JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 2, April 2006, p. 871 - 875

P-aminobenzoic acid/cyclohexanon/ formaldehyde resins as hardner for epoxy resins. Synthesis and characterization

F. MUSTATA[*], I. BICU
Institute of Macromolecular Chemistry "P. PONI", Aleea Gr. Ghica Voda 41A, 700487, Iasi, Romania

New formaldehyde resins with p-aminobenzoic acid and cyclohexanone that contain functional groups in structure were obtained at various molar ratios under acid catalysis. Mixture of DMF/toluene was used as reaction medium and as carrier for aqueous condensation. These polymers were characterized by IR, ^{1}H-NMR spectroscopy and elemental analysis. The obtained resins have low molecular weight and are soluble in medium and high polar solvents. Using these formaldehyde resins as hardener, the curing behaviours of some epoxy resins were investigated. The activation energies and the curing temperatures were studied by DSC using Ozawa and Kissinger methods. The thermal properties of cured product were also investigated.

(Received October 14, 2005; accepted March 23, 2006)

Keywords: Formaldehyde resins, Epoxy resins, Curing behaviour

1. Introduction

Because of their well-balanced properties including excellent heat, moisture and chemical resistance, superior electrical and mechanical properties and good adhesion to fibers and metal substrates, epoxy resin after crosslinking are widely used as composite matrices or as structural adhesives in numerous industrial applications including aero and hydrospace, car industry, electric industry, medicine and so on [1-3].

However, the conventional epoxy resins are inefficient to satisfy the requirement properties in special in the field of advanced materials of electronic devices. A viable alternative is to design the special polymers which to contain reactive groups on the polymeric chain and use of this as hardener for epoxy resins. The final properties of the crosslinked products will have high glass transition temperatures and low moisture absorption.

In the last years, a great deal of the efforts of the researchers has been extended to the introduction of a reactive functionality into polymeric structure (OH, NH_2, maleimide, epoxy groups), which could as sites for crosslinking [4-17].

The present paper describes the synthesis and characterization of formaldehyde resins of novolak type obtained from p-aminobenzoic acid and cyclohexanone, which present NH_2 and COOH groups of polymeric chain. The properties of the final product obtained from formaldehyde resin crosslinking of epoxy resins with this formaldehyde resins as hardener, were also investigated.

2. Experimental

2.1. Materials

Cyclohexanone (CH_x)(98% purity, Chimopar, Romania), p-aminobenzoic acid (p-ABA)(99% purity, Aldrich), hydrochloric acid (HCl)(35%, Chimopar, Romania), and organic solvents were chemical pure reagents and used as received or were purified by distillation. p-Formaldehyde resin (98% purity) was a commercial product and used without further purification. Diglycidylether of bisphenol A (DGEBA) was a commercial product (Sintofarm SA Romania) with epoxy equivalent weight of 190 $g\cdot eq^{-1}$ and was used as received.

2.2. Measurements

Nitrogen content (N%) was obtained according to Kjelhaldl method [18]. The epoxy equivalent weight was determined using pyridinium chloride-pyridine method and expressed in $g\cdot eq^{-1}$ [19]. The relative viscosity in DMSO was measured by means of Ubbelohde viscometer with suspended level at 25 ^oC under preliminary filtration.

Infrared spectra (FT-IR) were recorded using a Bio-Rad DigiLab Division (Portmann Instruments) spectrophotometer on KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on an Avance DRX 400 (BRUKER, Rheinstatten, Germany) at 50 ^oC using tetramethylsilane as internal standard and DMSO-d_6 as solvent. NMR chemical shift were expressed as ppm. Thermogravimetric analyses were obtained using a Paulik, Paulik-Erdey derivatograph type (MOM, Budapest), at heating rate of 10 $^oC\cdot min^{-1}$ in air on the range of 25 to 700 ^oC. The activation energy of decomposition process was calculated using literature equations [20,21]. The glass temperature transition and curing thermal properties were obtained by means of Metller 12E apparatus at 5,10,15 $^{o}C \cdot min^{-1}$ heating rate in nitrogen between 25 to 350 ^{o}C, using indium as standard. The kinetic parameters were obtained using DSC scans and literature equations [22,23]. The moisture absorption was determined by placing the cured disks (20 mm diameter, 1.5 mm thick) in boiling water for 72 h. The disks were removed, cooled to room temperature, dried with paper filter and weighted. The quantities of the absorbed water were determined as the ratio of the weight difference between the weight measurement before and after absorption and the initial weight.

