Multifunctional Formaldehyde Resins as Curing Agent for Epoxy Resins

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ABSTRACT: Formaldehyde resins (FR) at 1/1/2 molar ratios of monomers (Cl-phenol/amino monomers/*p*-formaldehyde) were synthesized under acid catalysis. The obtained resins were characterized using elemental analysis, FTIR and RMN spectroscopic methods, being used as crosslinking agents for epoxy resin formulations. The curing of epoxy resins with FR were investigated. The glass transition temperature (T_g) and decomposition behavior of crosslinked resins were studied by differential scanning calorimetry (DSC) and thermogravimetric (TGA) techniques. All DSC scans show two exothermic peaks, which implied the occurrence of cure reactions between epoxy ring and amine or carboxylic protons, in function of chemical structures of FR. The crosslinked products showed good thermal properties, high glass transitions, and low water absorption. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1787–1796, 2010

Key words: resins; kinetics; thermal properties

INTRODUCTION

Because of their excellent characteristics, like low moisture-absorbance and good chemicals' resistance after crosslinking, toughness, good adhesion to many substrates, dimensional stability, superior heat, mechanical and electrical properties, and excellent processability, epoxy resins (an important class of high performance, crosslinking polymers) used as structural adhesives or matrix resins, varnishes, paints, etc., are suited to special fields, such as, car industry, aero and naval engineering, military equipments, agriculture, medicine, and so on.[1–4] Generally, the ultimate properties of the crosslinked epoxy resins depend not only on their chemical structure but also on the harder chemical composition and the conditions of curing process. The most usable hardeners are amines (aliphatic, aromatic, and polyamines), anhydrides, acids, cyanate ester, Friedel-Crafts metal halides, etc.[3,5–7]

In the recent times, formaldehyde resins (FR) of novolac type (with OH and NH_2 as reactive groups) have been used as hardeners for epoxy resins, because the cured products present improved moisture resistant behavior, dimensional stability, and high glass transition temperature.[8–19]

In this article, the FR with NH_2, COOH, and Cl in their structure were obtained, characterized, and used as curing agents for epoxy resins. The thermal behavior of the cured products was also emphasized.

EXPERIMENTAL

Materials

Cl-phenol (*p*-ClPh) (Fluka), *p*-aminobenzoic acid (*p*-ABA) (Fluka), *p*-aminophenol (*p*-APh) (Fluka), aniline (AN) (Chimopar SA, Romania), and 4,4'methylenedianiline (MDA) (Aldrich) were used as received. *p*-Formaldehyde (pFA) 98% purity was obtained from a commercial source. Hydrochloric acid (HCl 36%), and all organic solvents were analytical grade products and were used as received or purified by distillation. The epoxy resins: (a) diglycidylether of bisphenol A (DGEBA) (SC Sintofarm SA, Romania) with average epoxy equivalent weight of 345 g equiv^{-1} was used without further purification; (b) diglycidylether of hydroquinone (DGEHQ) (average epoxy equivalent weight of 163 g equiv^{-1}) and diglycidyl aniline (DGAN) (average epoxy equivalent weight of 190 g equiv^{-1}) were obtained as in the literature.[20,21]

FR at molar ratio monomers/formaldehyde (1/1) were prepared according to a method reported, as follows.

Synthesis of formaldehyde resin

The FR containing different amounts of monomers (*p*-ClPh, *p*-ABA, *p*-APh, and AN) at molar ratio

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Sample	Molar ratio (AM/*p*-ClPh/*p*-FA)	Catalyst (HCl) (%)	Color	Number average molecular weight[a]	Cl (%)	Nitrogen (%)	Melting point (°C)
1	(*p*-ABA/*p*-ClPh/*p*-FA) (1/1/2)	3	reddish brown	710	12.45	4.95	135
2	(*p*-APh/*p*-ClPh/*p*-FA) (1/1/2)	3	brown	650	13.56	5.41	130
3	(AN/*p*-ClPh/*p*-FA) (1/1/2)	3	dark orange	590	15.09	5.89	119

[a] cryoscopic method, DMSO as solvent.

monomers/formaldehyde 1/1 were synthesized in the presence of HCl (3% based on the weight of monomers) as catalyst and DMF/toluene mixture (1/1 v/v) as carrier for reaction water, under slowly vacuum. A typical synthesis of the FR (Sample 1, Table I) was carried out as follows.

In a 0.5 L four-necked round-bottomed flask, equipped with thermometer, a mechanical stirrer, reflux water condenser, and oil bath, was charged with 27.43 g (0.2 mol) *p*-ABA, 25.71 g (0.2 mol) *p*-ClPh, and 12 g (0.4 mol) *p*-FA. The content of the flask was stirred at room temperature, and the temperature of the reaction mixture was raised at 70°C and maintained at this level for 15 min. After the temperature becomes stable, 2 mL of HCl (36%) was added in a three portion over 20 min. An exothermic effect ($\sim$ 10°C) was observed and the temperature was raised at reflux, when the reaction mass becomes transparent and orange in color. The reaction mixture was maintained at reflux under stirring for 2.5 h to obtain the base Mannich. Then, 25 mL of DMF/toluene mixture were added, a Dean-Stark trap was attached to the bottom of the water condenser and the temperature reaction mass was raised at reflux. In the meantime, the reaction water was removed from the system, under slowly vacuum, and the temperature rose up continuously to 135°C, when the base Mannich becomes a FR with NH_2 groups on the polymeric chain. Then, the solvents were removed by distillation under vacuum. The total resin preparation can be completed in 3 h. Finally, the hot fluid resin was transferred in a porcelain mold, cooled at room temperature, divided as fine powder, and extracted twice with hot distilled water, to remove the catalyst. The obtained resin (reddish brown) was removed by filtration, and dried under vacuum for over night at 80°C (Scheme 1).

