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PERFORMANCE OF HYPERBRANCHED DENDERTIC POLYESTERPOLYOLS ORGANIC COATINGS

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Abstract

The present article depended on designation of four branched unsaturated resins in two steps. The first step includes the preparation of eight hydroxy branched groups based on pentaerythritol as a core molecule and dimethylolpropionic acid as monomer. In the second step polycondensation reactions of 1 mole prepared eights hydroxy terminated sample with four different molar ratios of maleic & phthalic anhydride namely10:90, 30:70, 50:50&90:10 respectively assigned as H1, H2, H3 and H4. The chemical structures of the prepared polymers are confirmed using FTIR and ^{1}HNMR spectroscopic techniques. The particle sizes & molecular weights of the synthesized resins are determined. Four high reactive functional groups cross linked networks water based coating films are performed to improve their chemical and mechanical resistance.

***Keywords**: Hyperbranched polymers; water based organic coatings; unsaturated polyester; nanoparticle resins; dimethylolpropionic acid.*

1. Introduction

The creations and investigation of new polymeric architectures have a greet attention among polymer scientists over the last eras [1]. Dendritic polymers are attractive for industrial needed because they have high functionality, high solubility and sole rheological manners. Dendritic polymers divided into two different classes: the monodisperse dendrimers and the polydisperse hyperbranched polymers [2]. Dendrimers have regular star-like structure and need various steps for preparation which certainly lead to a relative high cost price, and limit their use in applications.

Hyperbranched polymers have irregular structures tree-like macromolecules ended with a great numbers of reactive functional groups prepared in one and simple step method [1-10]. Properties of branched macromolecules do not only attract the academic research through their simplicity and synthetic experiment [2], but they also get more and more attention in industrialized research applications [11-15]. Because of the sole behaviors, multifunctional terminal groups, narrow polydispersity and low cost with easy synthesis, hyperbranched polymers can to be used as coating resins [[2, 16, 17]].

On the other hand, the traditional unsaturated polyester resins (UP) prepared previously in literatures suffer from various problems such as rigidity, low acid & alkali resistances and low adhesion with steel when cured with vinyl monomers [18-24]. To solve these badly-behaved polymers, low cost hyperbranched resins with small particle size ended by various reactive functional groups with high surface area containing different chain lengths are synthesized in the present research. In this respect, the present paper aims to design four branched unsaturated polyester resins using simple method with various chain lengths and different nanosizes for coating stability based on pentaerythritol (PEL) as a core molecule and dimethylolpropionic acid (DMPA) as monomers.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

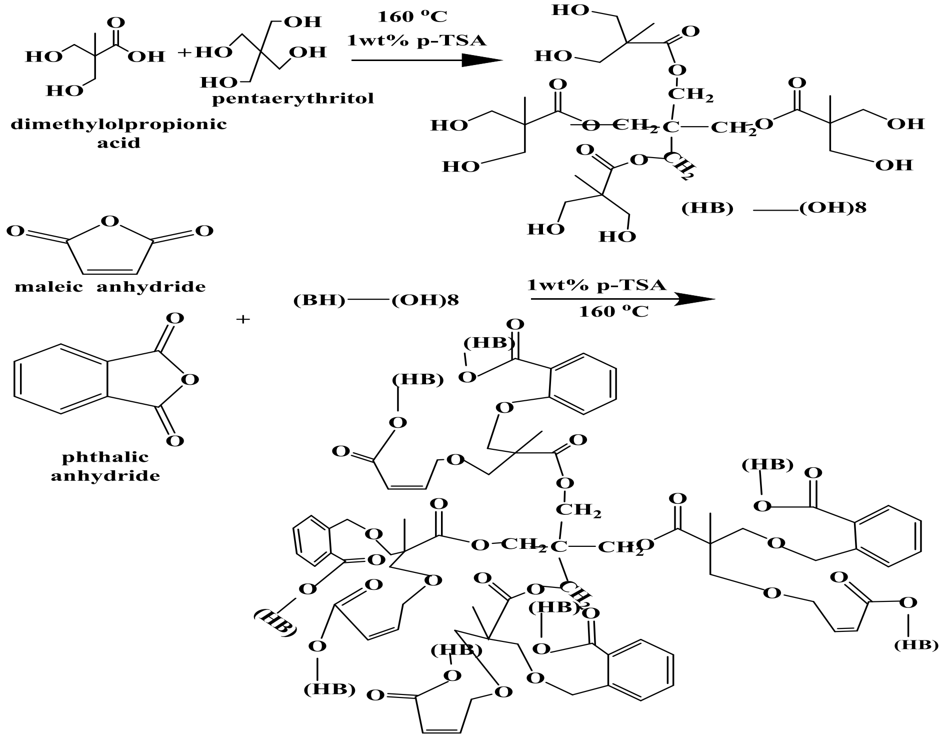
Pentaerythritol (PEL), dimethylolpropionic acid (DMPA), Phthalic anhydride, adipic acid, lauric acid and stearic acid, maleic anhydride, styrene, para-toluene sulphonic acid (p-TSA) was added as catalyst, 10% HCl and 5% NaOH aqueous solutions, methyl ethyle keton peroxide (MEKP) as initiators, cobalt octoate as accelerator. Dichloromethane ($CH_2Cl_{2)}$ and distilled water are used for purification. The Fluka chemical company supplied all chemical.