2.3. Curing procedure

DGEBA and corresponding formaldehyde resin as fine grain, at molar ratio r=1, were r= amine and carboxyl protons/ epoxy ring, were mixed under vigorous stirring, at 50 ^{o}C, for 15 minutes. Then, the mixtures were in moved in the aluminum mold and placed in a vacuum oven and maintained at level of temperature 1 h, to remove the air bubbles. Then the mixtures were divided in two parts; one part was cured at 120 ^{o}C for 1 h and at 180 ^{o}C for another 3h and used for TGA analysis and the second part were crosslinked in DSC apparatus.

2.4. Synthesis of p-aminobenzoic acid/ cyclohexanone /formaldehyde resins

The formaldehyde resins containing various molar ratio p-aminobenzoic acid/ cyclohexanone at molar ratio monomers/formaldehyde 1/1 were obtained in presence of HCl (3% based on monomer weight). The mixture of DMF/toluene (1/1 v/v) (40% based on monomer weight) were used as solvent and carrier for the reaction water. The reaction conditions and the main characteristics of the obtained resins are presented in Table 1. A typical synthesis is presented as follows:

Into a 1000-mL, 4-neked round-bottomed reaction flask, equipped with Dean-Stark trap and ascendent condenser, mechanical stirrer, thermometer and oil bath was added 39.26 g (0.4 mol) CH_x, 109.6g (0.8 mol) p-ABA, 24 g (0.8 mol) p-FA and 300 mL of solvents. The reaction mixture was heated under vigorous stirring at 75 ^{o}C and 15mL of HCl were added in four portions in 15 minutes. An exothermic effect (~18 ^{o}C) were observed, the temperatures were raised to reflux and the mixtures becomes transparent. Then, the reaction mass was maintained at reflux, the water was removed under low vacuum as toluene/water azeotrope. As a consequence of the water extraction, the temperature raised continuously up to 150 ^{o}C. Finally, the toluene was extracted and the reaction mass were transferred into 1000 mL of water /ice mixtures. Then, the obtained resins were filtered, broken as fine grain and extracted twice with hot cyclohexane. The resin was filtered and dried under vacuum at 60 ^{o}C over night. The resin of brown color was obtained at yield of 91%.

3. Results and discussion

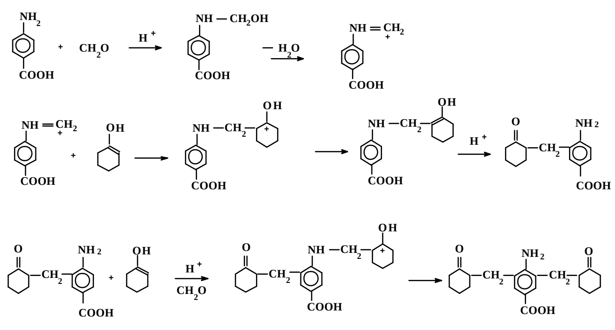
The condensation conditions and the main parameter of obtained resins is presented in Table 1. The obtained resins are solid materials, brittle with colours varying for pale yellow brown for resin with only cyclohexanone in structure to brown for resin with only p-aminobenzoic acid in composition. The probable chemical reactions involved in the synthesis of these resins are presented in Scheme 1. In the first step, in presence of acidic protons from HCl, all chemical reagents react with this. The p-ABA reacts with formaldehyde and becomes and unstable N-methylolic forms which rapidly rearranged in anhydroformaldehyde form by splitting off water. In presence of acidic protons, cyclohexanone becomes an enolic derivative, which react with the anhydroanilinformaldehyde form of p-ABA at double bond and a mono or bis base Mannich were obtained. At molar ratio CH_x/p-ABA>1 is more probable that mono Mannich base to be obtained, and at molar ratio CH_x/p-ABA<1 the bis base Mannich is probable to be obtained. In the second step, in presence of formaldehyde and acidic protons and under effect of the temperature, the mono and bis base Mannich becomes unstable and rearranges into oligomers and polymers with methylene bridges between aromatic and aliphatic rings.

Table 1. Reaction conditions and the main physical characteristics of obtained formaldehyde resins.

