Synthesis and Characterization of Novel Methylenedianiline/tert-butylphenol Formaldehyde Resins as Hardeners for Epoxy Resins

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New formaldehyde resins were synthesized by the polymerization of a mixture of 4,4’-methylenedianiline (MDA) and p-tert-butylphenol (p-TBPH) with formaldehyde (FA) (at a molar ratio monomers/formaldehyde, 1/1), in the presence of an acid catalyst (HCl).The mixture of DMF/toluene was used as reaction medium and as carrier for the aqueous condensation. These polymers were characterized by elemental, spectral and thermal analysis and used as hardener for epoxy resins (diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of hydroquinone (DGEHQ)). The obtained resins have low molecular weight and are soluble in medium and high polar solvents. The curing and the temperature behaviour of epoxy resin/formaldehyde resin systems were investigated using differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques. The activation energies of the curing reactions are situated in the range of 52 to 66 kJ×mol^{-1} for DGEBA systems and at 54 to 72 kJ×mol^{-1} for DGEHQ systems. The cured products have good thermal properties, and the activation energies of the degradation reactions have values between 36-65 kJ×mol^{-1} for epoxy systems.

Keywords: formaldehyde resins, epoxy resin, crosslinking reactions, thermal properties

Although formaldehyde resins are among the oldest polymers, as a consequence of their excellent physico-chemical properties in addition with a good processability they are used in many fields of industrial applications [1-3]. Epoxy resins, the most common crosslinked compounds are used as structural adhesives for electronic and electric industry, because of their good mechanical, electrical and chemical resistance [4-6]. The main constituents of the epoxy resin formulations are the epoxy resin and the curing agents, which confer them the ultimate properties of the crosslinked products.

The common curing agents are aromatic and aliphatic amines and anhydrides [6]. Recently, the multifunctional formaldehyde resins of novolac type with OH, COOH or NH_2 groups on the polymer chains were used as hardener for epoxy resins because the obtained products have high performance properties, after crosslinking [7-17]. A survey of the literature data shows that there are some references on the synthesis of the formaldehyde resin with MDA in its structure and used as hardener for epoxy resins [10,12,16,18,19].

The aim of this paper is to report the results of the synthesis and characterization of new formaldehyde novolac resins, which contain 4,4’-methylenedianiline (MDA) and p-tert-butyl phenol (p-TBPH) in the resin backbone. Our interest in these resins resulted from their applications as cross linked agents for epoxy resins. The thermal properties of the formaldehyde resins and of the crosslinked products were also investigated.

Experimental part

Materials

4,4’-Methylenedianiline (MDA) (Aldrich) and p-tert-butylphenol (p-TBPH)(Fluka) were used as received. p-Formaldehyde (FA) was commercial source, 98% purity. Hydrochloric acid (HCl 35 %), and all organic solvents were chemically pure reagents and used as received or purified by distillation before use. The epoxy resins (diglycidylether of bisphenol A)(DGEBA)(SC Sintofarm SA, Romania) and diglycidylether of hydroquinone (DGEHQ)(obtained as in literature [20]), with an average epoxide equivalent weight of 200 g×eq^{-1} and 250 g×eq^{-1} respectively were used as purchased. Formaldehyde resins at molar ratio monomers/formaldehyde (1/1) were prepared according to a method reported, as follows.

Measurements

Nitrogen content was determined in accordance with the Kjeldhal method [21]. Average molecular weight of formaldehyde resins was obtained by cryoscopic method using dimethyl sulfoxide as solvent [22]. The average epoxide equivalent weight was evaluated by pyridinium chloride-pyridine method and expressed in g×eq^{-1} [23]. Infrared spectra (FT-IR) were recorded using a Bruker Vortex 70 spectrophotometer from KBr pellets. ^{1}H-NMR spectra were obtained on an Avance DRX 400 (BRUKER, Rheinstatten, Germany) at 50°C using tetramethylsilane as internal standard and DMSO-d_6 as solvent. Thermal studies of formaldehyde resins and of the crosslinked products were evaluated on a STA 449 F1 Jupiter apparatus (Netzsch-Germany) at 10°C ×min^{-1} heating rate in the temperature range 25-600°C under static air atmosphere. The extent of curing was evaluated by means of a Pyris Diamond DSC, Perkin Elmer instruments at different heating rates (5, 10, 15 °C×min^{-1}), into the range of 20 - 400 °C in a nitrogen atmosphere (3 Lmin^{-1}). The instrument was calibrated using the melting point of high purity indium. Samples of about 7-10 mg were enclosed in the aluminium cells and scanned in the presence of aluminium empty cell as standard.

