels (15 cm x 10 cm) to evaluate the different properties of coatings. The panels are prepared according to British standard specification 1449. The other side of the panels is coated and protected against corrosion environments by using coal tar epoxy primer. Then the panels are subjected to different testing procedures to evaluate their mechanical properties (adhesion strength, pencil hardness test, impact resistance and T-bend test) and their durability.

Chemical resistance of organic coatings was evaluated from hot water resistance, solvent resistance and salt spray resistance according to ASTM of organic coatings. The coated panels were evaluated for salt-spray resistance in accordance with ASTM B117. The results of the salt-spray tests were evaluated by two methods. One method was to measure the area of disbonding around the scribed X. The other method was to evaluate the disbonded area in the lower half of the test panel in accordance with ASTM D1654 rating system. 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 degree of adhesion and visual inspection of blister and cracks were tested for the coated panels. The thickness of the polyurethane coatings was measured with an Electrometric ESM-12 magnetic thickness gauge.

III. RESULTS & DISCUSSION

HBPAE was synthesized via pseudo-one-step reaction between TMP as a central core and AB₂ prepolymerized monomer as shown in Fig. 1.

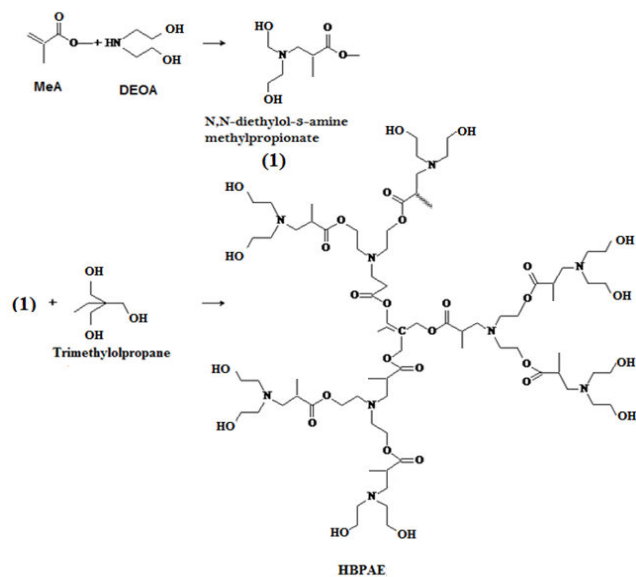


Fig. 1 Scheme of Synthesis of hyperbranched poly (amine-ester)

The HBPAE was characterized by GPC, FT-IR, $^1\text{H-NMR}$, TGA and DSC. FTIR spectrum of the prepared polymer showed as in Fig. 2 revealed that, the two bands at 2879 cm^{-1} and 2941 cm^{-1} were due to C-H stretching and the band at 1729 cm^{-1} represented the α -unsaturated carbonyl of the ester group. The broad absorption band at 3398 cm^{-1} was assigned to hydroxyl groups which were H-bonded and those bands at 1064 cm^{-1} , 1112 cm^{-1} and 1265 cm^{-1} were attributed to C-O and C-N stretches.

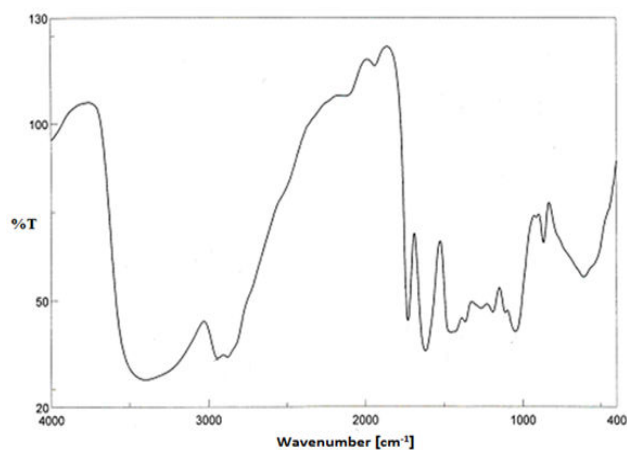


Fig. 2 FTIR spectrum of the prepared hyperbranched poly(amine-ester)

