

Synthesis of Bisphenol A Novolac Epoxy Resins for Coating Applications

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ABSTRACT: Bisphenol A novolacs were synthesized in both melting and solution processes using *p*-formaldehyde and formalin solution in presence of oxalic acid catalyst, respectively. Hydrogen nuclear magnetic resonance, ¹H NMR, investigations show a high methylene bridge contents in the novolacs synthesized in a melting process. These novolacs were analyzed by gel permeation chromatography (GPC) and fourier transform infrared spectroscopy (FTIR). The bisphenol A novolac was cured with 1-(2-amino ethyl) piperazine (AEP) as a curing agent for epoxy resins. The cured resins were evaluated as organic

coating for steel. The mechanical properties of the cured epoxy resins were evaluated. The chemical resistances of the cured resins were evaluated through salt spray resistance, hot water, solvents, acid and alkali resistance measurements. The data indicate that the cured epoxy resins have excellent chemical resistances as organic coatings among other cured resins. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 347–354, 2008

Key words: bisphenol epoxy; coatings; curing; novolacs; chemical resistance; mechanical properties

INTRODUCTION

Epoxy phenol novolac resins have attained commercial importance.^{1–3} When cured with polyamide or aliphatic polyamines and their adducts, epoxy novolacs show improvement over bisphenol A epoxies, but the critical performance of each cure is limited by the performance of the curing agent. Novolac-cured epoxy resins are widely employed in molding and sealing compounds for the production of electronic devices. Commercial novolacs are used on the basis of phenol or cresol.^{4,5} Modelling reactions of epoxy-phenol systems were investigated in the literature,^{6–8} but no researchs about bisphenol A novolac-cured epoxy resins are known.

Although the glycidyl ether derivatives are used as adhesives, they suffer from a lack of flexibility, which arises from short rigid aromatic groups in the chains.

Improvements in flexibility can be obtained by incorporation of long chain compounds into the resin before cure. The aim of the present study is directed to introduce methylene group between aromatic groups of bisphenol to improve both the adhesion and flexibility properties of epoxy resins. In this respect, bisphenol A novolacs were synthesized in a melting process using *p*-formaldehyde, and in a solution process using a formalin solution and oxalic

acid catalyst. The 1-(2-Amino ethyl) piperazine (AEP) was selected as suitable curing agent to produce organic coatings.

EXPERIMENTAL

Materials

Diglycidylether of bisphenol A (DGEBA) was recrystallized from an acetone-methanol mixture (20:80, v/v); m.p. 44°C.⁹ Epichlorohydrine (EC) was used as received. AEP was used as hardener. *p*-formaldehyde and formalin solution (37%) was used as received. High purity acetone, toluene, and pyridine were used as received. All chemicals were supplied by the Aldrich Chem.

Techniques

Methylation of bisphenol A

Different molar ratios between bisphenol A and *p*-formaldehyde were used for the syntheses of the novolacs. The mol ratio between *p*-formaldehyde and bisphenol A was varied between 0.167 and 0.495 mol formaldehyde to 0.438 mol bisphenol A. The mixtures were heated at 180°C in a one-necked flask with a reflux condenser and a drying tube only filled with glass wool. After 30 min the reflux condenser was removed and the water was distilled. After no more water could be distilled, the temperature of the reaction mixture was shortly (about 5 min) raised up to 200°C. Then the bisphenol A was removed from the flask and cooled to room temperature.

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For the bisphenol A novolac synthesis in the solution process, 0.5 mol of bisphenol A was reacted with 1.5 mol of 37% formalin solution and 1 g oxalic acid dehydrate were refluxed for 90 min. Then 100 mL water was added under stirring. After depositing, the water layer was decanted and the residual water of the lower viscous layer was removed in vacuum at 140°C. A colorless product was obtained in a yield of 65%.