Synthesis of formaldehyde resin

The formaldehyde resins containing different amounts of monomers (MDA/p-TBPH/p-FA) at molar ratio monomers/formaldehyde 1/1 were obtained under acidic conditions (~3 % HCl based on monomer weights) and DMF/toluene mixture (1/1 v/v) as carrier for reaction water, under moderate vacuum. The molar ratio and the

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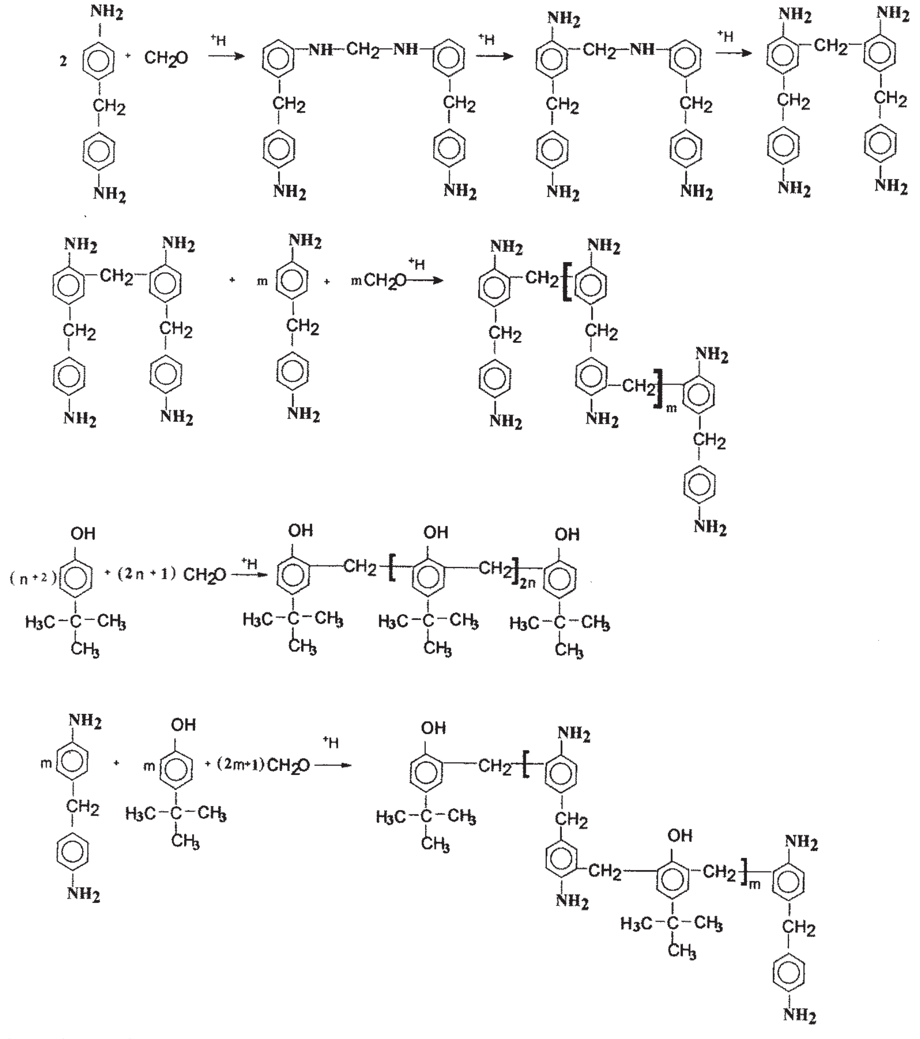
condensation conditions were presented in table 1. A typical experiment (Sample 2, table 1) was carried out as follows: a 4-necked round-bottomed glass reaction vessel, equipped with thermometer, oil bath, mechanical stirrer, reflux water condenser and dropping funnel, was charged with 39.6 g (0.2 mol) MDA, 30 g (0.2 mol) p-TBPH and 12 g (0.2 mol) p-FA. The content of the vessel was heated at 75°C under stirring and maintained at this level for 15 min . After the temperature becomes stable, 7.2 mL of HCl (37 % v/v) was added in three portions over 10 min. An exothermic effect (~18°C) was observed and temperature was raised at reflux when the reaction mass becomes transparently. 60 mL of DMF/toluene mixture (1/1 v/v) was added to the reaction mixture and maintained at reflux under stirring for another 2 h to obtain the Mannich base. Then, a Dean-Stark trap was attached to the water condenser and under moderate vacuum, the reaction water was extracted. Finally, the temperature rose up to 145°C. The total resin preparation can be completed in 3 h. The obtained formaldehyde resin was dissolved into 200 mL of warm (60°C) DMF/toluene mixture, washed twice with warm distilled water under vigorous stirring with the aim of the catalyst removal. Then, the solution was decanted and the solvents were removed by distillation under vacuum. Finally, the reaction mass was moved in an aluminium mold, cooled at the room temperature, divided as fine grains and extracted twice with cyclohexane. A reddish brown resin (table 1, scheme 1) is obtained.