Curing procedure of epoxy resins

The epoxy resins were mixed with a stoichiometric amount of FR obtained as in Table I. After this, the mixtures were heated under vigorous stirring at 50°C for 10 min for uniform dispersion of solid phase, poured into an aluminum cell and placed in a vac-

uum oven for another 10 min to remove air bubbles. Then, the mixture was quickly cooled at 0°C and kept for differential scanning calorimetry (DSC) and thermogravimetric (TGA) studies. A small quantity of the sample was weighed and used for DSC studies ($\sim$ 5–10 mg of the void-free sample) and was scanned at 20–400°C, with different heating rates (5, 10, and 15°C min^{-1}) under nitrogen atmosphere in the presence of an empty cell as standard. For TGA studies, 1 g of each DGEBA/FR system obtained as above was heated at 130°C for 1 h and post cured at 200°C for another 3 h. The cured product was ground into fine powder and used for thermal tests.

Characterization

Nitrogen content was determined in accordance with Kjeldhal method and chlorine was determined by Schöniger method.[22] The average epoxy equivalent weight was evaluated by pyridinium chloride-pyridine method and expressed in gram per equivalent.[23] The average molecular weight is carried
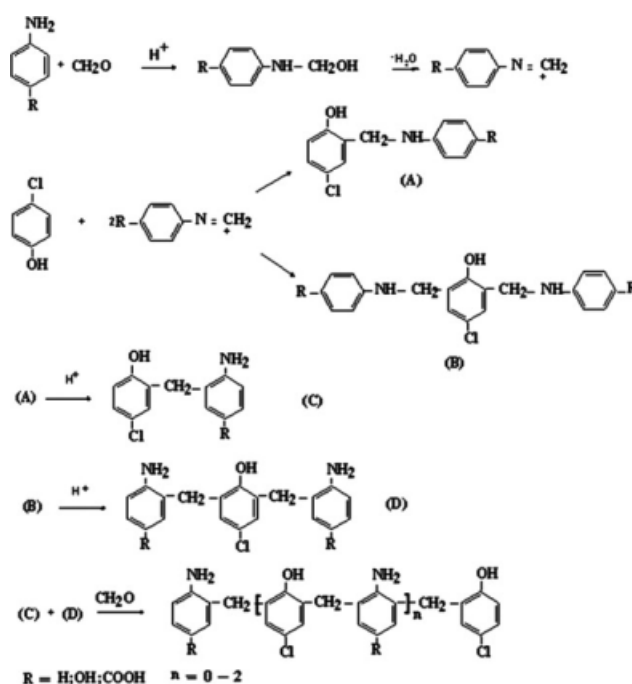
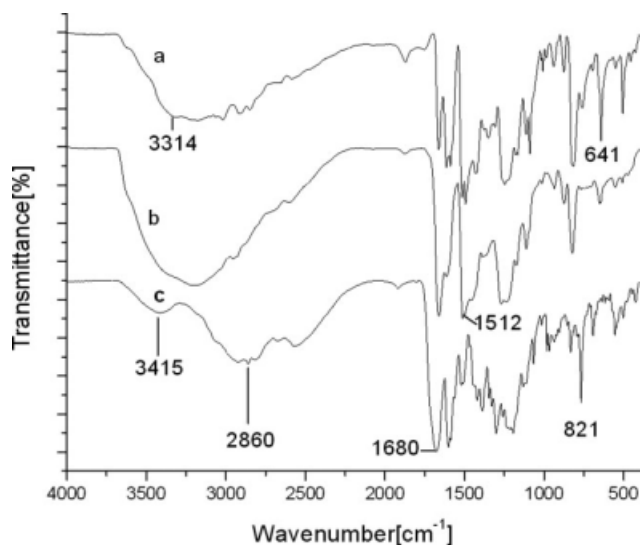**Scheme 1** Preparation of formaldehyde resins.

Figure 1 FTIR spectra for (a) (p-APh/p-ClPh/p-FA) (1/1/2); (b) (1/1/2) (AN/p-ClPh/p-FA) (1/1/2); (c) (p-ABA/p-ClPh/p-FA) (1/1/2).

out by cryoscopic method using DMSO as solvent.[24] ^{1}H-NMR and ^{13}C-NMR spectra of the synthesized novolacs were obtained on an Avance DRX 400 (BRUKER, Rheinstatten, Germany) at 50°C. Samples were analyzed in deuterated DMSO-d_6 using tetramethylsilane (TMS) as internal standard (NMR chemical shifts were expressed in ppm). Infrared spectra (FTIR) were recorded with Bruker Vertex 70 spectrophotometer using KBr disk technique. The extend of curing and glass transition temperature was evaluated by means of a Pyris Diamond DSC, Perkin Elmer instruments at different heating rates (5, 10, and 15°C min^{-1}), at the range of 20–400°C under nitrogen atmosphere (3 L min^{-1}). The instrument was calibrated using pure indium as a standard. Runs were always carried out using an empty cell as a reference. The initial temperature (T_i), the peak temperature (T_p), and the finish temperature (T_f) were recorded against the heating rate. Kinetic parameters of crosslinking reactions were estimated from DSC thermograms using the variable peak exotherm method of Kissinger and Ozawa.[25,26] Based on the obtained linear relationship between the reciprocal of exotherm peak temperature (T_p) and logarithm of the heating rate (log β) and ln(β/T_p^2), the activation energy of crosslinking reactions and the pre-exponential factor were calculated:

$$\ln(\beta/T_p^2) = E_a/RT_p - \ln(AR/E_a) \quad \text{(Kissinger equation)}$$
(1)

and

$$\ln \beta = C - 0.4567(E_a/RT_p) \quad \text{(Ozawa equation)} \quad (2)$$

where A is the pre-exponential factor, C is a constant, E_a is the activation energy for the curing reactions, T_p is the peak of exothermic temperature, R is the gas constant, and β is the heating rate. Previously, this calculation mode of the activation energy of crosslinking reactions is possible without knowing the reaction order. The TGA curves were recorded by a Paulik, Paulik-Erdey TGA analyser of MOM (Budapest) type, at a heating rate of 10°C min^{-1} in air, between 25 and 700°C. The kinetic parameters and activation energies of the degradation reactions for the obtained resins were calculated using Swaminathan and Modhavan and Coats and Redfern equations.[27,28] The general equations used are:

$$d\alpha/dT = A \exp(-E_a/RT)[\alpha^m(1-\alpha)^n][-\ln(1-\alpha)^p]$$
$$\text{(Swaminathan and Modhavan equation)} \quad (3)$$

and

$$\log[1-(1-c)^{1-n}]/(1-n) \times T^2$$
$$= \log(AR/\beta E_a) - 2.303(E_a/RT)$$
$$\text{(Coats and Redfern equation)} \quad (4)$$

where α is the conversion degree (ratio of the weight loss at time "t" and at the end of the process), A is the pre-exponential factor, c is the conversion, E_a is the activation energy of decomposition, n is the reaction order, m and p are the exponents of the conversion function, T is the temperature, β is the heating rate, and R is the gas constant.

The water absorption of cured products was determined by placing the cured disks (1.5 mm diameter, 1.0-mm thick) in cold water at 25°C for 14 days and in hot water at 100°C for 1 h.[29] Then, the disks were removed, dried with filter paper, and weighed. The quantities of the absorbed water were determined as the ratio between the final weight after water absorption and the initial weight.

RESULTS AND DISCUSSION

Synthesis of formaldehyde resins

The FR were synthesized at molar ratio monomers/formaldehyde 1/1 in the presence of HCl as catalyst. The condensation conditions and some characteristics of the resins are presented in Table I. The obtained resins are solid, brittle, with the color varying from dark orange (for the resin with aniline in the structure) to brown as a consequence of their chemical structure. They are partially soluble at room temperature in medium, polar solvents (acetone, methanol, and ethanol), soluble in high polar solvents (DMF, NMP, DMSO, DMAC, and chloroform), and insoluble in ethers (ether ethylic,
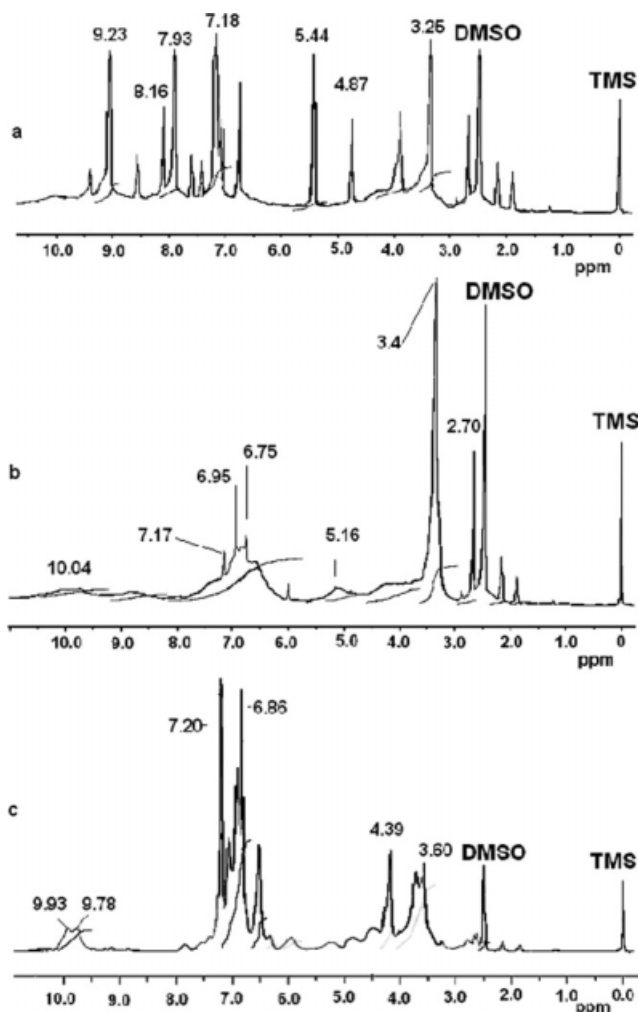
Figure 2 ^{1}H-NMR spectrum for formaldehyde resin: (a) (p-ABA/p-ClPh/p-FA) (1/1/2); (b) (p-APh/p-ClPh/p-FA) (1/1/2); (c) (AN/p-ClPh/p-FA) (1/1/2).