2.1.2 Synthesis of hyperbranched polyester

Equimolar ratio of pentaerythritol (PEL) as a core and dimethylolpropionic acid (DMPA) as monomers is placed in a 250 round flask equipped with a mechanical stirrer, thermometer, and condenser. 1wt% of p-toluenesulfonic acid (p-TSA) is added as catalyst. The temperature is adjusted to be constant between 140 and 160^{0}C in the end of the reaction, eight hydroxyls terminated hyperbranched polyester is yielded and named (HB)-(OH)8 after evaporating the small amount of water produced [25-28].

2.1.3. Synthesis of unsaturated hyperbranched polyester nanoparticles resin

The reaction system is evacuated using N_2 gas for 30 min before the beginning of the reaction. One mole of eight hydroxyl ended hyperbranched polyester (HB)-(OH)8 is reacted with four different molar ratios of maleic & phthalic anhydride namely10:90, 30:70, 50:50&90:10 respectively assigned as H1, H2, H3 and H4 in presence of 1wt% p-TSA of total weight reactants as catalyst at 160^{0}C. The prepared resin was purified using CH_2Cl_2, and distilled water. After the solvent was evaporated, the polyester nanoparticles were mixed with large amounts of styrene vinyl monomer to yield 60% solution of the polyester. The schematic presentation of the synthesis is shown in Figure 1.



(HU1)

Figure 1. The schematic presentation of the synthesis of unsaturated hyperbranched nanoparticles

2.1.4. Dynamic light scattering (DLS)

DSL is a technique in physics that can be used to determine the size distribution profile of small particles in suspension or polymers in solution. In the present study, the samples were dispersed in high dilution methanol and 2% diluted distilled water.

Gel permeation chromatography (GPC) was performed at 40°C using GPC-Water 2410, with a refractive index detector using 4 columns styragel HR tetrahydrofuran (THF) 7.8 x 300 mm, equipped with a water 515 HPLC pump. tetrahydrofuran and water were used as a mobile phase with a flow rate of 1 mL/min. Aliquots (1 ml) of each sample were diluted with an appropriate amount of THF or water and shaken vigorously. Afterwards, the samples were passed through a filter and injected into the GPC for analysis.

2.2. Testing of the coatings

Steel panels of (10 x 15 cm) are used to evaluate the behaviors of coatings. The panels are coated with tested polymers by using methylethyl ketone peroxide as initiators and cobalt octoate as accelerator. Then the panels are tested 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 water resistance, acid & Alkali resistance and Solvent & fuel resistance according to ASTM D870-69, ASTM D1647-89, and ASTM D 870-92 respectively. The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl aqueous solutions using distilled water. The duration of the test was 90 days at 38 ^{0}C. The degree of adhesion and visual inspection of blister and cracks were tested for the coated panels.

2.3. Surface morphology studies

The scanning electron microscopy (SEM) of model type JEOL 5410, JEOL, Japan are used to detect the surface morphology of the coated and uncoated panel samples after immersion in 10% of HCl and 5% of NaOH aqueous solutions for 90 days at 38 ^{0}C.

3. Results and discussion

3.1. Characterizations of the synthesized hyperbranched polyester

The FTIR spectrum of prepared hyperbranched polyester with 8 hydroxyl reactive ended groups (HB)-(OH)8 which is represents in Figure 2(a) shows the following characteristic peaks:- Absorption bands at 3500 cm^{-1} assigned for OH stretching band, the appearance of beak at 2900 cm^{-1} assigned for stretching vibration of the aliphatic CH bond and the appearance of beak at 1730 cm^{-1} assigned for C=O group indicate the completion of esterification reactions. The appearance of beak at 1105 cm^{-1} assigned for stretching vibration of the C-O, 1450 cm^{-1} assigned for stretching CH_2 and 1375 cm^{-1} assigned for CH_3 peak.

