

SYNTHESIS, CHARACTERIZATION AND SOME PROPERTIES OF EPOXY RESINS CONTAINING AZOMETHINE BONDING

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Abstract New epoxy resins were prepared from hydroxyl substituted Schiff base monomers in two steps. The first step is based on the synthesis of hydroxyl substituted Schiff base monomers *via* condensation reaction. The second step includes the reaction between Schiff base monomers with epichlorohydrine (EPC) to obtain epoxy resins. The structures of resulting compounds were confirmed by FTIR and ¹H-NMR. TG-DTA and DSC measurements were made for thermal characterizations of the compounds. Chemical resistances of the cured epoxy-amine systems in acidic, alkaline and organic solvents were determined for coating applications. HCl (aqueous solution, 10%), NaOH (aqueous solution, 10%), DMSO, DMF, *N*-methylpyrrolidone, ethanol, THF and acetone were used for corrosion tests. Chemical resistance data show that the synthesized resins have good chemical resistance against various acid, alkaline and common organic solvents.

Keywords: Epoxy resin; Thermal analysis; Poly(imine)s.

INTRODUCTION

Epoxy resins as one of the most important thermosetting polymers, are currently used in advanced composites, coatings, structural adhesives and microelectronics due to their high stiffness, high strength, good chemical resistance and dimensional stability^[1, 2]. However, epoxy resins have major drawbacks of lack of toughness, and their brittleness reduces many end-use applications^[3]. Recently, many attempts have been used to improve the toughness of epoxy resins. For this purpose various types of high-performance thermosetting resins, such as sulfone-containing epoxy, phosphorus-containing epoxy, polyimide-containing epoxy and polyester-containing epoxy have been explored^[4–7]. Polymerization of epoxy resins to form crosslinked polymers can be accomplished by using curing agents such as amines, carboxylic acid anhydrides and thermally catalysts. The anhydride cured resins are preferred for electrical and electronic applications due to their high thermal stability and transparency^[8, 9].

Amine-cured epoxies are one of the most commonly used matrix materials in engineering applications of fiber reinforced polymeric matrix composites, due to their excellent engineering performance and ease of processing prior to cure. The broad interest in epoxy originates from the extremely wide variety of chemical reactions and materials that can be used to form crosslinked networks and, resultantly, many different properties. Depending on the chemical structure of curing agents and curing conditions, it is possible to vary the mechanical properties ranging from extreme flexibility to high strength and hardness, and physical properties such as adhesive strength, chemical resistance, heat resistance and electrical resistance. Different chemical compositions and curing kinetics can permit the user to process over a wide range of temperatures and control the degree of crosslinking^[10].

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Schiff base inhibitors have been previously reported as effective corrosion inhibitors for steel, copper and aluminum^[11–13]. The mechanism of corrosion protection of these materials was referred to adsorption of these substances on metal surface. It was reported that the adsorption depended not only on the nature and charge of the metal but also on the chemical structure of the inhibitor. The main drawback of these materials was referred to poor thermal stability. These problems were exceeded by preparing Schiff base epoxy resins to enhance their thermal stabilities. The thermal characteristics and curing exotherms were measured in the presence of aromatic and aliphatic amines as curing agents. On the other hand, the cured Schiff base epoxy derivatives were evaluated as protective coating systems for steel. The chemical resistances were also evaluated to use these epoxy resins in the coating of petroleum equipments^[14].

In this paper, we synthesized new Schiff base epoxy resins and investigated their spectral, thermal properties and corrosion resistance against HCl (aqueous solution, 10%), NaOH (aqueous solution, 10%) and organic solvents.