$^1\text{H-NMR}$ Spectrum of HBPAE1 showed as in Fig. 3 distinguished signals of chemical shifts at 0.7 ppm which were assigned to $(\text{CH}_2-(\text{CH}_3)\text{CH}-\text{NCH}_2-)$, while signals of chemical shift at 1.1 corresponding to $(\text{CH}_3\text{CH}_2-)$ and other signals at 1.7 were assigned to $(\text{CH}_3\text{CH}_2\text{CR}_3)$, signals at 2.0 – 2.2 and 2.3 – 2.5 were ascribed to $(-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2)$ and $(-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2)$, those at 2.83.0 and 3.2 -3.4 were ascribed to

$(-\text{OCOCH}_2\text{CH}_2\text{NR}_2)$ and $(\text{R}'\text{R}_2\text{CCH}_2-\text{OCO})$ and at 4.5 were assigned to $(-\text{CH}_2\text{CH}_2\text{OH})$.

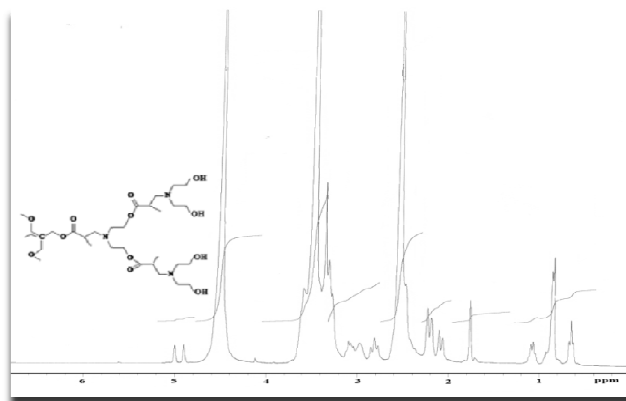


Fig. 3 $^1\text{H-NMR}$ spectrum of the prepared hyperbranched poly (amine-ester)

TGA of HBPAE as shown in Fig. 4 exhibited relative thermal stability till $200\text{ }^\circ\text{C}$, where the weight loss is 20%, TGA curve of the hyperbranched poly (amine-ester) descended when the temperature reached the range of $250\text{ }^\circ\text{C}$ - $320\text{ }^\circ\text{C}$. DSC as shown in Fig. 5 measurements recorded T_g value as $23\text{ }^\circ\text{C}$. The previous data confirmed the expected structure of the resulting polymer

TGA data as shown in Table II, observed that temperature corresponding to 50% decomposition of the prepared PU modified HBPAE with different of TDI ratios exhibit high thermal stability which would increased with the TDI ratios increase. This means that the incorporation of HBPAE in to PU coatings offer a stabilizing effect against decomposition.

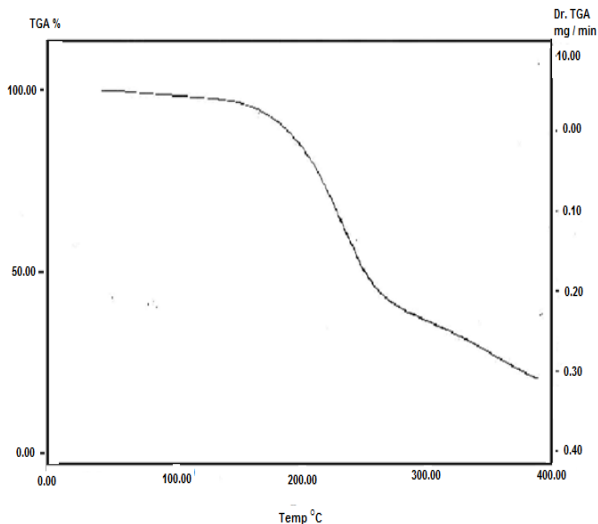


Fig. 4 TGA spectrum of the prepared hyperbranched poly (amine-ester)