Moreover Figure 3 shows ^{1}HNMR chart Protons of (HB)-(OH)8 polymer. Hydroxyl terminated protons appears at the peaks of (4.8–5.2 ppm), CH_3 protons at (1.00 –1.10 ppm), CH_2-O-C=O protons at (4.00–4.22 ppm) and CH_2-OH protons at (3.35–3.56 ppm), the peak at about 2.5 ppm is certified to the remaining hydrogen protons of the solvent (DMSO). All the above peaks approve the construction of hyperbranched polymer.

On the other hand the constituents of the four performed hyperbranched unsaturated polyesters show the same FTIR charts. Figure 2(b) represents FTIR bands for H1 as representative sample, the spectrum shows absorption bands at 2982 cm^{-1} (assigned for stretching vibration of the aliphatic CH bond). The appearance of peak at 1620 cm^{-1} (assigned for stretching vibration of the (C=C) indicate the presence of unsaturation, 1450 cm^{-1} (assigned for stretching CH_2), 1375 assigned for CH_3 peak and the appearance of beak at 1730 cm^{-1} assigned for C=O group. The appearance of hydroxyl and protons confirm hyper branched polyols terminated performance. Furthermore the synthesized unsaturated hyperbranched polymers have a more complex structure, and more types of repeating units so it may be difficult to elucidate the exacted chemical structure using ^{1}HNMR spectroscopy technique accordingly the signals overlapped with each other so no definite peaks appears [15] .

The size and distribution of the performed nano particle resins are estimated as shown in Table 1. Figure 5 give an example for DLS chart for H4 resin. It is clear from the data of particle size that, the particle size increase in order of H1>H2>H3>H4 this means that, the size of prepared resins increase by increasing terminal aliphatic chains (maleic moiety) .This may be attributed that, as the terminated ended chains increase the regular structure (ordering structure) may be formed with large surface area and small particle size [15].

The molecular weights of the synthesized hyperbranched resins decrease by increasing maleic anhydride moiety and all samples have polydispersity more than one as shown in Table1. This result may be attributed to the disordering of the arrangement of branched molecules by decreasing ended chain length as mentioned in our previous work [15].

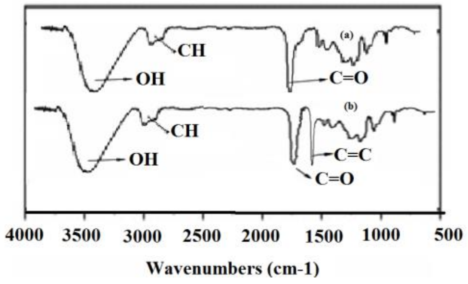


Figure 2. FTIR spectrum of (a) HB-(OH)8 and (b) H1 respectively

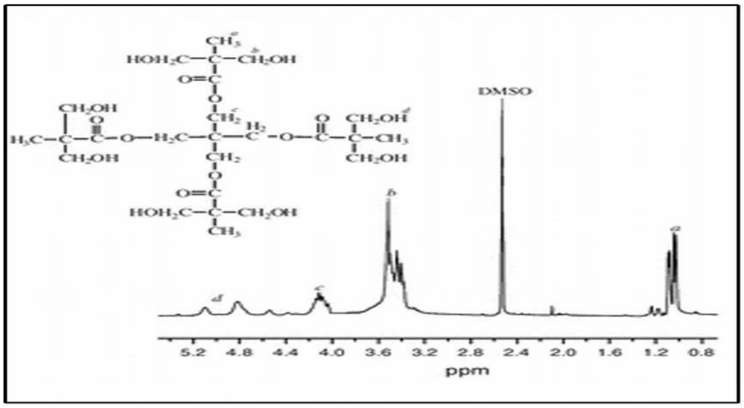


Figure 3. ^{1}HNMR spectrum of HB-(OH)8

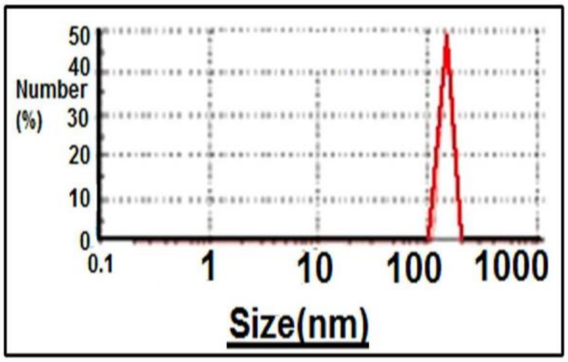


Figure 4. DLS Image of H4

Table 1. Molecular weights and diameter of the synthesized hyperbranched unsaturated nano particles polyester resin