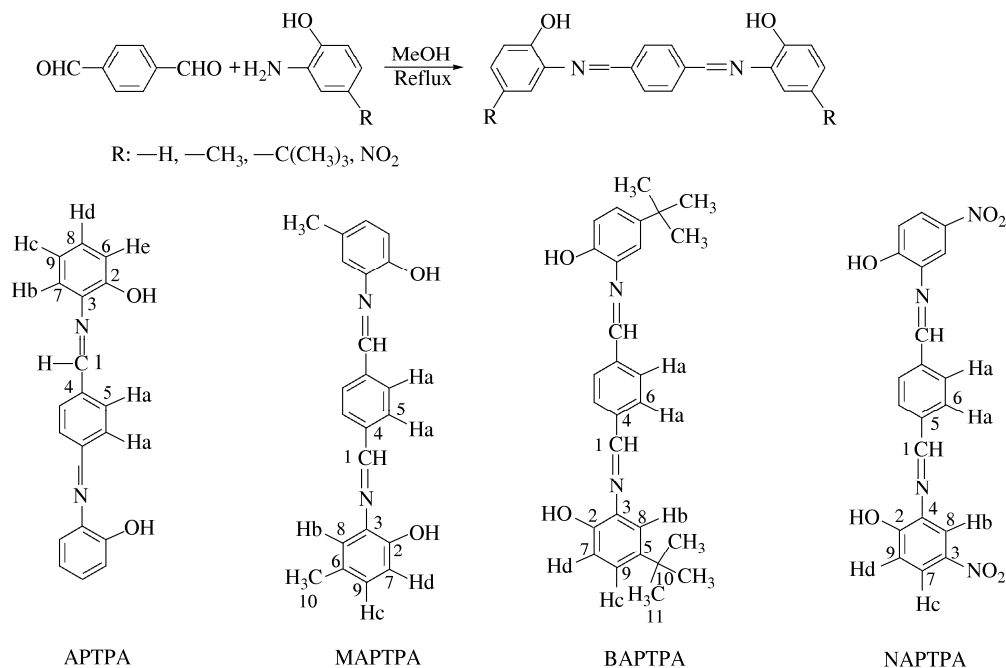
EXPERIMENTAL

Materials

Terephthalaldehyde (TPA), *p*-phenylenediamin (PPDA), epichlorohydrine (EPC), 2-aminophenol (AP), 2-amino-4-*t*-buthylphenol (BAP), 2-amino-4-methylphenol (MAP), 2-amino-4-nitrophenol (NAP), NaOH, ethanol, acetone, DMSO, DMF, HCl, *N*-methylpyrrolidone (NMP), THF and methylethylketone (MEK) were supplied by Merck Chemical Co. (Germany).

Preparation of Schiff Bases

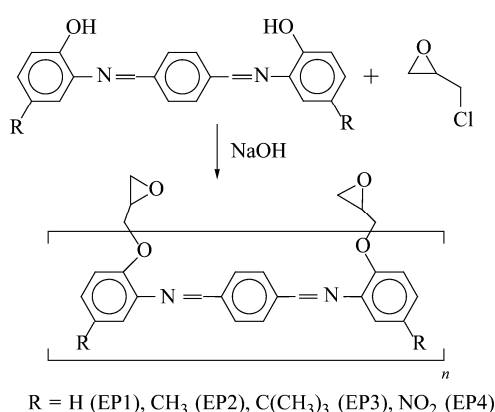
The APTPA, MAPTPA, BAPTPA and NAPTPA were prepared by the condensation of terephthalaldehyde with 2-aminophenol, 2-amino-4-methylphenol, 2-amino-4-*t*-buthylphenol and 2-amino-4-nitrophenol using stoichiometric values for each compound in methanol (25 mL) by boiling the mixture under reflux for 3 h at 70 °C (Scheme 1)^[15]. The solutions were filtered and recrystallized from methanol and dried in vacuum desiccators. The yields of APTPA, MAPTPA, BAPTPA and NAPTPA were found as 96%, 93%, 94% and 90%, respectively.