Sample	Molar ratio (p-ABA /CHx /p-FA)	Solvent Toluen/ NMP (1/1) (%)	Catalyst (HCl) (%)	Melting point (^{o}C)	Culour	Nitrogen (%)	Relative viscosity a)
1	1/0/1	15	3	125	White opaque	0	1.019
2	1/1/2	15	3	100	pale red brown	2.66	1.023
3	2/1/3	15	3	87	red brown	3.37	1.03
4	1/2/3	15	3	91	brown	6.81	1.029
5	0/1/1	15	3	92	dark brown	10.23	1.040

a) DMSO as solvent, 25 ^{o}C

The possible structures of these polymers confirmed by elemental analysis and IR and ^{1}H-RMN spectroscopy are presented in Scheme 1.



Scheme 1

The IR spectra of these resins are shown in Fig. 1. In the range of 3450-3500 cm^{-1}, a strong absorption band indicates the presence of amino and OH groups present in p-ABA moieties. At 2860-2980 cm^{-1} an intense band specific to CH and CH_2 groups located in cyclohexanone ring and methylene bridges are observed. The peaks specific to CO groups from CH_x and p-ABA are presented in the range of 1730 and 1700 cm^{-1}. The peaks characteristic to para substituted benzene exhibit specific vibrations in the range of 840 cm^{-1} and 760 cm^{-1}.

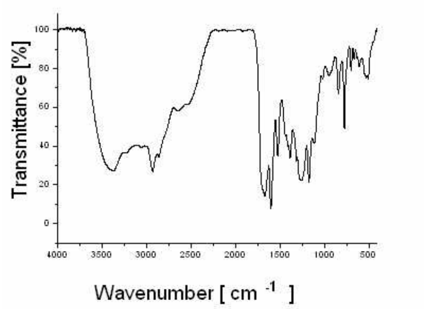


Fig. 1. The IR spectrum of formaldehyde resin at molar ratio ((p-ABA/CHx/p-FA; 1/1/2).

The ^{1}H-NMR spectra (Fig. 2) shows a large unsolved peak centered in the range of 0.9-2.15 ppm chemical shift, which is specific to the CH and CH2 protons of cyclohexanone, ring. The peaks located in the range of 1.5-1.75 ppm chemical shift are specific to CH_2 protons situated in the neighborhood of CO groups and the peaks located in the range of 1.75-2.2 ppm chemical shift is located in another CH and CH_2 groups of cyclohexanone ring. The CH_2 protons which appear in the range of 3.35-4.2 ppm chemical shift can be assigned to the CH_2 bridges between aromatic or/and aliphatic rings an are specific to formaldehyde resins. The minor peak situated in the range of 4.3-5.05 ppm chemical shift can be attributable to the unreacted methylol groups. The protons specific to NH_2 moieties bonded to aromatic ring appear in the range of 5.9 ppm chemical shift. The aromatic protons introduced by p-ABA moieties are present in the range of 6.55-7.76 ppm chemical shift and in the range of 7.95-8.5 ppm chemical shift. The protons specific to carboxylic groups are located as an weak peak in the range of 9.75 ppm chemical shift.

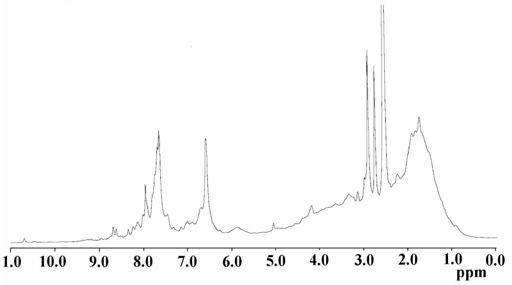


Fig. 2. The ^{1}H-NMR spectrum for formaldehyde resin at molar ratio ((p-ABA/CHx/p-FA; 1/1/2).

In the ^{13}C-NMR spectra (Fig. 3) the characteristic signal attributed to CH_2 group located in cyclohexanone moieties appear in the range of 26-35.83 ppm chemical shift. The signals observed in the range of 38.85-42.32 ppm are characteristic to the DMSO-$_{d6}$ and to the CH_2 groups situated between aromatic or aliphatic ring. The peaks specific to CH groups located in the aromatic ring can be seen in the range of 110-116 ppm. The methylene group linked the aromatic ring is presented in the range of 128-131 ppm. The C-NH_2, C- OH and C=O linkages are presented in the range of 153, 162 and 167.6 ppm chemical shift respectively.