Sample	Molecular weight (g/mol)	Polydispersity	Diameter (nm)
H1	9 760	1.3	350
H2	9 850	1.3	350
H3	12 564	1.2	200
H4		1.2	150

3.2. Evaluation of synthesized unsaturated polyester resins for coating applications

Hyperbranched polyolesters can be prepared using simple and low cost method. They have greatly branched strength and huge functional hydroxyl groups, which gives entree to a large number of reactive groups. Their construction makes them excellent in water based organic coatings.

3.3. Chemical resistances

The effects of surrounding solutions are very important especially on durability. In this respect, four panels coated with the prepared resins and immersed to alkali, acid, solvent (acetone test) solutions to study the stability of coats at three months. The initial change of the panels was affected by the environmental conditions. With contact to the surrounding media, the appearance of all the panels changed to show color variations and roasting. The observations at 3 months are summarized in Table 2. It is obvious from the results that the four coated panels with the performed nanoparticle polymers stable and not affected by acid, alkali, water or solvent for 90 days but in case of coated panel with H1 stable for 60 days only and after that, the coated samples affected by acid and alkali solutions this may be attributed to its hardiness which disappointed the stability of samples.

3.4. Surface morphology studies

Figure 5 shows the image of uncoated steel and four tested coated panel after immersion in 10% of HCl for 90 days. It is clear from the images that, the uncoated panel surface is highly corroded. Whereas smoother surface is seen for H2, H3 and H4 attributed huge functionality on the surface area with high moiety of maleic anhydride as aliphatic polymers. These results indicated that, the constituents of aliphatic chains molecules inhibit the cracking of the coated protective film on the steel surface after long time of immersion in hard environmental conditions [29-31]. But in case of H1 sample after 90 days cracking on coated film surface is occurred this is may be attributed to the rigidity of H1 sample due to the high content of phthalic acid moeity.

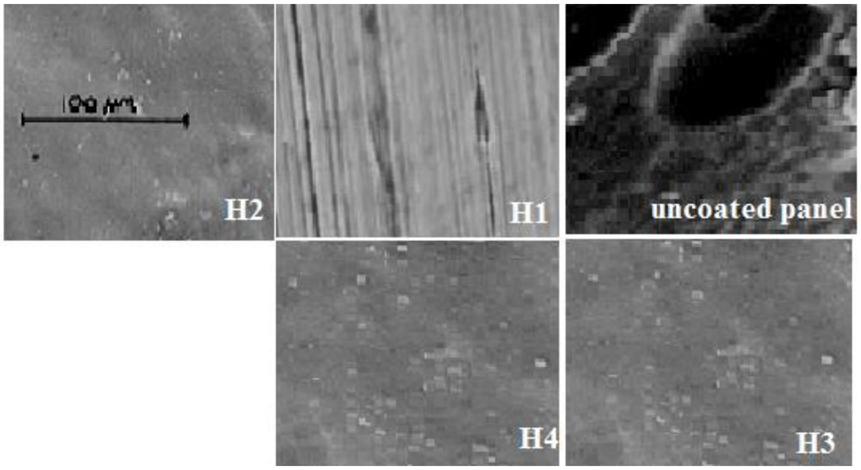


Figure 5. SEM images of uncoated panel, coated panel with H1, H2, H3 and H4 sample after immersion in immersion in 10% of HCl for 90days.

Table 2. Chemical resistance tests of the performed hyperbranched unsaturated polyester cured with styrene

Sample	Acid resistance (days)	Alkali resistance (days)	Water resistance	Solvent resistance
H1	60	60	+	+
H2	90	90	+	+
H3	90	90	+	+
H4	90	90	+	+