Curing procedure

The epoxy resin and formaldehyde resins (FRs) at 40-50°C, as fine grain were vigorously mixed for about 0.5 h in a proportion corresponding to a stoichiometric equivalent amine proton/epoxy ring using a mechanical stirrer. The homogeneous mixture was moved in an aluminium cell and placed in a vacuum oven at 50 °C for 1 hour to release the air bubbles. Then, the mixture was quickly cooled at 0°C and kept for TG and DSC studies. The freshly prepared samples (4-10 mg) were used for recording DSC traces in nitrogen atmosphere at a programmed heating rate from 20 °C up to 350 °C. A large part of the samples were cured at 140°C for 1h, and post cured at 220 °C for 4 h. The cured product was ground into fine grains and used for thermal tests.

Results and discussions

FRs were synthesized at various molar ratios of MDA/*p*-TBPH in the presence of HCl as catalyst. The condensation conditions and the main characteristics of the resins are presented in table 1. The obtained resins are solid with colour varying from brown orange for the FR with MDA/*p*-TBPH at molar ratio 1/ 2 to dark brown orange for the FR with MDA/p-TBPH at molar ratio 2/1. The obtained products are soluble at room temperature in high polar solvents (chloroform, methylpirrolidone, dimethylformamide, dimethylsulfoxide, dimethylacetamide) and insoluble in ethers (ethyl, petroleum), acetone, alcohol, cyclohexane, n-hexane. The chemical reactions involved in the synthesis of these resins and their structure are presented in scheme 1. In the first step, in the presence of small quantities of acidic protons, MDA reacts with formaldehyde and forms NH-CH_2OH groups. Under the action of temperature, CH_2OH groups react with *p*-TBPH and split off water, resulting a mono and bis Mannich base [23-24]. It is more probable, that the bis Mannich base to be formed instead of the mono Mannich base in the



Scheme 1. The syntheses of the MDA/*p*-TBPH/formaldehyde resins

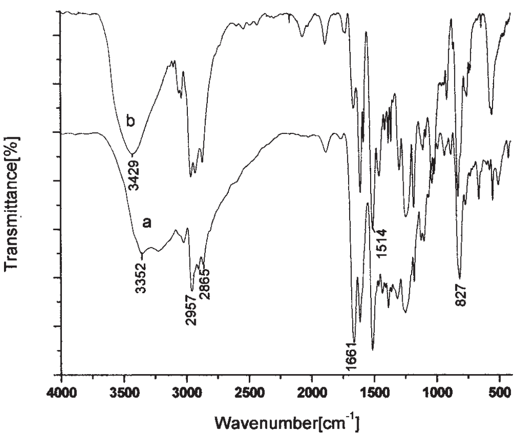


Fig.1. FT-IR spectra of (a)MDA/p-TBPH (1/1) formaldehyde resin and of (b)DGEBA crosslinked with MDA/p-TBPH (1/1) formaldehyde resin

Table 1

THE REACTION CONDITIONS USED AT THE CONDENSATION BETWEEN MDA/*p*-TBPH/ FORMALDEHYDE AND SOME PHYSICAL CHARACTERISTICS OF THE OBTAINED RESINS