Scheme 1 Syntheses of Schiff bases

Syntheses of Epoxy Resins

Epoxy resins were synthesized from Schiff bases *via* reaction with epichlorohydrin as follows (Scheme 2). A three-necked flask (0.1 L capacity) equipped with a condenser, magnetic stirrer, thermometer and dropping funnel was charged with Schiff base monomer (0.01 mol) and epichlorohydrin (0.1 mol). The reaction solution was stirred at 40 °C under nitrogen atmosphere for 1 h. Then, the reaction temperature was raised up to 90–100 °C. 50% concentrated sodium hydroxide solution (containing 0.02 mol of NaOH) was transferred into dropping funnel and added to the reaction flask within 2 h with stirring. The reaction temperature was increased to reflux for 1 h at 90–100 °C. The obtained viscose (liquid) resins were isolated from solvent under pressure by rotary evaporator. The products were cleaned with distilled water for removing from the medium the inorganic salts such as sodium chloride. The yields of EP1, EP2, EP3 and EP4 were found as 85%, 82%, 75% and 79%, respectively.



Scheme 2 Syntheses of epoxy resins

Curing of Epoxy Resins

p-Phenylenediamine (PPDA) was used as curing agent for the curing of epoxy resins. Epoxy binders were mixed with PPDA in methyl ethyl ketone (MEK) as solvent to prepare 90% solution of the reaction mixture. After evaporation of the solvent at room temperature, the mixture was dried perfectly in vacuum oven and stored at –10 °C before use to prevent the curing reaction of the mixture. The weight ratios of epoxy binders were 4:1 (epoxy: curing agent). Cured network of epoxy binders was prepared after curing at 150 °C for 2 h and post-curing at 250 °C for 1 h.

Characterization Techniques

The infrared spectra were measured with a Perkin Elmer Spectrum One FTIR system. The FTIR spectra were recorded by using a universal ATR sampling accessory within the wavelength range of 4000–550 cm^{–1}. Schiff bases and epoxy resins were characterized by using ¹H-NMR and ¹³C-NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25 °C by using deuterated DMSO as solvent. TMS was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 15 °C and 1000 °C (in N₂, rate 10 K/min). DSC analyses were carried out by using Perkin Elmer Pyris Sapphire DSC. DSC measurements were made between 25 °C and 420 °C (in N₂, rate 20 K/min).

Corrosion Tests of Epoxy Resins

It is common to use mild steel panels (3 × 3 cm) to evaluate the different properties of coatings. The panels, then, are subjected to chemical resistance procedures. The acid, alkali and solvent resistances of coated panels were determined after immersion in 10% of HCl, 10% of NaOH aqueous solutions, DMF, DMSO, *N*-methylpyrrolidone, THF, ethanol and acetone organic solvents. The panels were weighed before immersions

into these solutions. The duration of the test was 90 days at 311 K. Then, the panels were weighed again. The chemical resistance properties were evaluated for the coated panels. These epoxy resin samples were sprayed by using air spray gun, and their wet film thickness was found as 210 μm on blasted steel panels^[14].

RESULTS AND DISCUSSION

Corrosion Tests of Epoxy Resins

Examining the data of corrosion tests of the resins, we observed all resins had high resistance against aqueous acidic and alkali solutions as well as common organic solvents such as DMF, DMSO, *N*-methyl pyrrolidone, THF, ethanol and acetone. Although EP2 and EP4 resins are not affected by acidic, alkali solutions and organic solvents, EP1 and EP3 resins are a little affected by the same solutions. Corrosion test data of the synthesized resins are given in Table 1. The number of the panels used for chemical resistance tests was three at each measurement. Solvent and chemical-resistant films are obtained by epoxy resin at ambient and elevated temperatures. Epoxy resins had passed impact resistance tests.

Table 1. Corrosion test data of epoxy resins synthesized

Assignment	EP1	EP2	EP3	EP4
HCl (10%)	Pass	Pass	Pass	Pass
NaOH (10%)	Pass	Pass	Pass	Pass
DMSO	Pass	Pass	Pass	Pass
DMF	Pass	Pass	Pass	Pass
NMP	Pass	Pass	Pass	Pass
THF	Pass	Pass	Pass	Pass
Ethanol	Pass	Pass	Pass	Pass
Acetone	Pass	Pass	Pass	Pass

Structures of Schiff Bases and Epoxy Resins

In the present investigation, some of Schiff base epoxy resins derivatives from reaction of hydroxyl aromatic amine, aromatic dialdehyde and epichlorohydrine were prepared in the hope that some of these derivatives might show enhanced thermal stabilities. In this respect, Schiff bases monomers were prepared from condensation products of AP, MAP, BAP and NAP with TPA. Then, epoxy resins were prepared from Schiff base monomers. In this series all derivatives were prepared and purified as illustrated in experimental section.

