



SYNTHESIS AND CHARACTERIZATION OF SOME EPOXY RESINS BEARING AZOMETHINE GROUPS

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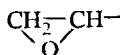
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Abstract—New epoxy resins bearing azomethine groups were synthesized by the reaction between the diglycidyl ether of bisphenol-A (DGEBA) and some aromatic azomethines, in the presence of *n*-butylamine as catalyst. The azomethines were obtained through the condensation reaction of aromatic diamines with 2-hydroxybenzaldehyde. The epoxides synthesized at 100°C were characterized by i.r., u.v. and ¹H-NMR spectral techniques, as well as by DSC and TG thermoanalytical methods. Some other properties of the resins are presented, such as epoxy equivalent, melting points and nitrogen content. The epoxy resins containing azomethine groups show an apparent higher thermal stability than that of crude DGEBA epoxy resin, and some of them show a pronounced tendency towards crystallization. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Epoxy resins are among the most important thermosetting polymers in wide use as a matrix for fibre-based composites, structural adhesives, surface coatings, etc. [1, 2]. Most of the commercially available epoxy resins are oligomers of DGEBA [1–3]. The epoxy resins are characterized by the presence of the oxirane group,



which is able to react with compounds possessing active hydrogen atoms, including amines, amides or mercaptans. Various glycidyl esters, glycidyl amine derivatives and thioethers have been synthesized using this approach [3, 4].

The synthesis, characterization and polymerization of epoxy resins of various glycidyl ethers and esters bearing azomethine groups have already been reported [5–7]. Owing to the relatively high thermal stability given by the presence of azomethine linkages [8–11], heat-resistant epoxides were prepared by reacting hydroxy and/or carboxy substituted azomethines or bis-azomethines with epichlorohydrin in the presence of a quaternary ammonium bromide as catalyst.

The present paper deals with the synthesis of some new epoxy resins with azomethine linkages included in the main chain. The products, obtained by the direct reaction between DGEBA epoxy resin and various aromatic azomethines, were characterized by both spectral and thermoanalytical techniques, the results being related to the chemical structure of the synthesized polymers.

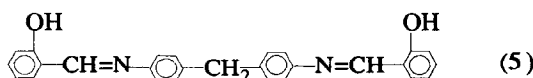
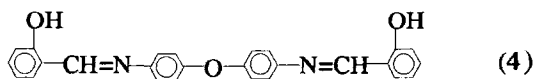
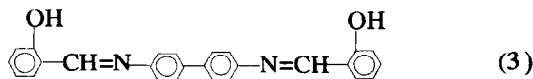
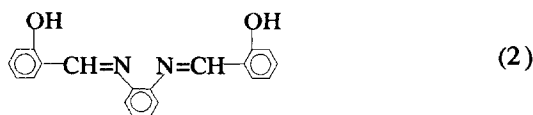
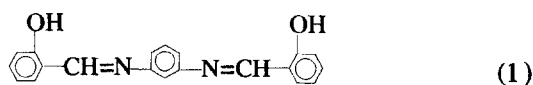
EXPERIMENTAL PROCEDURES

Preparation of DGEBA epoxy resin

The DGEBA epoxy resin was synthesized starting from bisphenol-A and epichlorohydrin, in basic medium, according to the procedure described elsewhere [12] for the preparation of *para*-nonylphenol formaldehyde novolac epoxy resins. The DGEBA resin obtained had an epoxy equivalent (EE%) of 0.211, a number-average molecular weight of 432, and a softening point ranging from 60 to 64°C.

Preparation of azomethine compounds

The following azomethine bisphenols were used:



The azomethine compounds 1 up to 5 were synthesized using commercially available aromatic diamines (Merck, Germany), namely, 1,3-phenylenediamine (purified by vacuum distillation), 1,2-phenylenediamine (recrystallized from

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Table 1. Properties of the azomethines used in the synthesis of epoxy resins

Azomethine	Raw formula	Recrystallization solvent	Melting interval (°C)	Elemental analysis					
				C (%)		H (%)		N (%)	
				Calculated	Found	Calculated	Found	Calculated	Found
1	C ₂₀ H ₁₆ O ₂ N ₂	EtOH/H ₂ O (1:1)	180–182	75.92	75.82	5.10	5.26	8.86	8.92
2	C ₂₀ H ₁₆ O ₂ N ₂	EtOH/H ₂ O (1:1)	163–165	75.92	75.85	5.10	5.05	8.86	8.70
3	C ₂₆ H ₂₀ O ₂ N ₂	Xylene	295–297	75.96	79.73	5.14	5.28	7.14	7.31
4	C ₂₆ H ₂₀ O ₃ N ₂	EtOH/H ₂ O (1:1)	212–214	76.45	76.26	4.93	4.72	6.86	6.60
5	C ₂₇ H ₂₂ O ₂ N ₂	EtOH/H ₂ O (1:1)	213–216	79.77	80.12	5.46	5.27	6.89	6.72

