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Curing and thermal properties of novolak epoxy resins

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Formaldehyde resins at various molar ratios of monomers p-aminophenol/cyclohexanone/p-nonylphenol/p-formaldehyde (p-AP/CH_x/p-NF/p-FA) under acid catalysis have been obtained. The resulted resins were reacted with a large excess of epichlorohydrin and transformed in a multifunctional novolak epoxy resins. These resins were characterized by ^{1}H-NMR, infrared spectroscopy and elemental analysis. The curing and thermal behaviour of these epoxy resin/ DDM 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 54-75 kJ/mol. The cured products have good thermal properties, and activation energies of degradation reactions have values between 32 to 52 kJ/mol.

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1. Introduction

In recent years, owing to their properties including good processability, good chemical and thermal resistance, superior electrical and mechanical behaviour in addition with good adherence to many substrates, both formaldehyde resins and epoxy resins have been widely used as engineering macromolecular compounds in aeronautic and naval industry, military and civilian applications, electric and electronic industry and so on. [1-6] Unfortunately, these resins after crosslinking are relatively brittle. Modification of the chemical structure of these resins has been recently paid much attention with the aim of to enhancing the physical-chemical properties of these cured resins and multifunctional epoxy and epoxy novolak were synthesized because this type of structure offers many possibilities for modification and preparing of products with a large variety of physico-chemical properties [7-19].

The aim of the present study is the synthesis of multifunctional resins which contain epoxy units as pendant groups on the novolak resins. The presence of ether, nitrogen and propyl moiety in chemical their structure is also expected to impart additional degrees of flexibility of crosslinked resins.

2. Experimental

2.1. Materials

p-Amino phenol (p-AP), cyclohexanone (CH_x), epichlorohydrin (ECl), diamino-diphenylmethane (DDM), hydrochloric acid (HCl, 35%), sodium hydroxide (NaOH), were analytical grade reagents and were used as received. Dimethylformamide (DMF), toluene and other solvents were analytical grade products used as received or distilled before use. p-Nonylphenol (p-NP) (d^{15} =0.955 $g\cdot cm^{-3}$; n_D^{20} =1.511) and p-formaldehyde (p-FA) (98% purity) were obtained from commercial sources and were used as received.

2.2. Measurements

The chemical structure of obtained resins was identified using IR (Specord M80, Carl Zeiss, KBr disk), ^{1}H-NMR (JEOL-JNMC 60HL, Japan, $CDCl_3$ as solvent, tetramethylsilane as internal standard, room temperature) and elemental analysis (nitrogen content, Kjeldhal method) [20]. The epoxy equivalent weight was recorded using the literature method and was expressed in $g\cdot eq^{-1}$[7]. Thermogravimetric study was done with a MOM-Budapest derivatograph of Paulik-Paulik Erdey type, in air at a heating rate of 10 °C·/min and temperature range of 25-600 °C. The relative thermal stability of the formaldehyde resins and cured epoxy resins was estimated by comparing TG parameters such; the activation energy of the degradation process with equations of Coats-Redfern and Swaminathan-Modhavan) and T_{10} (temperature for 10% weight loss), T_{50} (temperature for 50% weight loss), weight loss at 500°C(WL_{500}). [21,22]. The literature equations used are:

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

and

$$d\alpha/dT = A\exp(-E_a/RT)[\alpha^m (1-\alpha)^n][-\ln(1-\alpha)^p] \quad (2)$$

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, β is the heating rate, 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 and R is the gas constant. DSC studies were performed using a Mettler 12E apparatus. All experiments were obtained in nitrogen atmosphere (3 $l\cdot min^{-1}$) between 30 to 400 °C at various heating rate (5, 10, 15 ^{o}C· min^{-1}). Kinetic parameters for the curing reactions were estimated using Kissinger and Ozawa methods [23,24].