FTIR spectra of APTPA, MAPTPA, BAPTPA, and NAPTPA Schiff bases are examined and given in Fig. 1. The stretching vibration peaks of $-\text{OH}$ groups are observed at 3360, 3337, 3342 and 3319 cm^{-1} , respectively. The imine ($-\text{HC}=\text{N}-$) peaks of APTPA, MAPTPA, BAPTPA and NAPTPA observed at 1620–1626 cm^{-1} confirm the Schiff base structures. Characteristic epoxy peaks of APTPAE (EP1), MAPTPAE (EP2), BAPTPAE (EP3), and NAPTPAE (EP4) are also observed at 1045, 1041, 1040 and 1036 cm^{-1} , respectively. FTIR and UV-Vis spectral data of the synthesized Schiff bases are summarized in Table 2.

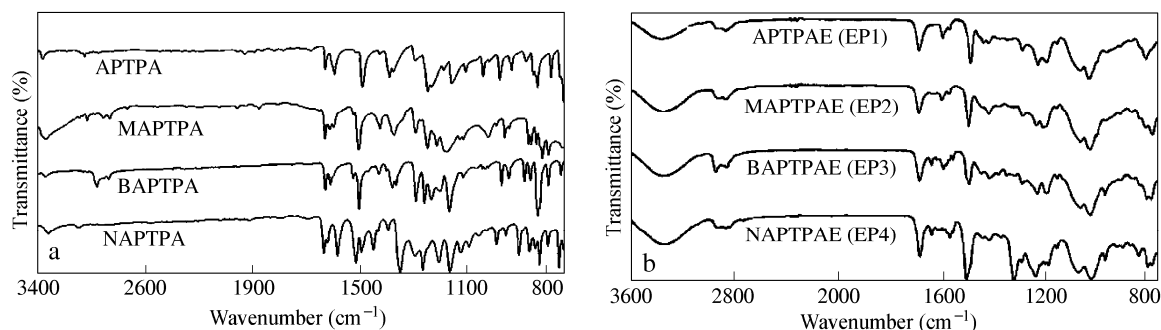


Fig. 1 FTIR spectra of Schiff bases (a) and epoxy resins (b)