Sample	Molar ratio of monomers: MDA/p-TBPH/p-FA	Toluene/ DMF (1/1) (%)	Catalyst (HCl) (%)	Colour	Number average molecular weight [a)]	Nitrogen (%)	Yield (%)	Melting point (°C)
1	1/2/3	40	3	reddish orange	805	3.21	94	69
2	1/1/2	40	3	brown orange	1020	5.86	93	78
3	2/1/3	40	3	dark orange	1080	7.79	96	84

a) cryoscopic method, 25°C, DMSO as solvent

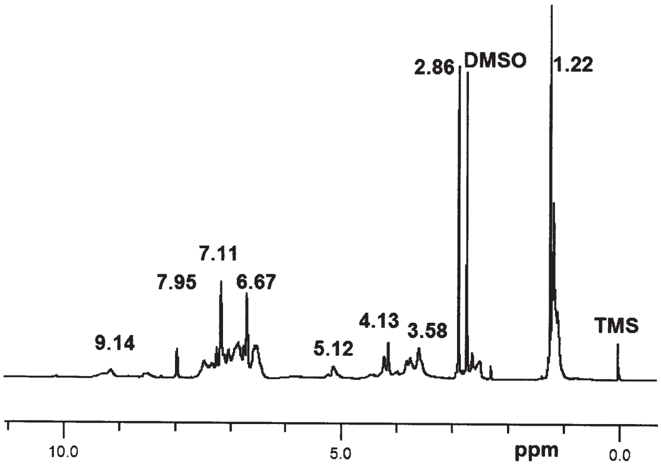


Fig.2. ^{1}H-NMR spectrum of MDA/p-TBPH (1/1) formaldehyde resin

conditions of a molar ratio of MDA/*p*-TBPH 2/1 (scheme 1). In the second step, in the presence of acidic protons and under the effect of temperature, the bis Mannich base becomes unstable and rearranges into oligomers with methylene bridges between aromatic or aromatic/aliphatic rings [25, 26]. When p-FA is in excess, the CH_2OH groups appear; by rising the temperature, the reaction water splits off and the methylol groups are transformed in methylene bridges thus, resulting the formaldehyde resins. The chemical structures of MDA/*p*-TBPH/*p*-FA resins were identified using^{1}H-NMR and FT-IR spectroscopic methods and elemental analysis (%N). The FT-IR spectrum of FR (fig 1a, Sample 2 from table 1) shows the analogous stretching vibration bands, specific to MDA and *p*-TBPH monomers. The main characteristic absorptions bands are as follows:

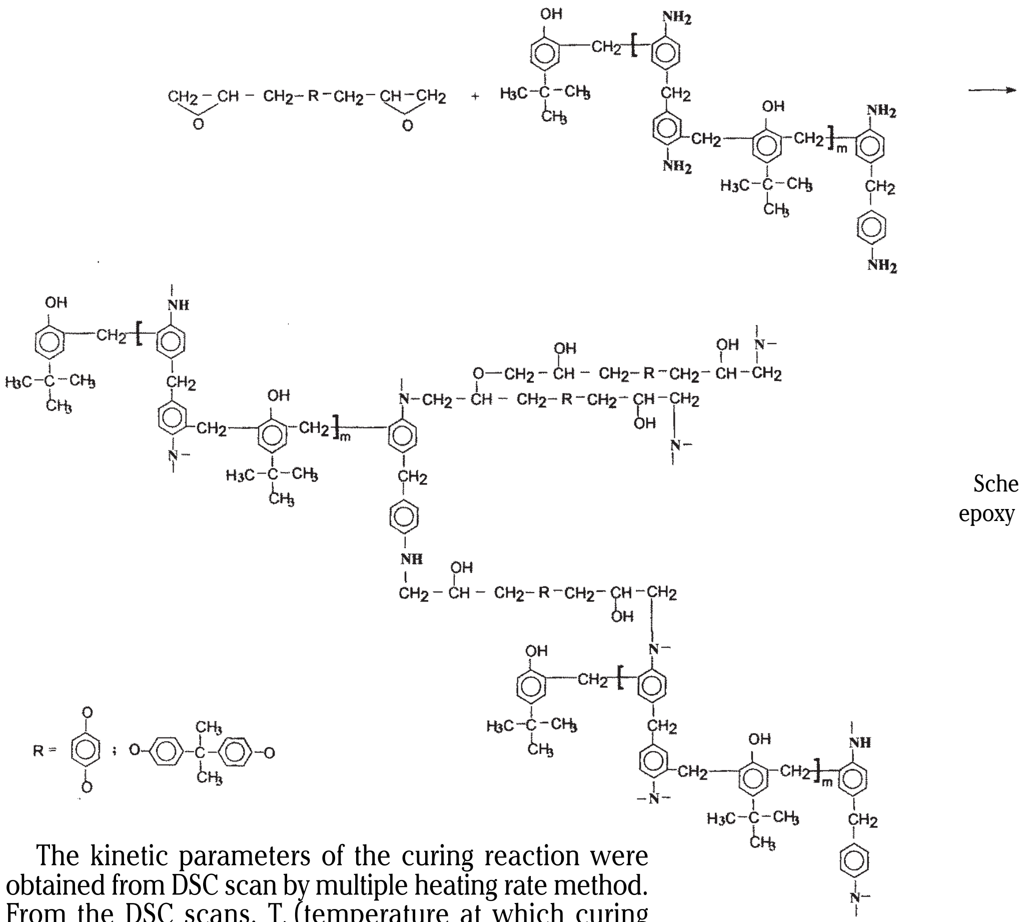
-two vibration bands situated in the range of 3350 and 3225 cm^{-1} which can be assigned to the NH_2 and OH groups;