2.3. Curing procedure

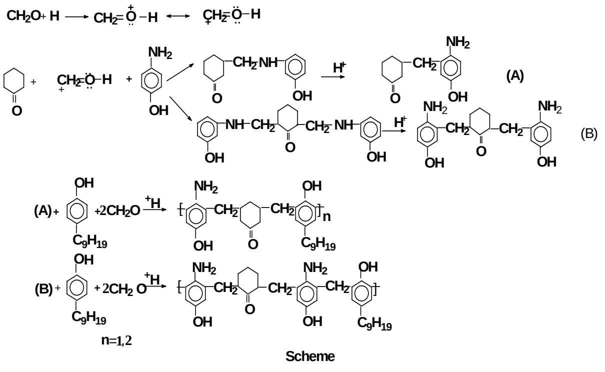
The multifunctional epoxy resins were powdered as fine grain and were mixed with corresponding DDM as hardner at molar ratio r = 1 where “r” is epoxy ring group/amine hydrogen, in presence of 15% chloroform, and placed in an aluminium mould. Then, the mixture was introduced in a vacuum oven at 60 ^{o}C and maintained there for 20minutes to remove residual chloroform. A small quantity of sample was taken for DSC studies. The remaining mixture wse cured at 120 ^{o}C for 2 hours, 2 hours at 140 ^{o}C and post cured at 200 ^{o}C for another 4 hours. Finally, the cured products were powdered and used for TGA studies.

2.4. Synthesis of multifunctional epoxy resins

The synthesis of multifunctional epoxy resins was a two-step process: synthesis of novolak formaldehyde resin and epoxidation to epoxy novolak resins.

2.4.1. Synthesis of formaldehyde resins

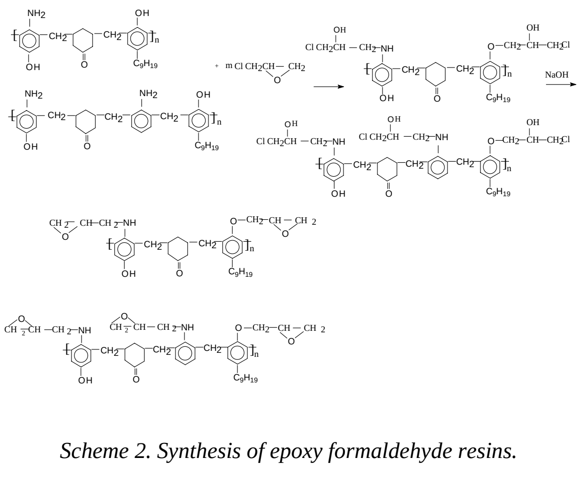
The novolak type resin was prepared by a standard procedure used in the synthesis of formaldehyde resins, at different molar ratio of monomers (p-AP/CH$_x$/p-NF), at molar ratio 1/1 for monomers/formaldehyde, in the presence of 3% (w/w, based on the weight of reactants) hydrochloric acid as catalyst. Reaction conditions and some physical-chemical characteristics are presented in Table 1. In a representative experiment (Sample 1, Table 1), a 0.5L four-necked round-bottomed flask equipped with thermometer, mechanical stirrer, water condenser and heating mantle was charged with 10.8g (0.1 mol) p-AP, 19.6g (0.2mol) CH$_x$, 6g (0.2 mol) p-FA, and were mixed at room temperature. Then, the mixture was heated slowly at 70^{o}C and the catalyst was added in three portions in 15 minutes. As a consequence, the mixtures become transparent and an exothermal effect was observed (Δt=12 ^{o}C). Then, the temperature was raised to the reflux under stirring and maintained at this level for 1 h. To the resulting mixture, 22g (0.1mol) p-NP and 6g (0.2 mol) p-FA were added and cooled at 70 ^{o}C, when the catalyst was added. The exothermal effect is not observed and the reaction mass was heated at reflux for 1 h when over the reaction mass, 50 mL of DMF/toluene (1/1, v/v) was added and a Dean-Stark separator was attached to the top of the water condenser. During the reaction (2h), the generated water was extracted as toluene azeotrope and the final reaction temperatures increased at 150^{o}C. Finally, DMF, toluene and water were evaporated under high vacuum and the resin was poured in an aluminium mould, cooled, broken as fine grain and extracted twice with warm distilled water (Scheme 1).