Preparation of diglycidyl ether bisphenol A

In a humidity-protected 500-mL glass reactor equipped with a mechanical stirrer, dropping funnel, and condenser, the purified methyl derivatives of bisphenols (0.11 mol) were mixed with 1% (wt% reacted to weight of methyl bisphenols) of $\text{BF}_3 \cdot \text{ET}_2\text{O}$ and heated at 40°C. EC (10 mol) was gradually added to the reaction mixture during 2 h. The reaction mixture was heated at 65°C for 30 min and after cooling to 40°C, 0.22 mol of NaOH (as 50% of aqueous solution) was added to the reaction mixture. Temperature of the reaction mixture was raised up to 80°C for 30 min. After cooling, the mixture was neutralized with 50 mL of acetic acid (50%); and 150 mL of toluene was added and the reaction mixture was filtered to remove sodium salts. The filtrate was washed four times with 150 mL of hot water (60–80°C), toluene evaporated off from organic layer by rotary evaporator. The products were obtained as viscous products and the epoxy content (EC) was determined as reported method.¹⁰

Physical measurements

The prepared epoxy resins were dissolved in CDCl_3 and analyzed using a Jeol ^1H NMR spectrometer model JNM-EX (270 MHz) to determine their chemical structures. GPC analyses of the novolacs were carried out on a column set (PS 4/PS 20 HI BAR columns, Merck) with exclusion limits from 100 up to 20,000 g/mol (polystyrene in tetrahydrofuran). Tetrahydrofuran as eluent and a refractive index detector were used. The glass transition temperatures (T_g) of the synthesized novolacs were measured on a Perkin Elmer DSC in a temperature range of 30–210°C with a scanning rate of 298 K/min.

Testing of the coatings

It is common to use mild steel panels (15 cm × 10 cm) to evaluate the different properties of coatings. The other side of panels were coated and protected against corrosion environments by using coal tar epoxy primer. The tested side was blasted and cleaned to apply the coating materials. Then the panels were subjected to different testing procedure to evaluate

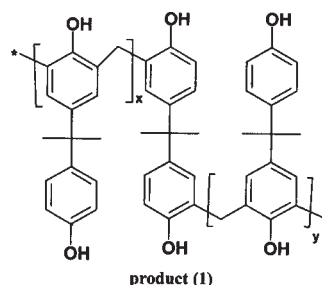
their mechanical properties and their durability. Adhesion strength (pull-off ASTM D 4541), mechanical properties (pencil hardness ASTM D3363, impact ASTM D 2794, T- bend tests ASTM D 522, chemical resistances (hot water ASTM D 870, acid and alkali resistance ASTM D 1647 and solvent resistance ASTM D 2792) were measured as reported in a previous study.^{11–13} The coated panels were evaluated for salt-spray resistance in accordance with ASTM B117. The test conditions were 35°C ($\pm 1.5^\circ\text{C}$), ($95 \pm 5\%$) relative humidity, and 5% weigh percent of aqueous sodium chloride solution.

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 evaluated for the coated panels.

RESULTS AND DISCUSSION

The reaction of bisphenol A with formaldehyde in a basic medium leads to formation of the resol-type resins.^{14,15} It was reported that, the resol bisphenol A-formaldehyde resins formed in the presence of catalysts, but novolac-type formed in the absence of a catalyst.¹⁶ The novolac formation by catalysis of the bisphenol A formaldehyde reaction with oxalic acid has already been investigated,^{17,18} but no information about the structure of these novolacs was given. We synthesized bisphenol A novolacs in the absence of solvent and catalyst because these compounds must be removed to use the novolacs for production of epoxy resins. Bisphenol A and *p*-formaldehyde were converted to the bisphenol A novolac as represented in Scheme 1. The molar ratio between bisphenol A and *p*-formaldehyde used for the syntheses of the novolacs was varied between 0.167 and 0.495 mol formaldehyde to 0.438 mol bisphenol A (Table I).

The number average molecular weight of the novolacs synthesized (M_n) rises with increasing concentration of *p*-formaldehyde in the reaction mixture. The glass transition temperatures of the novolacs (T_g) do not significantly depend on the molar ratio



Scheme 1 Chemical structure of bisphenol A novolacs.

TABLE I
Synthesis of Novolac Resins from Bisphenol A and *p*-Formaldehyde in a Melting Process

Novolac	Formaldehyde (mol)	Bisphenol A (mol)	M_n (g/mol)	T_g ($^{\circ}\text{C}$)	ΔH (JK/g)
BP-5	0.167	0.438	380	33.0	0.71
BP-7.5	0.25	0.438	590	54.3	0.55
BP-10	0.33	0.438	620	54.4	0.44
BP-15	0.495	0.438	820	59.1	0.40