acetic acid), 4,4'-benzidenediamine (recrystallized from xylene), 4,4'-diaminodiphenylether (recrystallized from tetrahydrofuran) and 4,4'-diaminodiphenylmethane (purified by vacuum sublimation). The above-mentioned azomethines were reacted with 2-hydroxybenzaldehyde (Loba, Fischamend, Austria), the last one being purified by recrystallization from distilled water. A 500 ml round-bottomed flask fitted with a stirrer, reflux condenser, heating system, and thermometer was charged with diamine and 2-hydroxybenzaldehyde (molar ratio 1:2). The reactant mixture was refluxed in ethyl alcohol for 4–6 hr. The synthesized azomethines were usually recrystallized from various solvents and the crude final products were dried in vacuum at 60°C for 24 hr. The yields varied between 80 and 85%. Table 1 presents the solvents used for recrystallization, as well as other characteristics of the synthesized azomethine compounds.

Preparation of the epoxy resins bearing azomethine groups

Preparation of the epoxy resins with azomethine groups in the main chain of the polymer was carried out in bulk using DGEBA epoxy resin and the azomethine compounds, synthesized as previously described. The reagents, taken in the molar ratio DGEBA/azomethine of 2:1, were first heated at 100°C for 1 hr, then *n*-butylamine, used as a selective catalyst for the ring opening of the epoxide compound [13], was added. The mixture was stirred at 100°C for 2–4 hr, and at 130°C for 1 hr to complete the polymerization process. The product, obtained as a solid glassy resin, was purified by dissolution in acetone, filtered several times and precipitated in toluene. Finally, the product was dried in vacuum at 80°C for 2 hr. The yields ranged from 75 to 80%.

Analysis

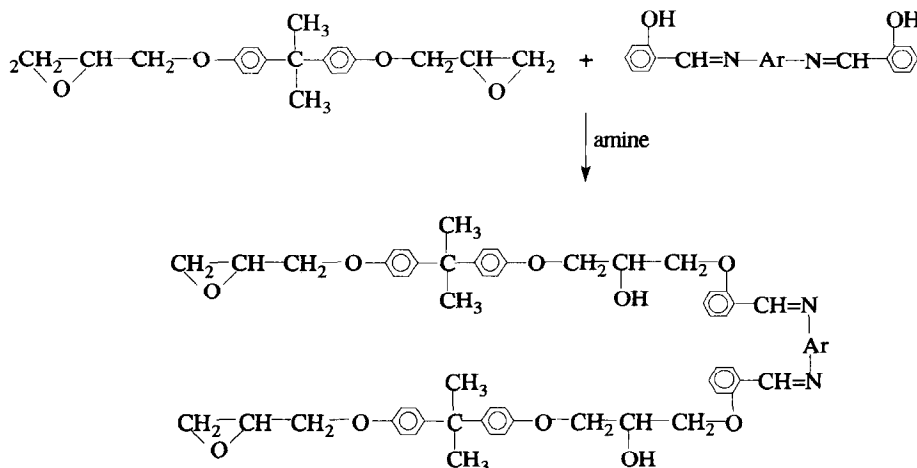
The i.r. spectra of the newly synthesized epoxy resins were recorded on an M 80 Specord spectrophotometer, using

KBr pellets, while the u.v. spectra were obtained with an M 42 Specord spectrophotometer. The ¹H-NMR spectra were obtained on a JEOL-JNMC 60-HL apparatus at 55°C, from CDCl₃ epoxy resin solutions. The glass transition temperature (*T*_g) was obtained by differential scanning calorimetry (DSC) by means of a Mettler 12 E instrument at a heating rate of 10°C min⁻¹, in a nitrogen atmosphere. The *T*_g value was taken as that corresponding to the half increase of the thermal capacity. The thermogravimetry (TG) experiments were performed with a MOM-Budapest derivatograph, under the following conditions: sample weight 50 mg, heating rate 12°C min⁻¹ and reference material α-Al₂O₃. The epoxy equivalent was evaluated by dissolution of the sample in pyridine (HCl solution) and titration with aqueous NaOH solution in the presence of phenolphthalein, as previously described [12]. Carbon and hydrogen contents of the azomethine compounds were determined by the modified Pregl method, while the content of nitrogen for both azomethines and epoxy resins was evaluated by the Kjeldahl method.