-a significant signals located in the range of 2865 to 2956 cm^{-1} assigned to the CH_2 and CH_3 groups presented in the tert-butyl groups and between the aromatic ring;

- three sharp intense bands at 1515, 1610 and 1660 cm^{-1} which can be assigned to the aromatic ring;

-a sharp intense band situated at 815 cm^{-1} specific to para substituted aromatic ring.

The structure was also confirmed by high resolution ^{1}H-NMR spectra of the FRs. Figure 2 (^{1}H-NMR spectrum) shows some important peaks centered in the range of 1.05-1.311 ppm chemical shift which represents the tertiary butyl groups linked to the aromatic rings. The methylene bridges located between the aromatic rings specific to formaldehyde resins are observed in the range of 2.82-2.90 ppm chemical shift. The primary amine protons from MDA moieties appear at 3.58-3.78 ppm. The phenol OH hydrogen from the TBPH moieties are situated in the range of 4.10 to 4.23 ppm chemical shift. The weak bands situated in the range of 5.12-5.34 ppm can be attributed to a small percentage of unreacted CH_2OH groups. Major signals as a large complex pattern were observed in the domain of 6.65-7.22 ppm and can be attributed to the aromatic protons situated in the aromatic rings of MDA or *p*-TBPH. The minor signals observed at 8.56 and 9.14 ppm chemical shift can be attributed to the aromatic protons of MDA located in orto position to nitrogen substituent. The chemical reactions which took place in the synthesis of the cured products and their possible structure are presented in scheme 2. The reaction between the epoxy ring and the amine protons has a complex mechanism and it is autocatalytic in nature. In the first step, the primary amine protons react with the epoxy ring and produce a secondary amine group and a secondary hydroxyl group. In the second step, the amine secondary protons react with another epoxy ring and produce the tertiary amino groups, new hydroxyl group and the crosslinked resins. In the IR spectrum (fig 1b) the absence of the peaks at 910-915 cm^{-1} (specific to the oxirane ring) and the presence of the signal situated at 3429cm^{-1} (specific to OH groups) suggest that the polymerization reaction took place.



Scheme 2. The curing reaction of epoxy resins with the MDA/*p*-TBPH / formaldehyde resins

The kinetic parameters of the curing reaction were obtained from DSC scan by multiple heating rate method. From the DSC scans, T_i (temperature at which curing started), T_M (the exothermic temperature peak), T_f (temperature at which cured was completed) were observed. In figure 3 the typical examples of DSC thermograms for DGEBA/ formaldehyde resins at 10 °C × min^{-1} heating rate are presented. The activation energy of the curing reaction and the pre-exponential factor were calculated using Kissinger and Ozawa method by assuming the following equations [28, 29]:

$\ln(\beta \times T_M^{-2}) = E_a/RT_M - \ln(AR/E_a)$ (Kissinger equation) (1)
and
$\ln\beta = -0.4567(E_a/RT_M) + C$ (Ozawa equation) (2)

where:
A is the pre-exponential factor;
β - the heating rate;
C - a constant;
E_a - the activation energy for the curing reactions;
T_M - the peak exothermic temperature;
R - the gas constant.