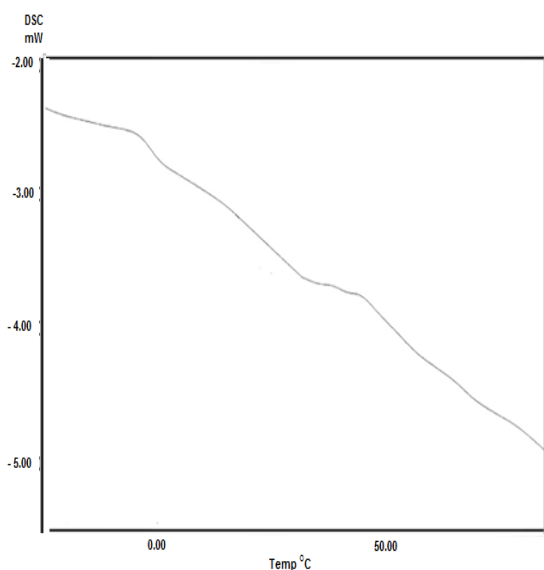


Fig. 5 DSC spectrum of the prepared hyperbranched poly (amine-ester)

TABLE II
THERMAL ANALYSIS (TGA & DSC) OF CURED PU RESINS

POLYURETHANE RESIN	DSC MEASUREMENTS (Tg °C)	TGA measurements At 50 % Wt. loss (°C)
PU1	136	400
PU2	199	405
PU3	201	413
PU4	216	418
PU5	217	421

A. Mechanical Properties of the Cured Hyperbranched Polyurethane Resin

Among the different resinous materials utilized in polymeric applications, hyperbranched 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 HB polymers as precursors with a compact architecture instead of linear polyether or polyester polyols results in HBPU with different material properties [6]. In fact, new PU systems with hyperbranched polymers, incorporated in a PU matrix as blends or introduced in the network as a cross linker, so in our present work the hyperbranched aliphatic polyesters (HBPs) was prepared using AB2 monomer and core moiety TMP. These HBPs are cured with TDI by different ratios forming a hyperbranched polyurethane network. 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 the hyperbranched polyurethane resins has been carried out on two aspects of the polyurethane resins namely, development and modifications of newer hyper branched water born polyurethane resin and their applications in manufacturing composites, coatings, adhesives,

paints, varnishes, construction materials and some other advanced fields. The present work aims to synthesis of water born hyperbranched polyamine ester with toluene diisocyanate to produce cured hyper branched polyurethane film having good durability with excellent mechanical properties. The compositions of the different hyperbranched polyurethane resins are listed in Table I. 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, 150 μ m on blasted steel panels. The tests for measuring the mechanical properties were evaluated after 24 h at ambient temperature. The data reported on adhesion and mechanical properties are listed in Table III. The data indicate that all cured hyper branched polyurethane resins PU5 based on TDI 50% 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 hyper branched polyol which meet the suitable quantity with TDI.

Where PU5 give the best results with impact and T-bend tests. These characteristics indicate that the ratios between hyperbranched polyol 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 (by pencil test) from softer (minimum cross links) to hardener coatings (maximum cross-link-density).

TABLE III
COATING TESTS OF PU RESIN CURED BY TDI

POLYURETHANE RESIN	TDI %	IMPACT (JOLE)	PULL OF RESISTANCE (MP)	T-BEND	HARDNESS
PU1	10	6	5	-	H
PU2	20	7	7	+	HB
PU3	30	9	10	+	2H
PU4	40	10	11	+	3H
PU5	50	15	16	+	3H
PU6	60	5	4	-	F