Table 2. NMR, FTIR and UV-Vis spectra data of Schiff bases

Compounds	Spectral data (δ)
APTPA	$^1\text{H-NMR}$ (DMSO): 9.14 (s, $-\text{OH}$), 8.81 (s, $-\text{CH}=\text{N}-$), 8.19 (d, $-\text{Ha}$), 7.28 (d, $-\text{Hb}$), 6.87 (t, $-\text{Hc}$), 7.14 (t, $-\text{Hd}$), 6.97 (d, $-\text{He}$)
	$^{13}\text{C-NMR}$ (DMSO): 158.86 (C1), 152.00 (C2-ipso), 139.10 (C3-ipso), 138.05 (C4-ipso), 129.57 (C5), 128.33 (C6), 120.00 (C7), 119.50 (C8), 116.65 (C9)
	FTIR (cm^{-1}): 3360 ν -OH; 1620 ν -CH=N; 1237 ν Ph-O
	UV-Vis (nm): 201, 294, 382
MAPTPA	$^1\text{H-NMR}$ (DMSO): 8.85 (s, $-\text{OH}$), 8.79 (s, $-\text{CH}=\text{N}-$), 8.16 (d, $-\text{Ha}$), 7.10 (s, $-\text{Hb}$), 6.92 (d, $-\text{Hc}$), 6.81 (d, $-\text{Hd}$), 2.26 (s, $-\text{CH}_3$)
	$^{13}\text{C-NMR}$ (DMSO): 158.59 (C1), 149.70 (C2-ipso), 139.09 (C3-ipso), 137.62 (C4-ipso), 129.48 (C5), 128.73 (C6-ipso), 128.58 (C7), 119.84 (C8), 116.39 (C9), 20.70 (C10)
	FTIR (cm^{-1}): 3337 ν -OH; 1621 ν -CH=N; 1238 ν Ph-O; 2906–2857 ν Aliphatic C-H
	UV-Vis (nm): 204, 296, 382
BAPTPA	$^1\text{H-NMR}$ (DMSO): 8.90 (s, $-\text{OH}$), 8.84 (s, $-\text{CH}=\text{N}-$), 8.17 (d, $-\text{Ha}$), 7.26 (s, $-\text{Hb}$), 7.13 (d, $-\text{Hc}$), 6.85 (d, $-\text{Hd}$), 1.30 (s, $-\text{C}(\text{CH}_3)_3$)
	$^{13}\text{C-NMR}$ (DMSO): 158.76 (C1), 149.44 (C2-ipso), 142.29 (C3-ipso), 139.12 (C4-ipso), 137.29 (C5-ipso), 129.46 (C6), 124.87 (C7), 116.65 (C8), 116.05 (C9), 34.41 (C10-ipso), 31.88 (C11)
	FTIR (cm^{-1}): 3342 ν -OH; 1620 ν -CH=N; 1223 ν Ph-O; 2950–2867 ν Aliphatic C-H
	UV-Vis (nm): 202, 295, 391
NAPTPA	$^1\text{H-NMR}$ (DMSO): 10.95 (s, $-\text{OH}$), 8.93 (s, $-\text{CH}=\text{N}-$), 8.15 (d, $-\text{Ha}$), 8.28 (s, $-\text{Hb}$), 8.13 (d, $-\text{Hc}$), 7.11 (d, $-\text{Hd}$)
	$^{13}\text{C-NMR}$ (DMSO): 162.49 (C1), 158.23 (C2-ipso), 151.14 (C3-ipso), 140.37 (C4-ipso), 139.00 (C5-ipso), 130.48 (C6), 129.96 (C7), 116.77 (C8), 115.78 (C9)
	FTIR (cm^{-1}): 3319 ν -OH; 1626 ν -CH=N; 1255 ν Ph-O
	UV-Vis (nm): 202, 286, 419

In order to identify the structures of Schiff bases and their epoxy resins, $^1\text{H-NMR}$ spectra were recorded in DMSO- d_6 and are given in Fig. 2. When looking at the $^1\text{H-NMR}$ spectra of the Schiff bases, the proton signals are very sharp. After epoxidation the peaks get broad and increase in number. These cases are ascribed to epoxidation. The FTIR spectral data and the results of the $^1\text{H-NMR}$ spectra of the Schiff bases and their epoxy resins confirm each other. The characteristic signals of azomethine ($-\text{CH}=\text{N}$) protons of APTPA, MAPTPA, BAPTPA, and NAPTPA are observed at $\delta = 8.81, 8.80, 8.84$ and 8.91 , respectively. Hydroxyl groups are also observed at $\delta = 9.14, 8.85, 8.90$ and 10.95 , respectively. $^1\text{H-NMR}$ spectral data of the synthesized Schiff bases are also summarized in Table 2. The proton signals of epoxide groups of resins ($-\text{OCH}_2$, $-\text{CH}-$ and $-\text{CH}_2-$) are observed at about $\delta = 2.5$ – 4.0 . Moreover, $^1\text{H-NMR}$ spectra can be used to determine the epoxy functionality of the resins through integration of the characteristic signals. This procedure is applied to determine the chemical compositions for graft or block copolymers. Accordingly, the same procedure is applied hereinafter to determine the epoxy functionality of glycidyl ethers. In this respect, the analysis is based on the integration of two signals at $\delta = 4.0$ (assigned to $-\text{CH}$ proton of oxirane ring) and $\delta = 10.6$ (assigned to unreacted $-\text{OH}$ protons of hydroxyl methyl group). The ratio of integrations of these proton signals shows that both hydroxyl groups of the Schiff bases react with epichlorohydrine. Also, the signals of hydroxyl groups disappear after the epoxidation. These cases indicate that the reactions end with EPC^[16]. At the NMR spectra, the proton signals of oxirane ring $-\text{CH}$, $-\text{OCH}_2$ and $-\text{CH}_2$ of EP4 compound was observed in $\delta = 3.92, 3.55$ and 3.36 , respectively. According to proton integrations (16.03/147.80) of hydroxyl and oxirane groups, % conversion of EP4 was found as 89.17% from NMR spectra.