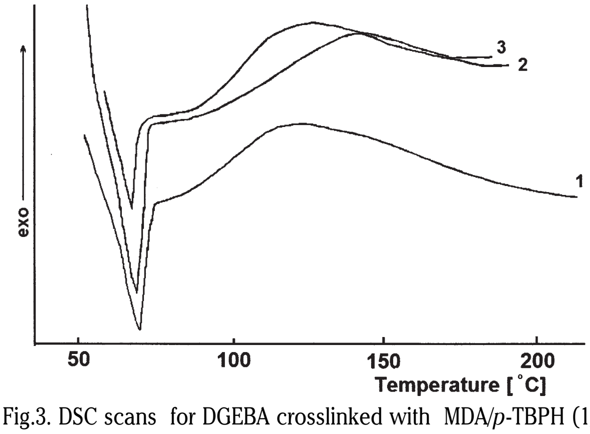


Fig.3. DSC scans for DGEBA crosslinked with MDA/*p*-TBPH (1/1) at (1) 5°C×min^{-1}; (2)10°C×min^{-1}; (3)15°C×min^{-1}

From the graph lnβ versus 1/T and $\ln(\beta \times T_M^{-2})$ versus 1/T, the energies of curing and the pre-exponential factor were obtained (table 2 and 3). These data show that for all systems, the maximum peak temperature is shifted to greater values with the increase of the heating rate and depends on the epoxy resin type. The data are presented in table 2 and 3 and show that the temperature at which the cure started is relatively lower for the DGEHQ systems in comparison with DGEBA systems. This can be attributed to the fact that DGEHQ has a lower molecular weight than DGEBA and the DGEHQ/FRs systems become homogeneous at lower temperature in comparison with the DGEBA/FRs systems. The T_M dimensions reveal that they depend on the type of epoxy resins, having minimum values for DGEHQ/FRs systems. As it can be seen from figure 3, DGEBA/FRs systems present a single large exothermic peak for each system. This fact may lead to the conclusion that the chemical reactions of the primary and secondary amine protons with epoxy ring occur simultaneously and can be explained by the small mobility of FRs (with great dimensions). The activation energy of the curing reactions is situated in the range of 52-72 kJ×mol^{-1}, depending on the chemical structure of FRs hardener and epoxy resins, in agreement with the data reported in literature [32-35]. The influence of FR structures on the thermal properties of the cured epoxy resin was also examined. The TGA curves and the main thermal parameters for the FRs and for the cured polymers are shown in tigures 4 and 5 and in tables 4 and 5. The relative thermal stability of the formaldehyde resins and of the cross-linked resins is estimated using TG parameters (T_{10}-temperature at 10% weight loss, T_{50}-temperature at 50% weight loss, WL_{500} - weight loss at 500° C), the activation energies of decomposition and the pre-exponential factor

Table 2
THE KINETIC PARAMETERS FOR DGEBA CURED WITH FORMALDEHYDE RESIN FROM DSC SCANS
(MOLAR RATIO EPOXY GROUP/AMINE PROTON=1/1)

Formaldehyde resins (molar ratio of monomers MDA/p-TBPH/p-FA)	Heating rate (^{o}Cxmin^{-1})									Activation energy of curing reaction (kJxmol^{-1})		Pre-exponential factor (min^{-1})
	5			10			15					
	T_I	T_M	T_F	T_I	T_M	T_F	T_I	T_M	T_F	Ozawa	Kissinger	Kissinger
Blank test a)	78	130	235	83	140	231	77	155	260	61.33	54.78	4.09
1/2/3	54	126	216	65	142	236	75	156	239	52.45	45.56	1.69
1/1/2	48	121	203	59	135	223	68	143	227	66.41	61.08	6.25
2/1/3	44	115	198	55	121	219	64	135	221	63.08	56.77	5.45