of the reacting components, but the specific heat capacities (ΔH) determined in the glass transition state are lowered with increasing *p*-formaldehyde content in the reaction mixture (Table I). The oligomer distribution of the novolacs was estimated by GPC. It can be seen that the novolacs contain a relatively high concentration of unreacted bisphenol A. From the literature the possibility of a quantitative determination of the low-molecular-weight oligomers in phenol or *p*-cresol-formaldehyde resins^{19,20} and of the phenol content²¹ is known. A calibration with model substances is a prerequisite. Therefore, only the area% of the bisphenol A peaks in the GPC-chromatograms as measured for the bisphenol A content were determined and related to the reaction conditions. The dependence of this bisphenol A peak area% on the molar ratio of the reacting components shows that the content of unreacted bisphenol A decreases if more *p*-formaldehyde is used in the synthesis (Fig. 1). The higher conversion of bisphenol A using more *p*-formaldehyde during synthesis of the novolacs leads to formation of a larger amount of higher molecular mass product (Table I). The concentration of the methylene bridges in the novolacs synthesized was estimated from ^1H NMR spectra. In this respect, ^1H NMR spectrum of BP-10 was represented in Figure 2. The ratio between the peaks at chemical shift 2.2 and 1.8 ppm, which represent methylene and methyl groups, was used to determine the methylene content. The concentration of the methylene bridges in the novolacs synthesized was estimated from ^1H NMR spectra. Figure 3 shows the ratio of the methylene and methyl protons determined from the integrals of the ^1H NMR spectra versus the formaldehyde: bisphenol A ratio. The content of methylene bridges increases up to 0.8 ratio of formaldehyde to bisphenol A. Further raising of the formaldehyde content in the reaction mixture is not more effective. FTIR spectra of the novolacs (Fig. 4) show a band between 850 and 900 cm^{-1} , which is not present in the spectra of bisphenol A [Fig. 4(a)]. This band is attributed to three- or tetra-substituted aromatics. Further, the hydroxylic band between 3200 and 3500 cm^{-1} is broader in the novolac spectra than in those of bisphenol A. This means even stronger hydrogen

bridges in the novolacs than in bisphenol A attributed to methylene bridges in the ortho position to the hydroxylic group in the bisphenol A structure, which is already known for other phenolic resins.^{22,23}

The other way of novolac preparation is the synthesis using formalin solution, bisphenol A, and oxalic acid catalyst^{17,18} as described in the experimental section. The amounts of formaldehyde used as 37% formalin solution and bisphenol A used in the synthesis are 3 and 1 mol, respectively. The methylene bridge concentration of this novolac determined from the ^1H NMR spectrum is lower compared with the novolacs synthesized in a melting process through the formaldehyde excess is higher in the solution process. Using a formaldehyde content of 3.77 mol relative to 1 mol bisphenol A, the methylene bridge concentration can be increased, but high contents of hydroxymethyl groups and oxymethylene bridges were determined as 1.89 referring to 1 mol of bisphenol A. Therefore synthesized novolacs from solution process were used for the synthesis of the DGEBA was represented in Scheme 2 and designated as BPFE.

Synthesis of Novolac BP-A epoxy resin

Epoxy resins are prepared by the reaction of compounds containing an active hydrogen group with EC followed by dehydrohalogenation in presence of

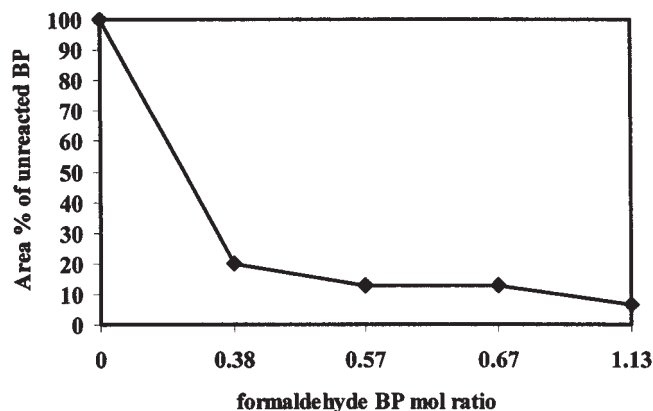
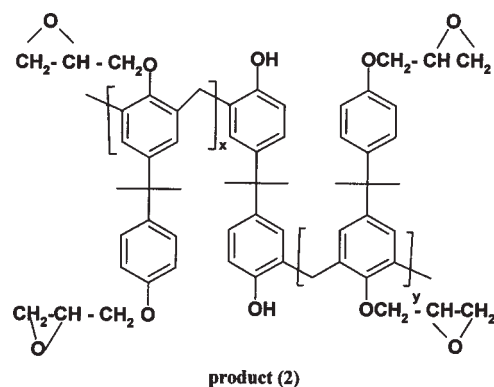


Figure 1 Area% of unreacted bisphenol A in the novolacs determined from GPC chromatograms.