RESULTS AND DISCUSSION



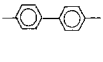
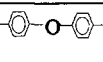
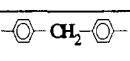
The general reaction yielding the epoxy resins bearing azomethine linkages is given in Scheme 1.

The chemical nature of the Ar radical and some other properties of the synthesized epoxy resins are listed in Table 2. The epoxy equivalent values show the presence of the final epoxy groups, while the content of nitrogen confirms the presence of azomethine segments in the main resin chain. The melting points determined using a Böetius microscope show low values. The data summarized in Table 2 show good agreement between the experimental and theoretical values.



Scheme 1

Table 2. Some characteristics of the epoxy resins bearing azomethine linkages

Sample	Ar	i.r. (cm ⁻¹)	EEW ^{a,b}	EE (%) ^a	N (%) ^a	m.p. (°C)	T _g (°C)
A ₁		3500 - 3300, 1050: -OH 3100, 1500: aromatic 3000 - 2900: (CH ₃) ₂ C=; 1625: -CH=N- 1100, 575: ether; 1200, 890: epoxy	490.19 (498.57)	0.204 (0.200)	3.15 (2.81)	80 - 85	35
A ₂		3500 - 3200, 1050: -OH 3050, 1520: aromatic 2950: (CH ₃) ₂ C=; 1615: -CH=N- 1100, 575: ether; 1200, 900: epoxy	543.47 (498.57)	0.184 (0.198)	3.11 (2.81)	78 - 83	45
A ₃		3600 - 3200, 1050: -OH 3025, 1530: aromatic 2975: (CH ₃) ₂ C=; 1620: -CH=N- 1120, 580: ether; 1250, 910: epoxy	609.75 (537.63)	0.164 (0.186)	2.95 (2.61)	70 - 73	56
A ₄		3600 - 3100, 1050: -OH 3050, 1575: aromatic 2950: (CH ₃) ₂ C=; 1610: -CH=N- 1115, 580: ether; 1200, 920: epoxy	480.76 (543.47)	0.208 (0.184)	2.91 (2.57)	82 - 87	51
A ₅		3500 - 3300, 1050: -OH 3025, 1500: aromatic 2900: (CH ₃) ₂ C=; 1610: -CH=N- 1100, 580: ether; 1200, 890: epoxy	746.26 (543.47)	0.134 (0.184)	2.83 (2.58)	91 - 93	60

^aNumbers in parenthesis indicate the calculated values.

^bEpoxy equivalent weight (100/EE).

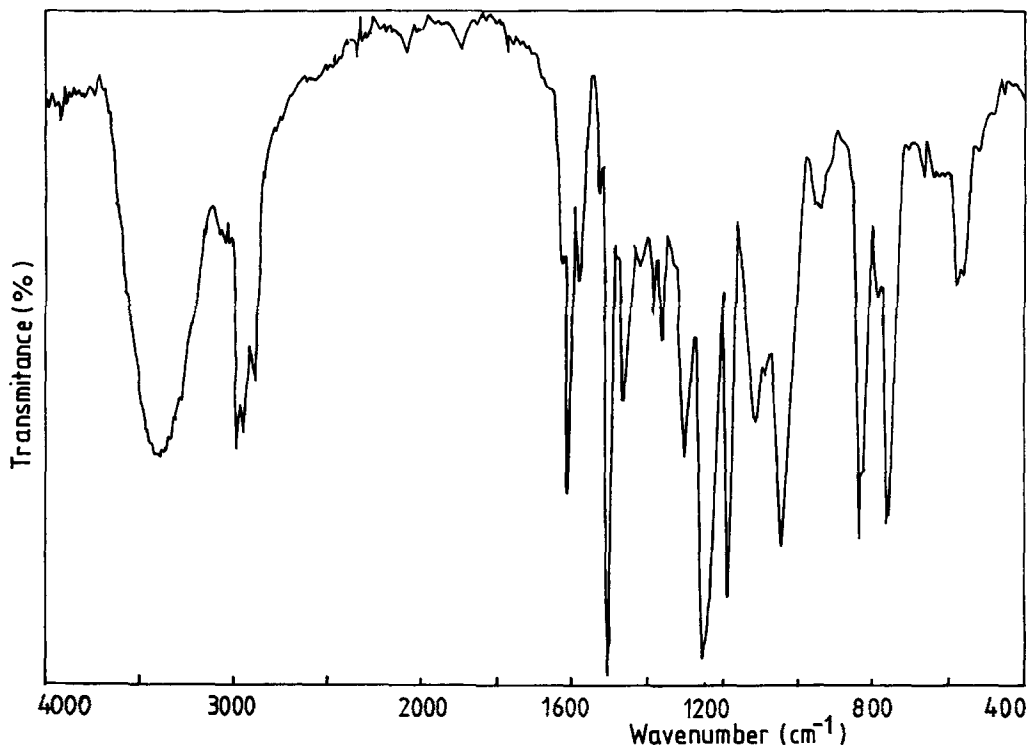


Fig. 1. Infrared spectra of sample A₅.