B. 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 their resistance 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 hyper branched poly (amine-ester) resins. In this respect, the chemical resistance data of the cured hyper branched polyurethane resins were listed in Table IV. It was found that all the prepared PU resins based HBPU 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 hyper branched poly (amine-ester) forming polyurethane resin from PU1 to PU5. we observed failure the chemical resistivity of the system which low TDI ratio (10%) to HBPAE 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 50% and at increasing TDI more than 50% the chemical resistivity decrease because the 50% TDI to is most efficient ratio. The data relating to acid and alkali chemical resistance for cured polyurethane hyper branched resins 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 IV
CHEMICAL RESISTANCE TESTS OF CURED PU

Polyurethane resin	Alkali resistance (days)	Acid resistance (days)	Pull of resistance (MP)	Solvent resistance (acetone test)	Hot water resistance 38 °C (days)
PU1	40	60	5	+	70
PU2	80	90	7	+	90
PU3	90	90	10	+	90
PU4	90	90	11	+	90
PU5	90	90	16	+	90
PU6	30	40	4	-	50

C. 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 hyper branched polyurethane systems based on hyper branched poly (amine-ester) resins and TDI which listed in Table V. Photos of the coated panels of PU5 after exposure to salt spray were selected and represented in Fig. 6 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.

The most familiar corrosion of this type is the rusting of iron exposed to moist atmosphere or water. The initial penetration of rust through the protective coating film is based on the coating constituents. The coating constituents must be able to resist the transfer of ions through the coating and be able to expand and contract with the underlying surface over which it is applied. These ions are chloride, sulfate carbonate, or similar ions which, on penetrating the film, would start under film corrosion. So the coatings must be highly adherent to the substrate and must have excellent resistance to water, ionic passage, osmosis, chemical weather and electroendosmosis [22]. Resistance to osmosis and electroendosmosis greatly affect coating life. In this respect water or dilute salt water are directed to the coating, they are semi permeable membranes, to which the principle of osmosis definitely applies. If the steel surfaces contain chlorides, sulfates or other ions (on which the coating is applied) will increase water penetration through the coating and leads to blistering and coating failure. So the strong adhesion is required to overcome the physical action of osmosis and electroendosmosis. Strong adhesion also prevents moisture vapor from passing through the coating and condensing in a poor area of adhesion, leading to a blistering of coating. This is of particular significance when it comes to the choice of suitable coating systems. 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. It was also observed that the increment of TDI ratio to hydroxyl groups of HBPAE until reach to 50% TDI (PU5) by comparing the salt resistance of cured PU1 10% 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 hyper branched polyester amine more than 50% 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 polyurethane hyper branched resin 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 tanks and tankers, salt barges and ships, general chemical tankers, as well as exterior coatings for the bottoms, boot-topping, and decks.

TABLE V
SALT SPRAY RESISTANCE OF CURED POLYURETHANE RESINS

Polyurethane resin	Exposure time (hours)	Disbonded area		Rating Number (ASTM D1654)
		Cm ²	%	
PU1	400	7.4	4.8	7
PU2	480	6.2	4	8
PU3	580	5.6	3.6	8
PU4	620	4.1	2.6	8
PU5	950	2.3	1.4	9
PU6	350	9.8	15	5



Fig. 6 Salt spray resistance of PU5 after 950 hours

IV. CONCLUSIONS

The following conclusions can be drawn from the previous results:

- 1) Hyperbranched polyurethane coating can be synthesized from hyperbranched poly (amine-ester) and TDI.
- 2) TGA data observed that temperature corresponding to 50% decomposition of the prepared PU modified HBPAE with 50% TDI ratio exhibit high thermal stability. This means that the incorporation of HBPAE in to PU coatings offer a stabilizing effect against decomposition.
- 3) The mechanical properties of the cured hyperbranched polyurethane resins are dependent on the degree of cross linking densities of the networks.
- 4) The high chemical and solvent resistance of the prepared resins can refer
- 5) The cured hyper branched polyurethane resins can be used as having high coating application on steel, and the results showed that the percentage of 50% TDI give high cross linked PU film.

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