Scheme 2 Chemical structure of glycidyl ether of bisphenol novolacs.

peak at 4.7 ppm in spectrum of BP, Fig. 5(b), and appearance of two peaks at 2.82 ppm (CH_2 epoxy), 2.94 ppm (OCH_2 epoxy), and 3.43 ppm (CH epoxy)^{11–13} indicates the formation of glycidyl ether group.

Evaluation of the prepared resins as organic coatings

The curing experiments of the prepared resins were formulated as liquid epoxy coatings with different ratios of curing agent. In all samples 1% of $(\text{ET})_3\text{N}$ (wt% based on weight of epoxy binder) was added as catalyst. These resins were sprayed (by using air spray gun) with wet film thickness, WFT, 350 μm on blasted steel panels.

The tests of cured coatings were evaluated after 24 h at room temperature (25°C). The data of mechanical properties (pull-off, impact, bending, and hardness) for cured epoxy resins based on methylated bisphenol A epoxy with curing agents were listed in Table III. The data reported on adhesions (pull-off) indicate that all cured epoxy resins based on novolacs bisphenol A epoxy resin have superior adhesion properties with steel. This can be attributed to the high epoxy functionality of the prepared epoxy binders based on novolacs bisphenol A.^{24,25}

It was also noted that the mixing ratios between epoxy resins and AEP hardener affect the impact resistance of coating films. This was determined by deformation of coating films when the mol% of AEP

TABLE II
Physico-Chemical Characterization of Glycidyl Ether of Novolacs Bisphenol A

Oligomers	EEW	Epoxy functionality	M_n (g/mol)	Yield (%)
BPE-5	295	2	590	73
BPE-7.5	242	2.8	680	62
BPE-10	243	3	730	70
BPE-15	212	4.8	1020	70
BPFE	200	4	800	83

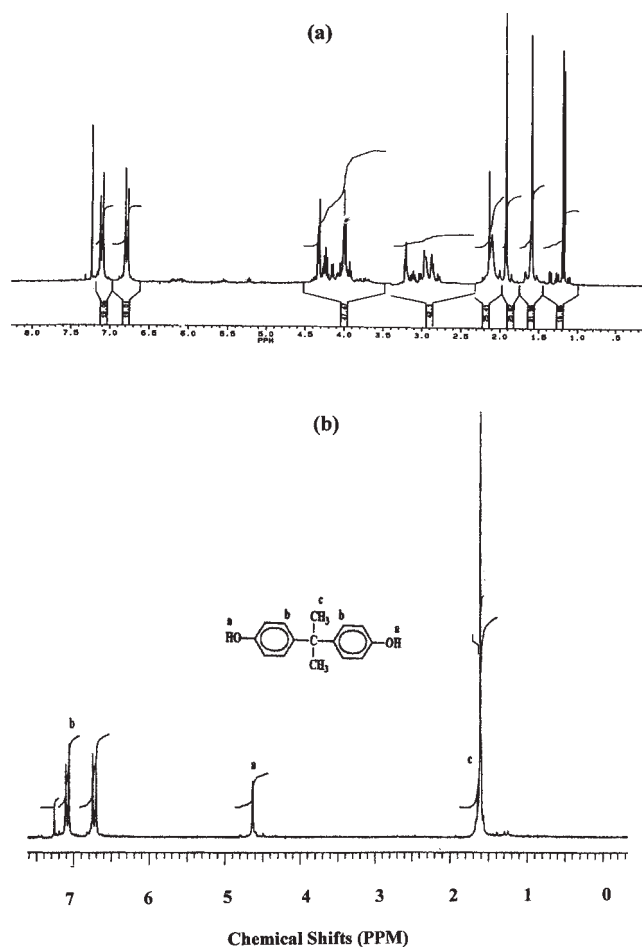


Figure 5 ^1H NMR spectra of (a) BPE-5 and (b) BP.

hardener was increased. Moreover, the films were deformed when mixing ratios were increased for methylated epoxy resins. While the mixing mol ratios between epoxy:hardener, were decreased to give the best results with impact and T-bend tests. These behaviors indicate that the ratios of cross-linking agent affect the mechanical properties of coatings. This behavior leads to speculate that the high cross-linking density networks decreases the mechanical properties of the formed network.^{11–13} The variation of hardness results (by pencil test) from soft (minimum cross-links) to hard coatings (maximum cross-link-density) indicate that the best results were determined at low mixing mol ratio for epoxy : hardener systems.