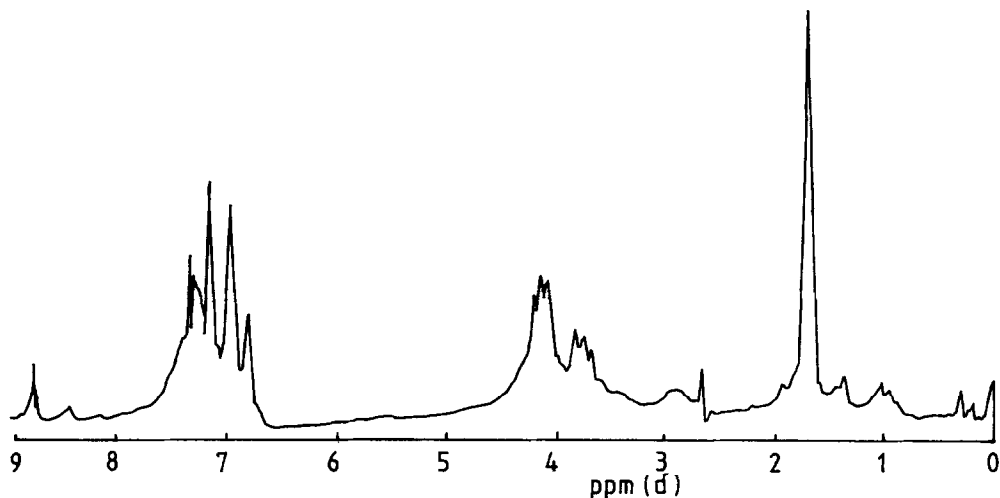


Fig. 2. $^1\text{H-NMR}$ spectrum of sample A_4 .

The ring opening of the epoxide compound (Scheme 1) is followed by the appearance of the secondary alcohol group [14, 15]. The degree of the selectivity of the reaction depends on the active hydrogen compound used, on the catalyst and on reaction temperature. The use of the selective amine catalyst and reaction temperatures higher than 90°C determines a 100-fold increase in the epoxide-phenol reaction rate over the epoxide-secondary hydroxyl groups reaction [13]. The experimental conditions used and the experimental data obtained confirm the linear structure of the obtained epoxy resins containing azomethine.

The main absorption bands observed in the i.r. spectra are listed in Table 1, while Fig. 1 shows, as an example, the i.r. spectrum of sample A_5 . As can be seen from Table 2 and Fig. 1, in addition to the valence vibrations of $-\text{OH}$ groups, the i.r. spectra of the epoxy resins bearing azomethine linkages show the presence of the characteristic absorption bands at 900 , 1200 and 1250 cm^{-1} , attributed to the epoxy group. The 575 – 585 cm^{-1} and 1120 cm^{-1} bands correspond to the vibration of the ether group

($-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-$), while the bands within the 1615 – 1650 cm^{-1} range can be assigned to the $-\text{CH}=\text{N}-$ bond. The bands indicating the presence of the aromatic ring are placed at 3100 and 1500 cm^{-1} , respectively.

The $^1\text{H-NMR}$ spectra of the synthesized epoxy resins show a singlet at 1.7 ppm , specific to the methylenic protons, a multiplet situated in the 2.6 – 3.8 ppm interval for the protons of the epoxy group, a multiplet placed in the 4.0 – 4.2 ppm interval for the protons of the ether bond, a multiplet observed in the 6.5 – 7.3 ppm interval for the aromatic protons and a singlet at 8.69 ppm , assigned to the azomethine protons. Figure 2 shows a typical $^1\text{H-NMR}$ spectrum recorded for sample A_4 .

The u.v. spectra of the epoxides show absorption bands placed in the 330 – 360 nm interval (characteristic to the azomethine groups) and around 285 nm (characteristic to the epoxy groups). As an example, Fig. 3 shows a typical u.v. curve obtained for sample A_3 , compared with the u.v. curve recorded for the DGEBA crude resin.