The broad peak appearing in the range of 3180–3415 cm^{-1} arises from the combined OH stretching and intermolecular hydrogen bonding vibrations. The vibrations of NH stretching from primary amine are masked in the same region. The absorption bands at 2850–2920 cm^{-1} due to CH$_2$ stretching vibrations, specific to the bridge between aromatic rings, are seen for all samples, as weak peaks. The characteristic vibration specific to C=O absorption present in carboxylic group of p-ABA appears at 1680 cm^{-1}, (it appears only in the resin with p-ABA in the structure). The peaks specific to the aromatic ring are located in the range of 1520–1612 cm^{-1}. Finally, all spectra show a sharp absorption bands in the range of 641–815 cm^{-1}, that is specific absorption to C—Cl group. The structure was also confirmed by the high

petroleum ether), n-hexane, and cyclohexane. The probable chemical reactions involved in the synthesis of these FR and their possible structure are presented in Scheme 1. In the first step, in the presence of the acidic protons, the amine monomers react with formaldehyde and form NH—CH$_2$OH groups. Under the action of temperature, CH$_2$OH groups react with p-ClPh and split off the water, resulting a mono and bis base Mannich.[30,31] In the conditions of a molar ratio of AM and p-ClPh 1/1, it is more probable that the mono base Mannich to be formed [phase (A), Scheme 1]. In the second step, in the presence of acidic protons and under the effect of temperature, mono and bis base Mannich becomes unstable and rearranges into oligomers with methylene bridges between aromatic rings.[32] The possible structure of the obtained resins was confirmed by FTIR, ^{1}H-NMR, ^{13}C-MNR, molecular weights measurements, and elemental analysis. The FTIR spectrum of the synthesized FRs is shown in Figure 1.

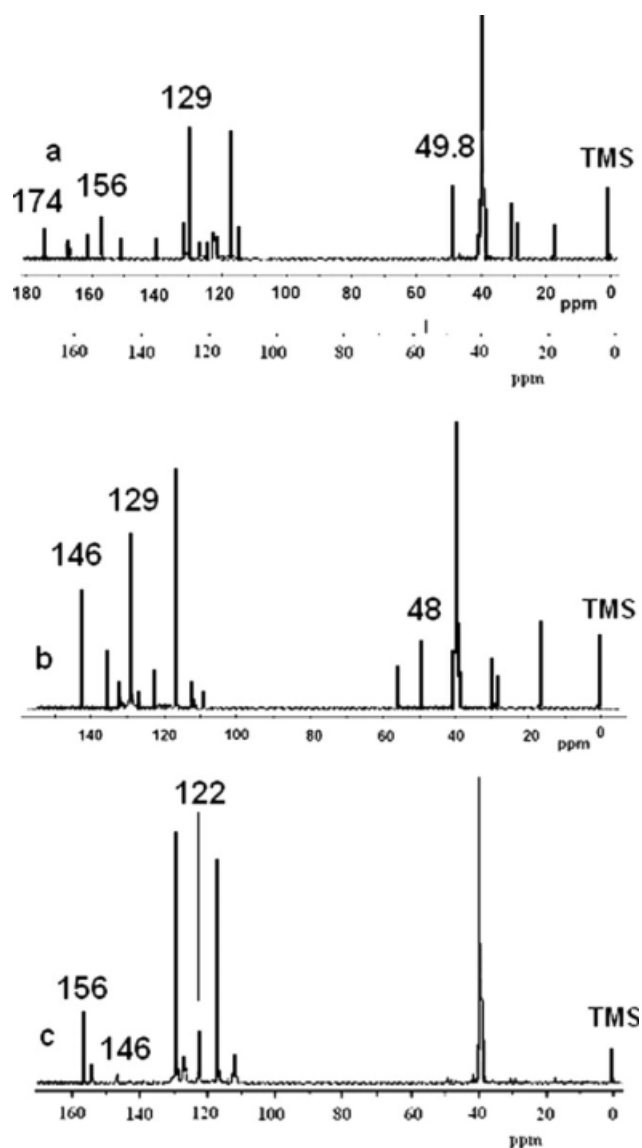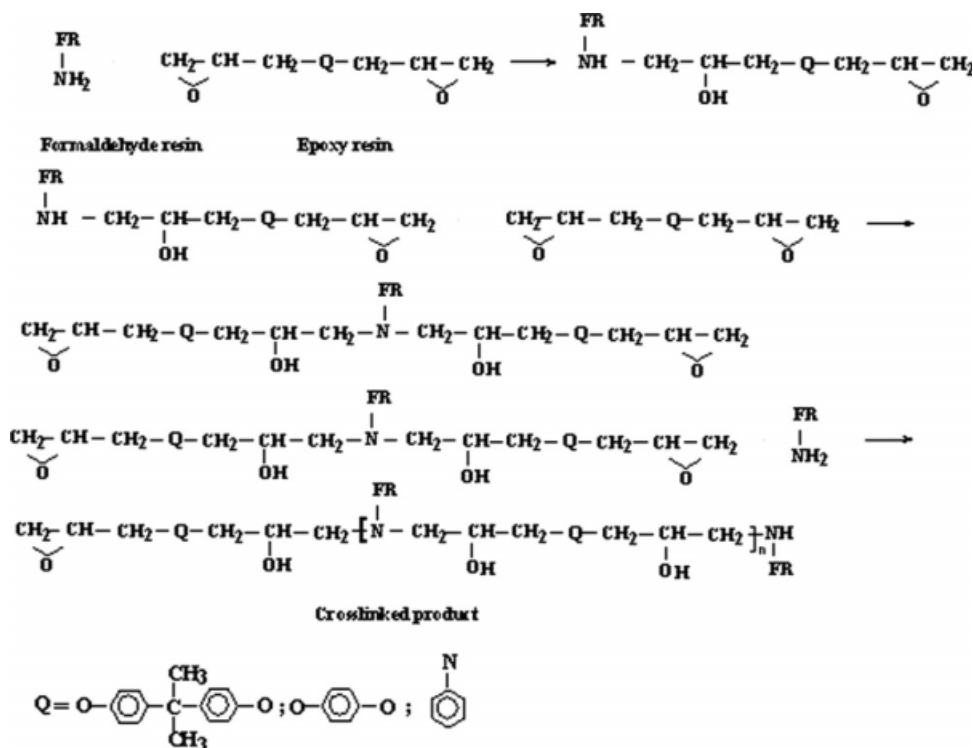**Figure 3** ^{13}C-NMR spectrum for formaldehyde resin: (a) (p-ABA/p-ClPh/p-FA) (1/1/2); (b) (p-APh/p-ClPh/p-FA) (1/1/2); (c) (AN/p-ClPh/p-FA) (1/1/2).