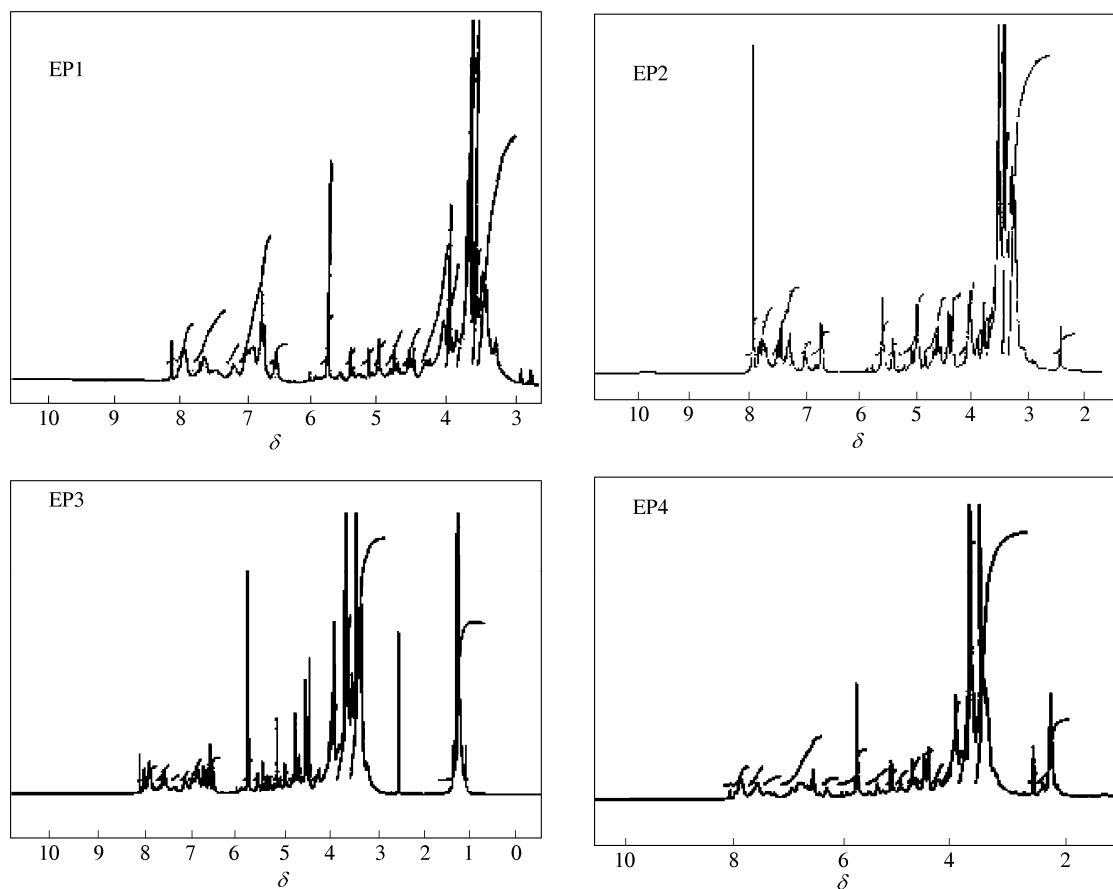


Fig. 2 ^1H -NMR spectra of epoxy resins

Thermal Studies

Thermogravimetric analysis is a useful method to determine the thermal stability of Schiff base derivatives and their epoxy resins. The thermal analysis results of the Schiff bases, epoxy resins and cured epoxy resins are summarized in Table 3 and the TG curves are given in Figs. 3, 4, and 5, respectively. DTG curves of epoxy resins and cured epoxy resins are given in Figs. 6 and 7, respectively. After the curing process the resins demonstrate higher thermal stabilities than the Schiff bases. The resins have higher char residues than the Schiff bases at 1000 °C. First, the decomposition start temperature of the Schiff base (APTPA) is 262 °C, while its epoxy resin (EP1) begins to decomposition at 75 °C. After the curing process, initial decomposition temperature of EP1 increases from 75 °C to 264 °C. As seen in the TG curves of the other Schiff bases and epoxy resins the same changes are observed. On the other hand, while the initial decomposition temperatures of the epoxy resins increase with curing, their weight losses decrease. Cured EP3 resin demonstrates higher thermal stability than the other resins. The initial degradation temperature and 66.43% weight loss temperature of cured EP3 resin are found to be 258 °C and 1000 °C. The presence of organic solvents can be clearly seen in TG and DTG curves of cured resins. 