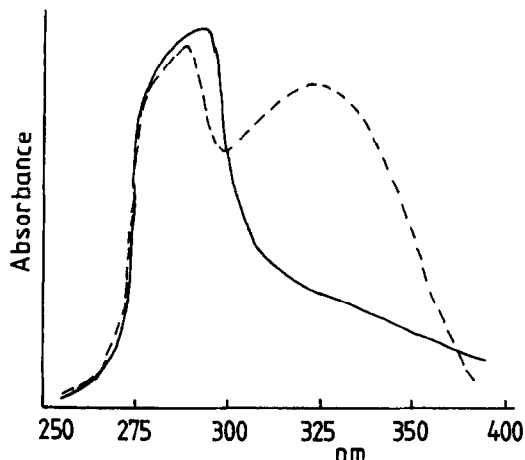


Fig. 3. Ultraviolet spectrum of sample A_3 (---) and DGEBA epoxy resin (—).

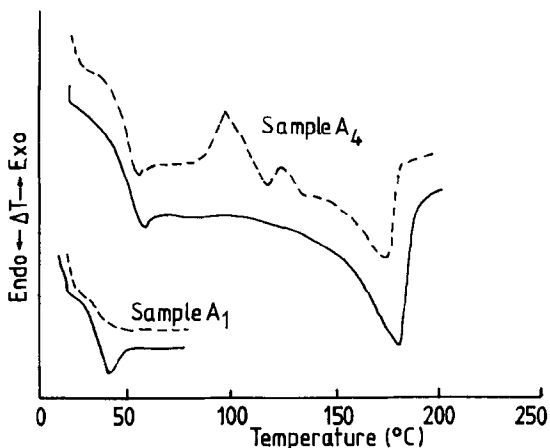


Fig. 4. DSC curves of samples A_1 and A_4 . (---) Cooling cycle; (—) heating cycle.

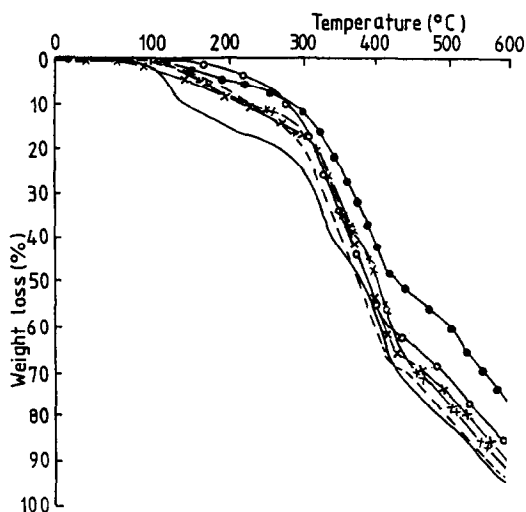


Fig. 5. TG curves for the decomposition of the DGEBA resin: (—) DGEBA; (●-●-●-●) sample A₁; (- - -) sample A₂; (xx-xx-xx) sample A₃; (o-o-o-o) sample A₄; (x-x-x) sample A₅.

The DSC curves recorded with repeated heating-cooling cycles allowed the evaluation of T_g values of the synthesized epoxy resins (see Table 2). The T_g values are situated in the 35–60°C temperature range. It is obvious that they depend on the structure of the epoxides, T_g increasing with increasing polymer molecular weight [16]. Figure 4 shows the DSC curves obtained for two of the synthesized samples. Sample A₄ has a special behaviour due to its semi-crystalline character and by exhibiting a crystallization phenomenon on cooling. Simultaneously, a shift in the glass transition was observed for sample A₃, towards higher temperatures and in the repeated heating-cooling cycles.

One might expect the polymers with azomethine segments in the main chain to have a high thermal stability. The thermal behaviour of the synthesized epoxides was evaluated by dynamic TG experiments in air. Figure 5 shows the TG curves recorded for both the epoxides with azomethine linkages and the DGEBA crude epoxy resin, respectively.

As can be seen from Fig. 5, the epoxides with azomethine groups in the main chain show an appar-

ent thermal stability higher than that of the DGEBA epoxy resin. The polymers A₁ to A₅ suffer a degradation starting from about 200°C, an increased decomposition rate being observed in the 300–450°C temperature range, when the weight losses reach about 60–70%. The very close similarity of the thermograms suggests that the heat stability of the synthesized epoxy resins is not significantly influenced by the structure of the azomethines introduced in the main chain of the DGEBA resin. Considering that the compounds incorporating azomethine groups (i.e. mesogenic units) and flexible spacers in the main chain could possess both heat resistance and liquid crystalline properties [17, 18], further investigations will concentrate on this aspect.

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