Scheme 2 Proposed reaction scheme for epoxy resin curing.

resolution ^{1}H-NMR and ^{13}C-NMR spectra of FRs. The ^{1}H-NMR spectrum for the AN/p-ClPh/p-FA) (1/1/2) FR is shown in Figure 2(c). The signals that appear in the region of the 3.59 and 3.72 ppm chemical shift can be assignable to the CH$_2$ protons that bridge the aromatic nuclei, specifically to the FR. The primary amine protons situated in the amino-monomers appear as the singlet at the 4.14-ppm chemical shift. The minor signals observed between

4.4 and 4.9 ppm chemical shift could be attributed to the residual uncondensed methylol groups and the peak located in the range of 6.5 ppm can be assigned to the secondary amine group. The aromatic protons assigned to the amino monomers and the p-ClPh nuclei appeared as a complex multiplet peaks in the range of 6.7–7.2 ppm denotes the aromatic protons ortho to the amino groups OH groups. The peaks

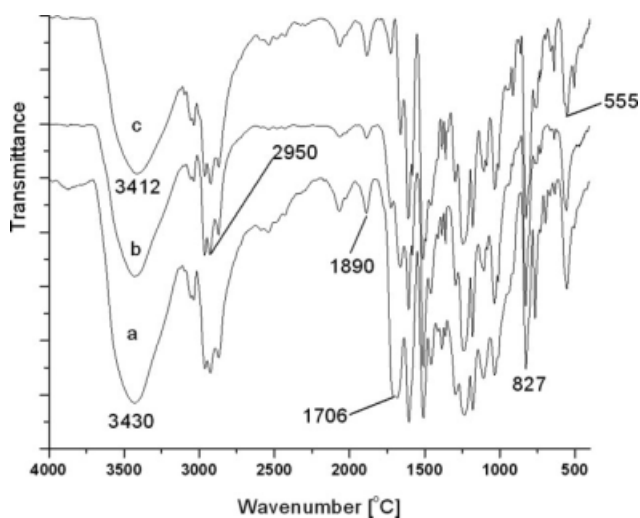**Figure 4** FTIR spectra for crosslinked DGEBA with formaldehyde resin: (a) (p-ABA/p-ClPh/p-FA) (1/1/2); (b) (p-APh/p-ClPh/p-FA) (1/1/2); (c) (AN/p-ClPh/p-FA) (1/1/2).

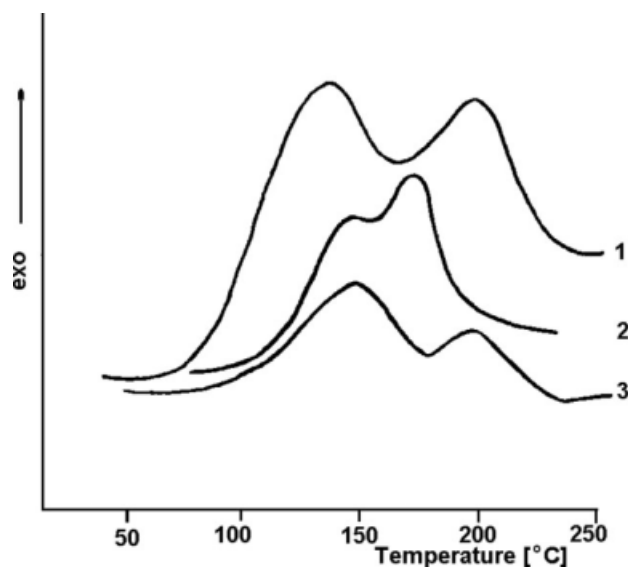**Figure 5** DSC thermograms (at heating rate of 10°C/min) of DGEBA crosslinked with formaldehyde resin: (1) (AN/p-ClPh/p-FA) (1/1/2); (2) (p-ABA/p-ClPh/p-FA) (1/1/2); (3) (p-APh/p-ClPh/p-FA) (1/1/2).