4.3% and 7% weight losses in the range of 30–170 °C indicate the removal of organic solvents. The thermal stabilities of the cured epoxy resins were changed as follows: EP1-C > EP3-C > EP4-C > EP2-C. Because of etheric C—O—C bonding, initial decomposition temperatures of EP1-C, EP2-C, EP3-C and EP4-C were found as 264, 219, 258 and 244 °C, respectively.

Table 3. Thermal degradation values of Schiff bases, epoxy resins and epoxy resins cured

Compounds	TG					DTA	
	T_{on}^a (°C)	T_{max}^b (°C)	20% Weight loss temperature (°C)	50% Weight loss temperature (°C)	% Weight loss at 1000 °C	Exo peak (°C)	Endo peak (°C)
APTPA	262	291, 575	290	461	70.08	—	219
MAPTPA	235	283, 445	267	328	90.82	—	222
BAPTPA	258	300, 452, 810	286	325	98.26	—	228, 807
NAPTPA	314	332	330	620	65.82	335	310
EP1	75	208, 445	195	342	71.87	276	467
EP2	70	170, 264, 589	171	300	83.42	—	—
EP3	97	165, 262	181	276	71.59	275	—
EP4	97	173, 234, 436	170	285	79.16	227	287
EP1-C	264	313	321	430	69.83	282, 391	—
EP2-C	219	287, 349	274	370	80.29	—	—
EP3-C	258	321, 443	321	462	66.43	—	—
EP4-C	244	312, 428	299	392	73.96	450	435

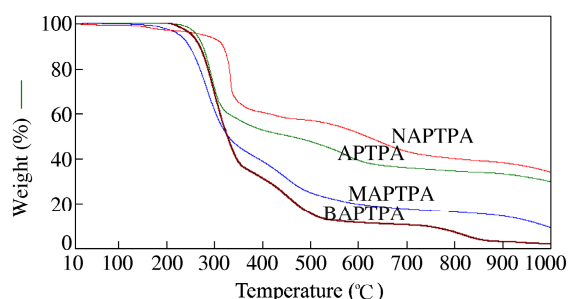
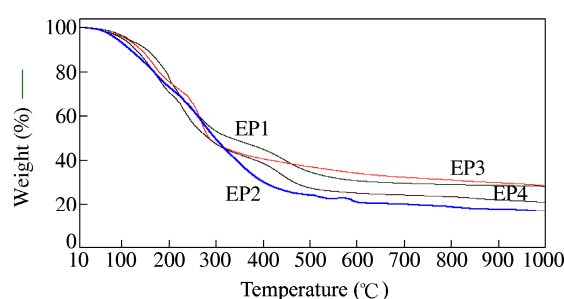
^a The onset temperature; ^b Maximum weight loss temperature

According to the DSC measurements of the cured epoxy resins, the glass transition temperatures (T_g) and ΔC_p values of EP1-C, EP2-C, EP3-C and EP4-C were found as 221, 202, 224, and 228 °C; 0.033, 0.050, 0.307 and 0.472 J/(g·K), respectively. DSC data are given in Table 4. Both T_g and ΔC_p values of EP4-C containing NO₂ groups were higher than those of the other epoxy resin cured.