T_I - initial temperature ^{o}C;

T_M - maximum peak temperature ^{o}C;

T_F - final temperature, ^{o}C.

a) DGEBA/MDA

Table 3
THE KINETIC PARAMETERS OF DGEHQ CURED WITH FORMALDEHYDE RESIN FROM DSC SCANS
(MOLAR RATIO EPOXY GROUP/AMINE PROTON=1/1)

Formaldehyde resins (molar ratio of monomers MDA/p-TBPH/p-FA)	Heating rate (^{o}Cxmin^{-1})									Activation energy of curing reaction (kJxmol^{-1})		Pre-exponential factor (min^{-1})
	5			10			15					
	T_I	T_M	T_F	T_I	T_M	T_F	T_I	T_M	T_F	Ozawa	Kissinger	Kissinger
Blank test a)	71	123	225	73	141	231	78	148	255	58.93	52.29	3.67
1/2/3	49	121	210	61	139	231	71	150	235	54.68	47.81	2.49
1/1/2	48	115	203	59	125	223	68	140	227	57.08	50.34	3.63
2/1/3	43	107	194	55	117	220	63	128	224	72.21	60.34	6.93

T_I - initial temperature ^{o}C;

T_M - maximum peak temperature ^{o}C;

T_F - final temperature, ^{o}C.

a) DGEHQ/MDA

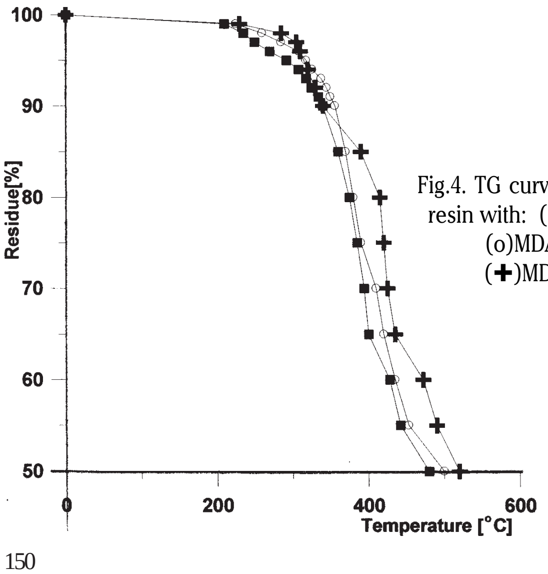


Fig.4. TG curves for formaldehyde resin with: (■)MDA/*p*-TBPH 1/2; (o)MDA/*p*-TBPH 1/1; (✚)MDA/*p*-TBPH 2/1

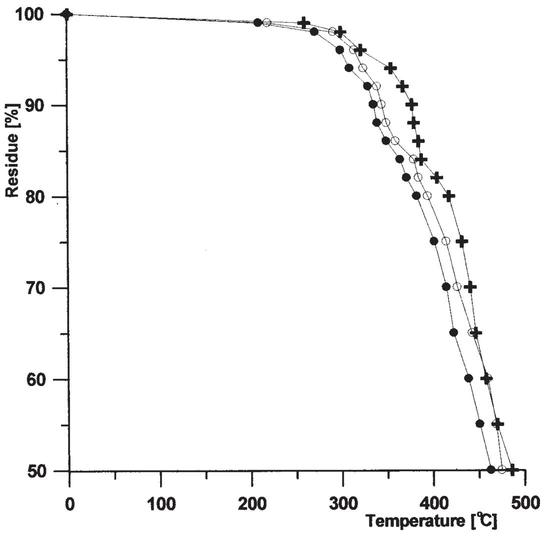


Fig.5. TG curves for formaldehyde resin with: (✚)MDA/*p*-TBPH 1/2; (O)MDA/*p*-TBPH 1/1; (■)MDA/*p*-TBPH 2/1

Table 4
THE THERMAL PARAMETERS OF FORMALDEHYDE RESINS

Sample	Formaldehyde resins (molar ratio of monomers) MDA/p-TBPH/p-FA	Temperature (^{o}C), at which weight loss is equal to:		Weight loss at 500^{o}C (%)	Reaction order	Decomposition activation energy (kJxmol^{-1})	
		10%	50%		Coats and Redfern	Swaminathan and Modhavan	Coats and Redfern
1	2/1/3	340	520	47	1.1	55.97	56.20
2	1/1/1	356	500	50	0.2	40.18	43.21
3	1/2/3	340	480	55	0.15	49.5	50.12