Scheme 1. Synthesis of formaldehyde resins

2.4.2. Synthesis of epoxy resin from formaldehyde novolak resins

0.1 equivalent of formaldehyde resin obtained as above and 1mol of ECl were introduced into a 0.5 L four-necked round–bottomed flask, equipped with water bath, thermometer, mechanical stirrer and dropping funnel, and dissolved at room temperature. Then, the solution was heated at 80-85^{o}C, kept at this level for 7h and cooled at 55 ^{o}C when 0.2 mol of a 50 wt-% aqueous sodium hydroxide solution was added to the resultant solution, dropwise under vigorous stirring, over a period of 6h. After sodium hydroxide completion the reaction mass was maintained at 60 ^{o}C for additional 1h. The resulted mixture was filtered from residual sodium chloride, washed twice with distilled water, under vigorous stirring, and decanted. Finally, the organic layer was distilled under high vacuum. The resulting mass was powdered, extracted with methanol and dried under vacuum at 60 ^{o}C overnight. (Scheme 2)



Scheme 2. Synthesis of epoxy formaldehyde resins.

Table1. Reaction conditions used on condensation of p-nonylphenol, cyclohexanone, p-aminophenol and formaldehyde and physical characteristics of obtained resins (toluen / DMF v/v, 1/1, 25% as solvent, HCl as catalyst, 3%)

No.	Molar ratio (p-NP/ CHx /p-AP /p-FA/ECl) (mol/mol)	Inherent a) viscosity	Epoxy equivalent weight (experimental) ($g\cdot eq^{-1}$)	Colour	Number b) average molecular weight	N (%)	Melting point (^{o}C)
1	1/2/1/4/0	0.13	-	pale brown	1160	2.43	82
2	1/1/1/3/0	0.12	-	pale brown	980	2.90	75
3	2/1/1/4/0	0.16	-	pale brown	1400	2.03	71
4	1/1/2/4/0	0.14	-	brown	1050	5.35	87
5	1/2/1/4/4	-	385	brown	-	2.10	56
6	1/1/1/3/4	-	350	brown	-	2.22	54
7	2/1/1/4/5	-	267	brown	-	1.66	50
8	1/1/2/4/7	-	230	brown	-	3.91	61

a) DMSO as solvent, c = 0.5w/w, 25^{o}C
b) cryoscopic method, DMSO as solvent

Table 2. Kinetic parameters of epoxy novolak resins cured with DDM from DSC scans (molar ratio epoxy group/amine proton =1/1).

No	Molar ratio ($p\text{-}NF/CH_x/p\text{-}AP/p\text{-}FA/ECl/ DDM$) (mol/mol)	Heating rate ($^{o}C/min$)			Activation energies of curing reactions (kJ/mol)	
		5	10	15	E_O	E_K
		T_M	T_M	T_M		
1	1/2/1/4/4/1	130	140	148	75	87
2	1/1/1/3/4/1	140	151	159	67	84
3	2/1/1/4/5/1.25	108	122	130	54	67
4	1/1/2/4/7/1.75	128	138	150	71	84

T_M- maximum peak temperature ^{o}C;
$E_{O,}$ E_K activation energies of crosslinking reaction calculated with Ozawa and Kissinger equation

Table 3. Thermal parameters of crosslinked epoxy novolak resins.

No	Molar ratio ($p\text{-}NF/CH_x/p\text{-}AP/p\text{-}FA/ECl/DDM$) (mol/mol)	Temperature corresponding to 10 % (T_{10}) and 50% (T_{50}) weight loss (^{o}C)		Weight loss at 500^{o}C (WL_{500}) (%)	Decomposition activation energy (kJ/mol		Reaction a) order	Pre- b) exponential factor lnA (min^{-1})
		T_{10}	T_{50}		E_C	E_S		
1	1/2/1/4/4/1	310	560	42	49	50	1.4	8.74
2	1/1/1/3/4/1	375	600	32	32	34	1.2	6.28
3	2/1/1/4/5/1.25	300	485	55	47	49	1.35	8.34
4	1/1/2/4/7/1.75	325	530	45	51	52	1.45	9.04

a) $E_{c,}E_s$, activation energies of decomposition reaction calculated with Coats and Swaminathan equation
b) calculated with Swaminathan equation

3. Results and discussion

The chemical reactions involved in these syntheses and the main characteristics of obtained resins are presented in Scheme 1 and 2 and in Table 1 and 2.