Table 4. DSC data of epoxy resins cured

Compounds	T_g (°C)	ΔC_p (J/(g·K))	Exo peak (°C)	Endo peak (°C)
EP1-C	221	0.033	280, 395	330
EP2-C	202	0.050	309	345, 359
EP3-C	224	0.307	322	396
EP4-C	228	0.472	275, 324	310, 342

The diglycidyl ether of bisphenol-A (DGEBA) is the most commonly used epoxy resin as it has many attractive properties such as fluidity, low shrinkage during curing and ease of processing. The cured products have good physical strength, excellent moisture, solvent and chemical resistance. Their main problem is relatively poor thermal stability and flame resistance which limits their applications in more demanding areas such as aerospace and electronic industry. Several degradation schemes are based on the cleavage of simple ethers and the products obtained from the pyrolysis study^[17]. When the TG curves of Schiff bases and their epoxy resins were examined, because of ether (—C—O—C—) linkage of resins, the initial degradation temperatures of epoxy resins were lower than those of the Schiff bases^[18–20].

**Fig. 3** TG curves of Schiff bases**Fig. 4** TG curves of epoxy resins

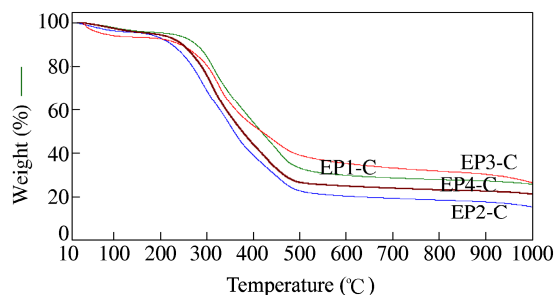


Fig. 5 TG curves of cured epoxy resins

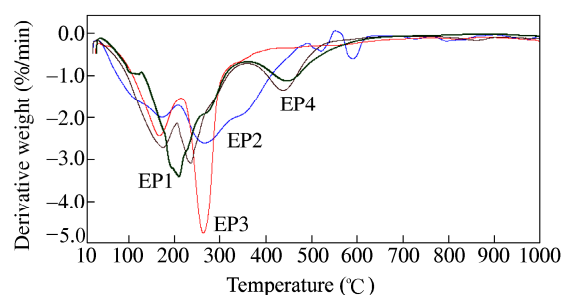


Fig. 6 DTG curves of epoxy resins

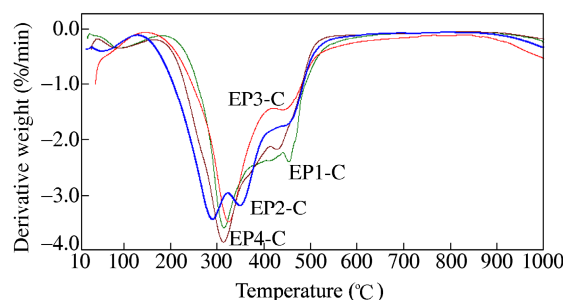


Fig. 7 DTG curves of cured epoxy resins

CONCLUSIONS

The epoxy resins were synthesized by condensation reaction of Schiff bases with epichlorohydrine. The monomers and epoxy resins were characterized by spectral and thermal studies. The epoxy resins demonstrated lower resistance against high temperature than the monomers. But after curing process, thermal stability of resins were highly increased because of high branched matrix formations. The synthesized resins demonstrated good chemical resistance for acidic and alkali aqueous solutions and various organic solvents. As a result, these epoxy resins may be used as coating materials in coating industry. The curing and determination of thermal properties of prepared epoxy resins and hardener based on Schiff base epoxy resins are another goals of this work.

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