Table 5
THE THERMAL PARAMETERS OF EPOXY RESINS CROSSLINKED WITH FORMALDEHYDE RESINS

Epoxy resin crosslinked with formaldehyde resins (molar ratio of epoxy ring/amine proton	Temperature (^{o}C), at which weight loss is equal to:		Weight loss at 500^{o}C (%)	Reaction order	Decomposition activation energy (kJxmol^{-1})	
	10%	50%		Coats and Redfern	Swaminathan and Modhavan	Coats and Redfern
DGEBA/ Sample 1 Table 1 (1/1)	335	463	60	0.3	59.54	57.64
DGEBA/ Sample 2 Table 1 (1/1)	345	475	57	1.1	65.19	64.49
DGEBA/ Sample 3 Table 1 (1/1)	378	486	55	0.8	57.21	55.98
DGEHQ/ Sample 1 Table 1 (1/1)	273	455	63	0.8	42.53	40.54
DGEHQ/ Sample 2 Table 1 (1/1)	285	460	61	0.9	38.54	36.55
DGEHQ/ Sample 3 Table 1 (1/1)	305	450	62	0.85	36.32	34.27

(estimated with Swaminathan & Modhavan and Coats & Redfern methods) [30, 31]. The general equations are used:

$$d\alpha/dT = A \exp(-E_a/RT)[\alpha^m (1- a)^n] [-\ln (1- \alpha)^p] \quad (3)$$

and

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

where:

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

Accepting T_{10}, T_{50}, WL_{500} as criteria of thermal stability, DGEBA/FRs systems can be considered relatively more stable in comparison with DGEHQ/FRs systems. These observations may be explained on the basis of the molecular mass of DGEBA, which confer a higher rigidity of the crosslinked polymers. The thermal stability of the cured products is relatively similar for all the systems with FR as hardener and the activation energy of decomposition is situated in the range of 36-65 k J/mol.

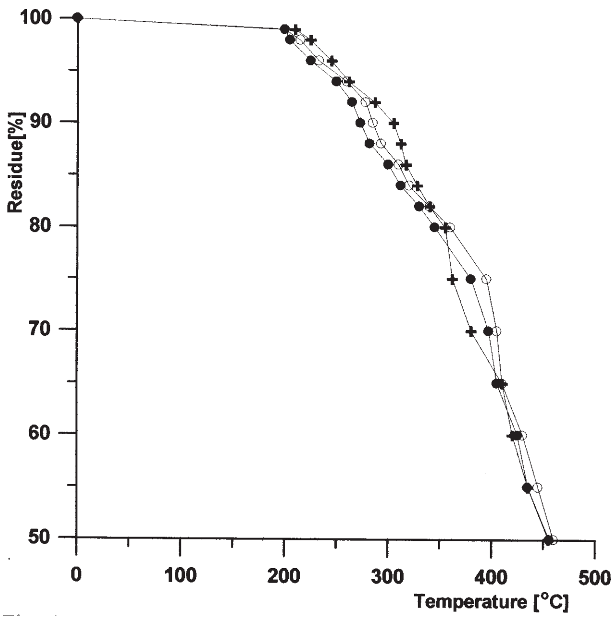


Fig.6. TG curves for DGEHQ cured with formaldehyde resin with: (✚)MDA/*p*-TBPH 2/1; (o)MDA/*p*-TBPH 1/1; (▪)MDA/*p*-TBPH 1/2

Conclusions

The new MDA/p-TBPH formaldehyde resins obtained in acid catalysis at various molar ratios of monomers were characterized by IR, H-NMR spectroscopy and elemental analysis. These resins were used as hardener for epoxy resins because they have NH_2 groups into the main chain. The apparent energies for the curing reactions were situated in the range of 52-72 $kJ\times mol^{-1}$ depending on the chemical structure of the two compounds. The formaldehyde resins and the cured products present a good thermal stability, the apparent energies for thermal degradation for cured products having values situated in the range of 36-65 $kJ\times mol^{-1}$.

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