3.1. Synthesis of formaldehyde resins

The novolak type resins were prepared under acid catalysis. In the first stage of the reaction, p-AP, p-FA and CH_x react with acidic protons and form mono or bis base Mannich [25,26]. (Scheme 1, A, B component). In the second step, in the presence of p-nonylphenol the base Mannich, reacts with formaldehyde and forms methylol groups. Under the action of the temperature the methylol groups split off water and rearrange into methylene bridges between aliphatic and aromatic rings and formaldehyde resins were obtained. The obtained resins are solid, brittle, brown colour and soluble in polar organic solvents and insoluble in aliphatic solvents. IR, 1H-NMR and elemental analysis confirm a possible structure of these resins. The IR spectra (Fig. 1) show a broad absorption band in the range of 3400-3450 cm^{-1} specific to OH and NH_2 groups presented in p-NP and p-AP. In the range of 2880-2970 cm^{-1} appears the band specific to the CH_2 and CH_3 groups located both in cyclohexanone and nonyl aliphatic substitute and in the methylene bridges specific to formaldehyde resins. The vibration specific to carbonyl group (at 1720 cm^{-1}) located in cyclohexanone ring is also present. The peaks presented in the range of 1660-1625 cm^{-1} and at 1525 cm^{-1} is frequent assigned to aromatic ring. In the range of 840 cm^{-1} and at 760 cm^{-1} appear the peaks specific to para substituted benzene. In the IR spectra of epoxy formaldehyde resin (Fig. 2, Sample 5, Table 1) in the range of 850 and 915 cm^{-1} appear the peaks specific to epoxy ring and in the range of 1150 to 1260 cm^{-1} are located the peaks specific to ether groups which appear as a consequence of reaction between ECl and Oh groups. In the ^{1}H-NMR spectra, the major signals attributable to aliphatic protons from cyxclohexanone and nonyl structure appear in the range of 0.875-2.15 ppm chemical shift. The CH_3 protons assigned to methyl groups are presented in the range of 0.9 ppm chemical shift while the protons assigned to CH_2 from nonyl moieties are presented in the range of 1.2-1.7ppm chemical shifts. The CH_2 protons assigned to CH_2 groups located in cyclohexanone ring in the neighborough of CO group are in the range of 1.7-1.8 and 2.25 ppm chemical shift while the CH_2 groups that are not adjacent to the keto group are presented in the range of 2.15-2,25ppm.

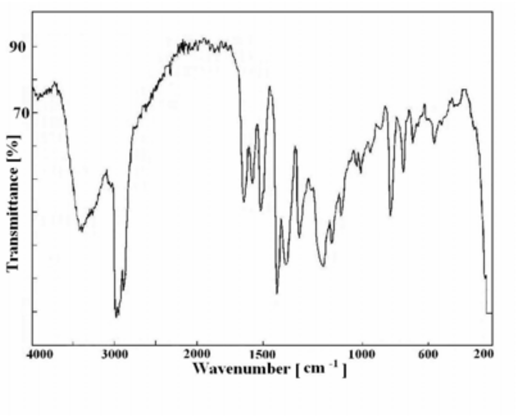


Fig.1. IR spectra for formaldehyde resin at molar ratio (p-NP/CH_x/p-AP),1/2/1.

For the methylene bridges between aromatic and aliphatic rings, the peak appears at 3. 85 ppm chemical shift. The aromatic protons located in p-AP and p-NP are represent as a broad peak in the range of 6.76-7.12 ppm chemical shift.

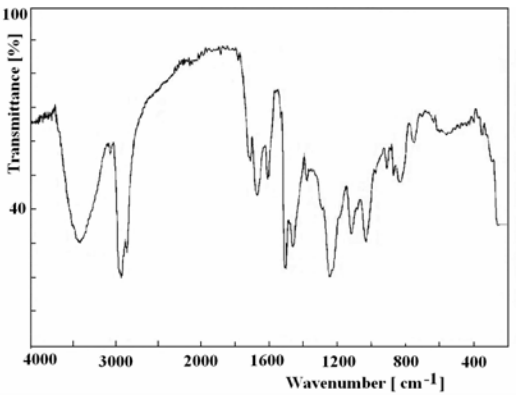


Fig. 2. IR spectra for epoxy formaldehyde resin at molar ratio (p-NP/CH_x/p-AP/ECl) 1/2/1/4.