+ pass; - fail

3.5. Mechanical tests

The mechanical properties of the performed hyperbranched resins have been tested by determining the impact, T-bend, adhesion and hardiness according to (ASTM D2794-04) (ASTM D 522/1999) (ASTM D 4541/20002) (ASTM D 3363/2000) respectively. The synthesized unsaturated hyperbranched polyester is transparent viscous liquid at room temperature it turn into solid state (cured) when adding 2g methyl ehyl keton peroxide initiator (MEKP) & 0.2g cobalt octoate activator to 100g of each tested resin containing 60% of styrene for 8-10 minutes for forming four cross linked networks coating films. In this respect, the tests for measuring the mechanical characteristics were evaluated after post-curing at 105°C for 24 h and standing for another 24 h at ambient temperature (25°C). The data of mechanical properties (adhesion, impact, and T-bending) for cured resins based are tabulated in Table 3. It is clear from the table that, the adhesion, impact at measured at 5.5&7.5J/mm and T-bond for the four unsaturated nanoparticles resins are all positive. This means that the prepared hyperbranched particles forming stable networks film with panels and having a good mechanical resistance. This may attributed to the nano size of the prepared polymers giving large surface area with stable networks which endorsed each to acts as excellent organic coatings. It is also obvious from the hardness results that the hardness decreases in the order of H4< H3 < H2 < H1. This may be owing to, increasing aliphatic and huge reactive functional ended segments chain length donate the flexibility to the coatings compounds. So the mechanical brittleness is effectively by stability and flexibility of hyperbranched crosslinked films forming coating. The data reported on adhesion indicates that the tested branched resins have superior adhesion network properties with steel. This can be attributed to the high functionality of resins which have beneficial effects on adhesion. It is obvious from hardness results that, H1sample is the hardest polymer. This behavior is according to the high crosslinking density networks formation. The reasons for hard& dense network formed for H1 attributed to high contents of aromatic phthalic moiety.

Table 3 Coating tests of hyperbranched unsaturated polyester cured with styrene

Sample	Adhesion	Impact (5.5 or 7.5 J/mm)	T-bond	Hardness
HU1	+	+	+	H
HU2	+	+	+	HB
HU3	+	+	+	HB
HU4	+	+	+	HB

+ pass; - fail

3.6. Abrasion resistance test

This method test the resistance of organic coatings to abrasion produced by the Taber Abraser on coatings applied to a plane, rigid surface, such as a metal panel according to (ASTM D 4060 – 95) using abrasion test instrument. Abrasion resistance is calculated as loss in weight at identified number of abrasion cycles, as loss in weight per cycle, or as number of cycles required to remove a unit amount of coating thickness. A result in Table 4 represents mass loss of tested samples. It is clear from abrasion test that, the mass loss of the synthesized resins is slightly decrease in the order of H1>H2>H3>H4, as for example the final mass loss of H1 was 0.95 g_m and H4 sample was 0.44g_m. These results relate to the slightly decrease of particle size and the stability of high functional reactive groups coated samples which give high surface area to resist the conditions such as loads and scratching material. These results also indicates that, H4 is most efficient due its highest flexibility according to high contents of aliphatic moiety, functionality of the surface of coating and its small particle size with regular hyperbranched structure which gives height surface area for coating resistance conditions.

Table 4. Abrasion resistance of hyperbranched unsaturated polyester cured with styrene

	Wight of coated panel before the test (g_m.)	Wight of coated panel after the test (g_m)	Wight loss of coated panel after the test (g_m)	Wight loss % of coated panel after the test
H1	80,23	79,29	0,95	1,20
H2	80,77	80,02	0,75	0,93
H3	81,79	81,12	0,66	0,81
H4	81,35	80,90	0,44	0,50

3.7 Mandrel bending test

Mandrel test performed according to ASTM D522 which contains two test methods used to determine the flexibility and resistance to cracking of organic coatings on substrates of sheet metal. Coatings attached to substrates are elongated when the substrates are bent during the manufacture of articles or when the articles are abused in service. These test methods used to examine the ability of coatings to attack cracking when stretched out. In this respect Figure 6 shows the four unsaturated nanoparticles coated panels when elongated with Mandrel bending tester. It is clear from this images that when aliphatic chains increase the panel become totally flexible and no cracks appear in order of H4>H3>H2>H1. This may be attributed to high contents of aliphatic moiety which decrease the hardness of coated samples.

Figure 6. Mandrel bend testing panel of HU1, HU2, HU3 and HU4 sample

4. Conclusions

Four samples of unsaturated hyperbranched polyester polyols resins are performed. The particle size of the synthesized resins decreases by increasing the molecular weights and by increasing maleic anhydride contents. The coated films showed excellent water, alkali, acid and acetone resistance. The prepared high functional reactive water based organic coatings have good adhesive and mechanical properties. H4 with high surface area and small particle size is the most stable sample with good chemical, mechanical, abrasion resistance. Moreover H4 is the best flexible sample and resistance to the cracking of organic coatings.

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