Evaluation of chemical resistance for cured resins

There are two test methods used to evaluate the durability of coatings, chemical resistance, and mechanical tests. In the previous section we have evaluated the mechanical tests of the cured epoxy based on methylated epoxy resins of bisphenol A. In the present section, the chemical resistance of the coated

TABLE III
Coating Tests of Glycidyl Ether of Novolacs Bisphenol A Epoxy Resins Cured with Hardener as Curing Agent at Different Mixing Ratios

Sample no.	Mol ratios of BP : EAP	Pull-off MPa	Impact (J/mm)	T-bend	Hardness
BPE-15a	1 : 1	10	10	+	HB
BPE-15b	2 : 1	12	12	+	H
BPE-15c	3 : 1	13	15	+	2H
BPE-15d	4 : 1	15	18	+	2H
BPE-10a	1 : 1	10	10	+	H
BPE-10b	2 : 1	5	5	+	HB
BPE-10c	3 : 1	3	1.5	+	B
BPE-10d	4 : 1	3	1.5	+	B
BPE-7.5a	1 : 1	13	12	-	H
BPE-7.5b	2 : 1	15	14	-	H
BPE-7.5c	3 : 1	18	15	+	2H
BPE-7.5d	4 : 1	20	20	+	2H
BPE-5a	1 : 1	15	12	+	2H
BPE-5b	2 : 1	8	8	+	H
BPE-5c	3 : 1	5	3	-	B
BPE-5d	4 : 1	5	3	-	B
BPFE	1 : 1	7	10	+	2H
	2 : 1	10	15	+	H
	3 : 1	12	20	+	H
	4 : 1	15	20	+	H

panels have subjected to chemical environments (alkali, acid, solvent, and salt spray) to study the durability of coats. The data of alkali, acid, and solvent resistance and water resistance were determined for cured epoxy systems (based on methylated epoxy resins of bisphenol A and listed in Table IV). The sign (-) indicates failure of tests, while (+) sign indicates the coatings pass the tests. The failure of test indicates that the coating films losses their adhesion with panels and show cracking and flaking of the film.

The use of polar solvents such as acetone has been used to determine the degree of curing of the present coating systems by both immersion and rub methods. The failure of tests was determined either by disruption or dissolution of the coating films from panels. The high cross-linking density indicates that less free volume and segmental mobility remain available in the polymer. The crosslink density can be controlled by change type of curing agents and functionality of epoxy resins.^{26,27} In this respect, it was found that the all prepared epoxy resins based on methylated epoxy resins of bisphenol A have good solvent resistance with all mixing ratios with AEP. It was also noted that the increasing of epoxy functionality from 2 to 4.8 for methylated epoxy resins of bisphenol A resins enhances solvent resistance for all epoxy resins and curing agents mixing ratios. This can be attributed to increasing of crosslink density by increment of epoxy functionalities, although the epoxy polarity is increased by increment of epoxy functionalities. Only specific functional groups

in the polymer may cause sensitization to such reagents. The acidic hydroxyl group in phenolic resins remains sensitive to alkali even after final cure.²⁸ In the present systems, the structure of network based on methylated epoxy resins of bisphenol A as epoxy binders and AEP as curing agent, have aliphatic ester groups, which are sensitive to both aqueous acidic and alkaline solutions. The data of acid and alkali chemical resistance for cured methylated epoxy resins of bisphenol A indicate that these networks have good resistance to alkaline and acidic aqueous solutions. The high alkaline and acidic resistance can be referred to high crosslink density of networks due to high epoxy functionalities. This can be attributed to high crosslink density of network decreases their exposure to environment.²⁹ This can be observed for fails of chemical resistance of cured epoxy based on methylated epoxy resins of bisphenol A at lower mixing mol ratios. On the other hand, the decreasing of hardener content decreases cross-link density of network and increase the attack of ester groups of network to acidic and alkaline solutions. The lower acid and base resistance of cured BPE-5 and BPE-7.5 can be referred to the formation of dangling chains (bonded from end and free from another end) which increase the attack of ester and amide groups with both acid and alkali media.¹¹ The data listed in Table V, indicate that the alkali and acid resistances were decreased when the mixing ratios between novolacs bisphenol A epoxy resin with AEP were decreased. This can be referred to

TABLE IV
Chemical Resistance Tests of Glycidyl Ether of Novolacs Bisphenol A Epoxy Resins Cured with Different Mixing Ratios