3.4. Thermal properties of the resins

The reaction between amine protons and epoxy ring is autocatalytic in nature and involves a complex mechanism [27,28]. The possible reactions are presented in Scheme 2. In the first step, at low temperature, amine protons react with epoxy ring and appear a secondary amine group and tertiary OH group. In the second step, the amine secondary proton reacts with another epoxy ring, a new tertiary OH group appears and crosslinked polymers are produced. The first and second steps have same reaction rate, but with the increase of temperature, it is possible that the epoxy ring to react with tertiary OH group and form ether linkage. These reactions led to high crosslinked structure. Information about chemical kinetics of polymerization and about crosslinked reaction were obtained from DSC technique. Some of the DSC results are shown in Table 2. From the DSC scans, the T_M (the maximum exothermic temperature peak) was used to calculate the energies of curing reaction. The presence of only one peak temperature in these systems indicates that the activation energy for initial polymerization process and for crosslinking reaction are equally the processes being developed in the same temperature range. The data presented in the Table 2 show that the T_M has different values and depends of chemical structure of epoxy resins. All the tested data showed a decrease of T_M with the increase of p-NP, and can be explained by the great mobility induced by nonyl moieties. The activation energy of curing reaction has values situated in the range of 54 to 75 kJ/mol, depending on chemical structure and are in agreement with literature data. [29-31]. The thermal stability of crosslinked resins was evaluated by the thermogravimetric analysis. (TGA). TGA data and the main parameters of degradation process, obtained in air atmosphere are shown in Fig. 3 and Table 3. The activation energy and the pre-exponential factor were obtained by applying the equation 1 and 2 [21,22]. The activation energies were calculated by both equations and have similar values. In odder to estimate the relative thermal stability, activation energy and TG parameters such as T_{10} (temperature for 10% weight loss), T_{50} (temperature for 50% weight loss) and weight loss at 500 ^{o}C(WL_{500}) were measured. Accepting $T_{10,}$ T_{50} and WL_{500} as the criteria of relative thermal stability, the ordering of thermal stability is Sample 2> Sample1 > Sample4 > Sample 3. As can be seen in Table 3, activation energy of thermal degradation process has a values situated in the range of 32 to 51 kJ/mol. These values are comparable with literature data for crosslinked novolak epoxy resins [15,18-32,33].

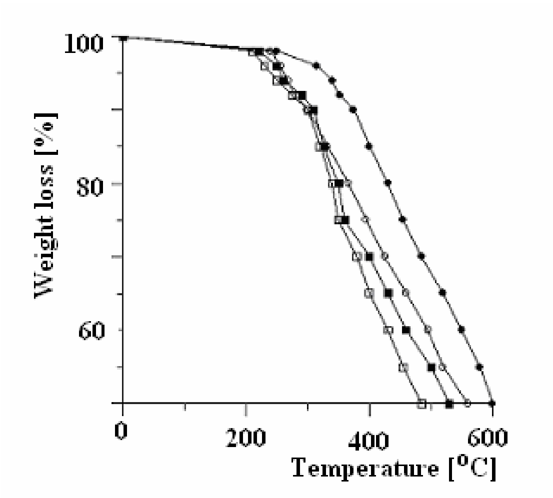


Fig. 3. TG curves for cured epoxy formaldehyde resin with DDM: (●) p-NP/CH_x/p-AP 1/2/1; (○)p-NP/CH_x/p-AP 1/1/1; (□)p- NP/CH_x/p-AP 2/1/1; (■)p-NP/CH_x/p-AP 1/1/2.

4. Conclusion

Polymers based on epoxy novolak resins were designed to polymerize in presence of catalyst without the formation of voids. The thermal study indicates these polymers present a relatively good thermal stability. The activation energy for thermal degradation of crosslinked resins has values situated in the range of 32 to 52 kJ/mol.

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