TABLE II
Kinetic Parameters for Epoxy Resins Cured with Formaldehyde Resin (AM/p-ClPh/p-FA) (1/1/2) from DSC Scans (Molar Ratio Epoxy Group/Amine Proton = 1/1) for the First Exotherm

Epoxy resin	Heating rate (°C min⁻¹)									Activation energy of curing reaction (kJ mol⁻¹)						Pre-exponential factor (min⁻¹)		
	(pABA/p-ClPh/p-FA)			(AN/p-ClPh/p-FA)			(pAPh/p-ClPh/p-FA)			(pABA/p-ClPh/p-FA)		(AN/p-ClPh/p-FA)		(pAPh/p-ClPh/p-FA)		(pABA/p-ClPh/p-FA)	(AN/p-ClPh/p-FA)	(pAPh/p-ClPh/p-FA)
	5	10	15	5	10	15	5	10	15	Oz	Kiss	Oz	Kiss	Oz	Kiss	Kiss	Kiss	Kiss
	T_M	T_M	T_M	T_M	T_M	T_M	T_M	T_M	T_M									
DGEBA	134	152	155	146	156	168	126	133	143	79.03	68.32	76.00	68.83	87.49	80.65	19.71	11.6	19.57
DGEHQ	135	145	165	110	127	138	115	126	135	51.57	44.37	51.60	44.98	72.21	65.62	15.11	5.71	12.14
DGAN	137	150	156	140	147	153	137	145	150	83.41	76.42	43.34	40.47	67.23	64.71	9.72	20.1	14.07
Blank test[a]	132	145	158	–	–	–	–	–	–	61.37	54.43	–	–	–	–	7.67	–	–

T_M, maximum peak temperature (°C); Oz, calculated using Ozawa equation; Kiss, calculated using Kissinger equation.
[a] DGEBA/MDA.

TABLE III
Kinetic Parameters for Epoxy Resins Cured with Formaldehyde Resin (AM/p-ClPh/p-FA) (1/1/2) from DSC Scans (Molar Ratio Epoxy Group/Amine Proton = 1/1) for the Second Exotherm

Epoxy resin	Heating rate (°C min⁻¹)									Activation energy of curing reaction (kJ mol⁻¹)						Pre-exponential factor (min⁻¹)		
	(pABA/p-ClPh/p-FA)			(AN/p-ClPh/p-FA)			(pAPh/p-ClPh/p-FA)			(pABA/p-ClPh/p-FA)		(AN/p-ClPh/p-FA)		(pAPh/p-ClPh/p-FA)		(pABA/p-ClPh/p-FA)	(AN/p-ClPh/p-FA)	(pAPh/p-ClPh/p-FA)
	5	10	15	5	10	15	5	10	15	Oz	Kiss	Oz	Kiss	Oz	Kiss	Kiss	Kiss	Kiss
	T_M	T_M	T_M	T_M	T_M	T_M	T_M	T_M	T_M									
DGEBA	161	176	184	182	196	204	175	188	195	78.08	71.20	88.55	80.90	95.54	86.94	13.65	13.05	14.68
DGEHQ	140	144	165	165	189	195	153	164	181	54.65	47.14	57.98	50.50	60.17	52.95	5.54	5.17	6.43
DGAN	151	166	172	157	173	183	150	170	177	79.84	72.68	69.12	61.75	61.2	54.05	14.28	9.81	6.76

T_M, maximum peak temperature (°C); Oz, calculated using Ozawa equation; Kiss, calculated using Kissinger equation.

TABLE IV
Thermal Parameters of Formaldehyde Resins

Sample	Molar ratio (AM/p-ClPh/p-FA)	Temperature (°C), at which weight loss is equal to:		Weight loss at 500°C (%)	Reaction order Swaminathan and Modhavan	Decomposition activation energy (kJ/mol)	
		(10%)	(50%)			Swaminathan and Modhavan	Coats and Redfern
1	(AN/p-ClPh/p-FA) (1/1/2)	342	555	45	1.57	69.82	67.23
2	(p-APh/p-ClPh/p-FA) (1/1/2)	290	520	48	1.55	62.06	60.46
3	(p-ABA/p-ClPh/p-FA) (1/1/2)	310	525	45	1.28	60.91	60.02

situated in the range of 7.17–7.2 ppm can be attributable to the aromatic protons situated in the aromatic rings in the meta position of the amine or OH groups. The peaks situated at 9.78–9.93 ppm could be attributed to the OH group from p-ClPh.

In the ^{13}C-NMR spectra (Fig. 3), the characteristic signal attributed to the CH_2 group bonded between the aromatic rings it appears in the range of 38–41 ppm chemical shift. The weak signals at 46.7–49.4 can be attributable to the carbon of the residual methylol groups. The peaks specific to the CH groups located in the aromatic ring can be seen at 115 ppm for the aromatic carbon situated in the ortho position of NH_2 and at 122 ppm for aromatic carbon situated in the ortho position of OH. The aromatic carbons located in the meta position of the C—NH_2 and C—OH groups are presented in the range of the 127 and 129 ppm chemical shift, respectively. The signals that appear in the region of the 146 and 156 ppm chemical shift are specific to the C—NH_2 and C—OH groups. The peak specific to the C—Cl link are presented in the range of the 122 ppm chemical shift and are masked in the same region by the NH_2 groups.