Sample no.	Acid resistance (day)	Alkaline resistance (day)	Water resistance	Acetone rub test
BPE-5a	7	7	-	+
BPE-5b	30	30	+	+
BPE-5c	45	45	+	+
BPE-5d	50	50	+	+
BPE-7.5a	14	14	+	+
BPE-7.5b	45	45	+	+
BPE-7.5c	60	60	+	+
BPE-7.5d	90	90	+	+
BPE-10a	45	45	+	+
BPE-10b	60	60	+	+
BPE-10c	90	90	+	+
BPE-10d	90	90	+	+
BPE-15a	90	90	+	+
BPE-15b	90	90	+	+
BPE-15c	90	90	+	+
BPE-15d	90	90	+	+
BPFE	90	90	+	+
	90	90	+	+
	90	90	+	+
	90	90	+	+

TABLE V
Salt Spray Resistance of Cured Glycidyl Ether of
Novolacs Bisphenol A Epoxy Resins

Sample no.	Exposure time (h)	Disbanded area (I)		ASTM D 1654 rating
		mm ²	%	
BPE-5a	300	67.4	58.1	2.5
BPE-5b	400	35.9	31	3
BPE-5c	500	5.2	4.4	7
BPE-5d	500	13	11	6
BPE-7.5a	646	2.33	2	8
BPE-7.5b	646	3.38	2.9	7.7
BPE-7.5c	646	5.2	4.4	7.2
BPE-7.5d	646	12.9	11	6
BPE-10a	350	67.4	58.1	2.5
BPE-10b	450	35.9	31	3
BPE-10c	550	5.2	4.4	7
BPE-10d	600	13	11	6
BPE-15a	750	2.33	2	8
BPE-15b	750	3.38	2.9	7.7
BPE-15c	750	5.2	4.4	7.2
BPE-15d	750	12.9	11	6
BPFE	1000	2.33	2	8
	1000	5.2	4.4	7.2
	1000	3.38	2.9	7.7
	1000	2.33	2	8

the high ability to form dangling chains which agree with the results discussed in previous work.¹¹⁻¹³

Testing corrosion resistance of coating

In the present work, 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 epoxy systems-based methylated epoxy resins of bisphenol A and listed in Table V. The test was stopped when the films show poor adhesion. The results of salt spray indicate the strong adhesion of coatings by increase of epoxy functionalities. This was observed from the improvement in coating performance from 75 to 95% for BPFE after 1000 h of exposure to the salt spray environment. 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. 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 epoxy systems, it was observed that increasing of epoxy functionality increases the adhesion of coat with steel. This can be referred to the curing of epoxy groups with AEP hardener produce hydroxyl groups. It has been shown that the concentration of resultant hydroxyl group has a deleterious

effect on the adhesion of the epoxy coating to the steel metal. The high salt spray resistance of cured epoxy resins can be attributed to the alicyclic structure of AEP that have high resistance to osmosis and electroendosmosis by comparing with aliphatic amines.³⁰ Essentially four types of epoxy materials are used in petroleum pipeline, tanker and marine coatings: the epoxy coal tar-type coating, the amine catalyzed ambient temperature cure coating, the polyamide epoxy coating, and the epoxy ester-type coating. Furthermore, an unlimited number of combinations can be formulated that are still called epoxy. In the present system of cured epoxy polyamine resins, based on both BPE-10 and BPE-15 have excellent alkali, acid, and solvent resistance and provide a dense hard coating with good adhesion. So from these points epoxy resins based on novolacs bisphenol A epoxy resin 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.

CONCLUSIONS

The following conclusions can be extracted from previous results:

1. The molar mass of the synthesized novolacs increased with increasing concentration of *p*-formaldehyde in the reaction mixture. The higher conversion of bisphenol A using more *p*-formaldehyde during synthesis of the novolacs leads to formation of a larger amount of higher molecular mass products.
2. The methylene bridge concentration of novolac synthesized in presence of formaline solution is lower when compared with the novolacs synthesized in a melting process.
3. It was determined that the epoxy functionality of the prepared epoxy resins varied from 2 to 4.8. These results indicate that the prepared methylated resins have polyfunctional epoxy groups.
4. The prepared novolac bisphenol epoxy resins have superior chemical resistances and good mechanical properties. The lower acid and base resistance of cured BPE-5 and BPE-7.5 can be referred to the formation of dangling chains (bonded from end and free from another end) which increase the attack of ester and amide groups with both acid and alkali media.

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