Curing of epoxy resins with FR

The chemical reactions involved in synthesis of the cured products and their possible structure are presented in Scheme 2. In the IR spectra (Fig. 4) the absence of the peaks at 910–915 cm^{-1} (specific to the oxirane ring) and the presence of peaks situated at 3415 cm^{-1} (specific to OH groups) suggest that polymerization reaction took place. The thermal cure behavior of epoxy resins with FR was studied by using DSC technique. The dynamic DSC scans were taken at three heating rates in a nitrogen atmosphere. All DSC scans show two exothermic peaks, which implied the occurrence of cure reactions between epoxy ring and amine or carboxylic protons, as function of chemical structures or FR. Figure 5 presents the DSC scan for DGEBA cross-

linked with (AN/p-ClPh/p-FA) (1/1/2) FR. The presence of the secondary exotherm can be attributed to the steric hindrance during the crosslinking reactions at the consequence of the high dimension of FR. In the presence of OH groups, the crosslinking reactions involved a complex mechanism[33] (Scheme 2). In the first step, the amine primary protons easy react at lower temperature with epoxy ring and secondary amine and tertiary OH groups appear. With the decrease of NH_2 concentration and the increase of the amounts of NH and OH groups, as a consequence of higher nucleophilicity of hydroxyl groups, the apparent reaction rate decreases, but at higher temperature, the tertiary amine groups, ether groups, and a crosslinked link appear. The fact that the maximum peak temperature for the second exotherm is situated under 200°C suggests the crosslinking reactions are not a consequence of the reaction between OH and epoxy ring. The data presented in Tables II–IV show the maximum peak temperature is specific to each epoxy resin and each FR and all the tested samples show a continuous increase of the maximum peak temperature with the heating rate. The kinetic parameters (activation energy, order of reaction, and pre-exponential factor) of the crosslinked reaction between epoxy resins and FR were evaluated using Kissinger and Ozawa methods for the two exotherms. The obtained results were listed in Tables II–IV. As it can be seen, the exothermic temperature peak is specific to each epoxy resins/FR system and has the minimum value (for the first exotherm) for the systems cured with the FR with AN in the structure (Table IV). For the second exotherm, the minimum value of exothermic temperature peak is for the systems cured with the FR with p-ABA in the structure (Table II). This fact can be explained by the great reactivity of FR with p-ABA in structure, because it contains three reactive groups in comparison with the other FR, which contain only two reactive groups. The activation energy of the curing reactions is situated in the range of 43–87 kJ mol^{-1} for the first

TABLE V
Thermal Parameters of DGEBA Crosslinked with Formaldehyde Resins

Sample	Formaldehyde resin/epoxy resin	Temperature (°C), at which weight loss is equal to: (10%)	(50%)	Weight loss at 500°C (%)	Reaction order Swaminathan and Modhavan	Decomposition activation energy (kJ/mol) Swaminathan and Modhavan	Coats and Redfern	Glass transition temperature (°C)[a]	**Water absorption (%) b	c
1	(AN/p-ClPh/p-FA) /(DGEBA)	345	585	42	0.71	40.04	41.75	140	1.47	0.77
2	(p-APh/p-ClPh/p-FA) /(DGEBA)	340	545	40	1.2	48.56	53.86	145	1.56	0.98
3	(p-ABA/p-ClPh/p-FA) /(DGEBA)	335	538	38	0.55	31.7	30.23	151	2.12	1.03
4	DGEBA/DDM	365	485	55	0.61	84.55	74.67	132	1.81	0.83

[a] measured after crosslinking at 130°C, 1 h, and at 200°C 3 h, by DSC method, at heating rate of 10°C min^{-1}.
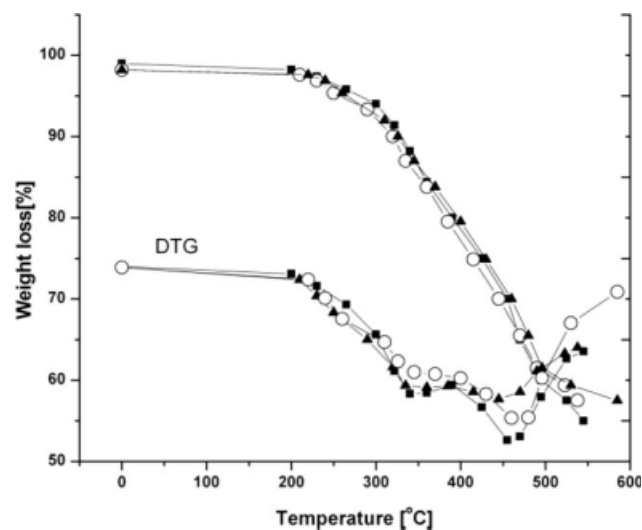[b] measured after14 days at 25°C.
[c] measured after 1h at 100°C.

Figure 6 Weight loss for formaldehyde resins: (■) (p-ABA/p-ClPh/p-FA) (1/1/2); (▲) (AN/p-ClPh/p-FA) (1/1/2); (○) (p-APh/p-ClPh/p-FA) (1/1/2).

exotherm and between 47 and 88 kJ mol^{-1} for the second exotherm depending on the chemical structure of epoxy resin and FR. About the same values of activation energies of curing process obtained from the second exotherm peaks in comparison with the values obtained from first exotherm demonstrated that this process is not composed by a summarization of exotherm effect of addition of amine to the epoxy ring and of the etherification process of OH groups with epoxy ring. The values of the activation energies of the curing are comparable with the other data reported in the literature for the epoxy resins, cured with the multifunctional FR (52–80 kJ mol^{-1}).[34,35] The influence of structure of
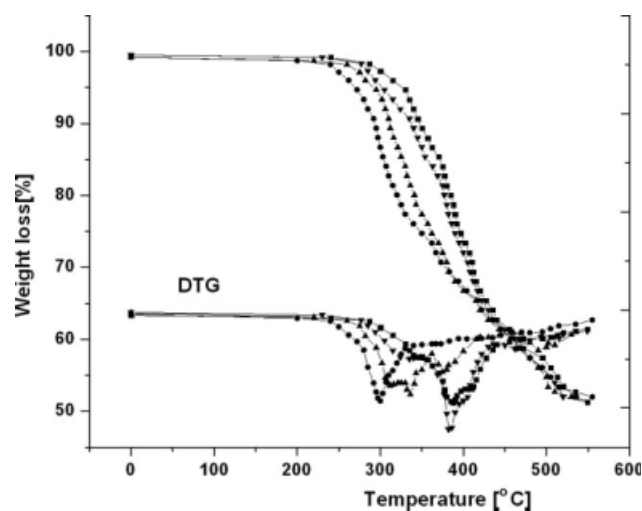

Figure 7 Weight loss for DGEBA crosslinked with formaldehyde resins: (■) (p-ClPh/p-ABA/p-FA) (1/1/2); (▲) (p-ClPh/AN/p-FA) (1/1/2); (●) (p-ClPh/p-APh/ p-FA) (1/1/2); (▼) DGEBA/MDA.

TABLE VI
The Solubility of the Formaldehyde Resins at the Room Temperature

Solvent	AN/p-ClPh/p-FA	p-ABA/p-ClPh/p-FA	p-APh/p-ClPh/p-FA
Cyclohexane	−	−	−
Petroleum ether	−	−	−
Acetone	−	±	±
Methyl alcohol	±	±	±
Ethyl alcohol	±	±	±
Dioxane	−	−	−
CCl$_4$	−	−	−
Chloroform	−	−	−
Benzene	−	−	−
Toluene	±	±	±
Diethyl ether	−	−	−
DMSO	+	+	+
DMF	+	+	+
DMAc	+	+	+
NMP	+	+	+

−, insoluble; +, soluble; ±, partially soluble by heating.

these cured resins were also examined by measuring the glass transition temperatures and the moisture absorption. As it can be seen in Table V, the glass transition temperatures (T_g) of the cured epoxy resin with FR which contains p-ABA in its structures was enhanced in comparison with cured epoxy resin with the FR containing AN and p-APh. This can be attributed to the fact that the FR resins with p-ABA have high functionalities and induce a high density of crosslinking, resulting in a more rigid structure in comparison with epoxy resins cured with FR which contain AN and p-APh. On the other hand, this crosslinked resin has a large moisture absorption in comparison with the resins which contain AN and p-APh. This is possible as a consequence of the fact that the cured resin with FR with p-ABA in its structure has the highest quantity of OH groups, hydrophilic in nature (produced by the ring opening of epoxy groups during the crosslinking reactions).

Thermal behavior of formaldehyde resins and of cured epoxy systems

The thermal behavior of FR and of the crosslinked products of DGEBA with FR was investigated between room temperature and 750°C, by thermal gravimetric analysis. The thermograms (TGs) along with their derivatives curves (DTG) of the three FR and as well of crosslinked resins are shown in Figures 6 and 7, respectively. The activation energy of the degradation reaction and the reaction order for the major degradation step were obtained using the eqs. (3) and (4), and their values are presented in Tables IV and V. The thermograms of FR show two stages of degradation, one of which comprises the major weight loss. The major weight loss registered at 500°C is located around 45%. It can be seen that the FR exhibited about the same thermal stability. This can be attributed to the same chemical structure and relatively the same molecular weights. The thermograms of crosslinked resins also show two stages of degradation. From the Figure 7, it can observe that DGEBA/MDA and DGEBA/(p-ClPh/p-ABA/p-FA) systems present the maximum of degradation peaks around 380°C, whereas the crosslinked resins DGEBA/(p-ClPh/pAN/p-FA) and DGEBA/(p-ClPh/p-APh/p-FA) present the maximum of degradation peaks around 300°C. A possible explanation of this behavior consist in the fact that these resins have a greater crosslinking density as a consequence of a large number of functional groups present on the polymeric chain take part to the crosslinking reactions. The major weight losses registered at 500°C are lower in comparison with that obtained for FR. The char yields have values situated in the range between 40 and 45%, with the exception of crosslinked product of DGEBA with FR, which contains p-ABA. The fact that these resins have a char yield value situated under 40% can be attributed to the three reactive protons presented in the molecular structure of p-ABA, which leads to the increase of the crosslinking degree.

Solubility of the formaldehyde resins

The solubility behaviors of the FR are presented in Table VI. As it can be seen, the obtained products are soluble at the room temperature in the most polar solvents and insoluble in petroleum ether, dioxane, carbon tetrachloride, and cyclohexane.

CONCLUSIONS

The new FR with Cl in their structure were obtained in the acid catalysis. Because these resins contain the multifunctional groups on the polymeric chain, they can be used as hardener for the epoxy resins, having the advantage of being relatively nontoxic and noninflammable as compared with other hardeners and thus inducing an improved pot life. The curing reactions of these multifunctional FR with the three epoxy resins are a complex process due to the different functionality present on the polymeric chain. The energies of the crosslinking reactions obtained from the DSC thermograms (depending on the chemical structure of the epoxy and FR) are situated in the range of 43–88 kJ mol^{-1} and are in good agreement with the literature data. The crosslinked resins show a relatively good thermal stability, high glass transition, and relatively low water absorption. The apparent activation energies of the degradation process have the values situated in the range of 61–70 kJ mol^{-1} for the FR and between 31 and 54 kJ mol^{-1} for the crosslinked products.

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