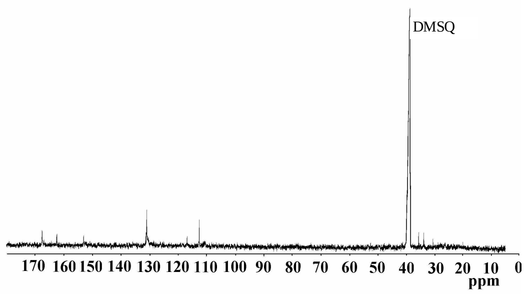
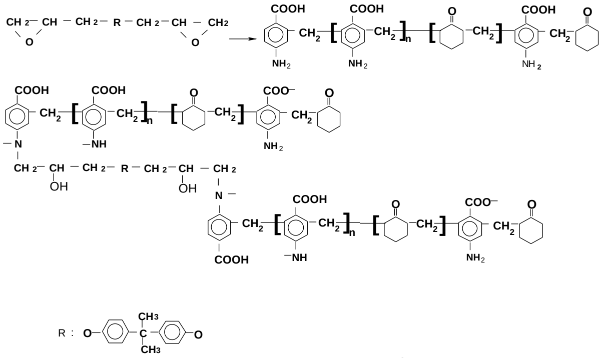


Fig. 3. The ^{13}C-NMR spectrum for formaldehyde resin at molar ratio ((p-ABA/CHx/p-FA; 1/1/2).

Chemical reaction involved in crosslinking reaction between NH_2 and COOH with epoxy ring is presented in Scheme 2. The reaction between epoxy ring and NH_2 and COOH groups are catalytic in nature and involves a complex mechanism [24,25]. In the first step, at medium temperature, NH_2 react with epoxy ring and secondary amine and tertiary OH groups appear. In the second step, secondary amine and COOH groups react with another epoxy ring and ester and tertiary amine groups appear. The presence of the only exothermic peak indicates that the activation energy for linear polymerization and for crossliking reaction is equal and takes place in the same range of temperatures.



Scheme 2

The activation energy for the cured products obtained by crosslinking with formaldehyde resin with more CH_x in structure have high values in comparison with the product obtained with formaldehyde resin which have more p-ABA in composition. This may be due to the fact that the formaldehyde resin with more CH_x in structures has a high rigidity of the polymeric chain. The activation energy of crosslinking reaction has values situated in the range of

54-62 kJ/mol and is comparable with the literature data [25-28].

Table 2. Kinetic parameters of epoxy resin of DGEBA type crosslinked with p-aminobenzoic acid/ciclohexanon/ formaldehyde resin obtained from DSC scans.

Molar ratio (p-ABA/CH$_x$/p-FA	Heating rate (°C/min)			Activating energy of curing (kJ/mol)		Moisture absorption (%)	Glass transition temperature (°C) (a)
	5	10	15				
	T$_M$	T$_M$	T$_M$	Ozawa method	Kissinger Method		
1/1/2	146	160	175	61.99	51.76	1.65	149
2/1/3	130	143	158	56.44	49.46	1.92	155
1/2/3	175	180	205	53.74	46.15	1.55	143

The thermal stability of the formaldehyde resin and crosslinked products was estimated by thermogravimetric analysis (TGA). The main parameter of thermal decomposition and the TGA curves are presented in the Table 3 and 4 and in Fig. 3 and 4.

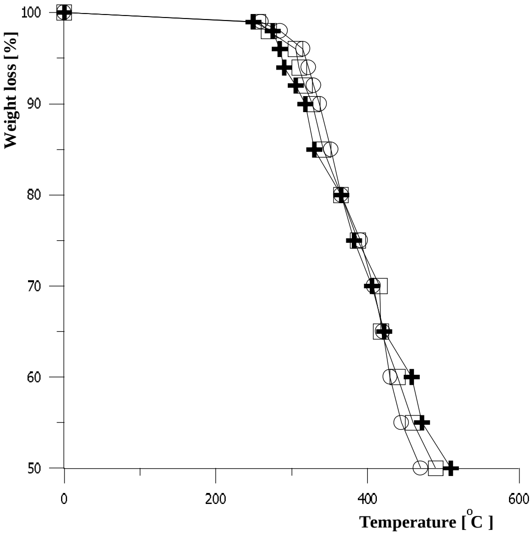


Fig. 4. The main thermal parameters of DGEBA crosslinked with formaldehyde resins: (O)*p-ABA/CH$_x$/p-FA,1/1/2,* (☐)*p-ABA/CH$_x$/p-FA,2/1/3,* (✚)*p-ABA/CH$_x$/p-FA,1/2/3.*

Table 3. The main thermal parameters of DGEBA crosslinked with formaldehyde resins.

Molar ratio (p-ABA/CH$_x$/p-FA)	Temperature corresponding to 10%(T$_{10}$) and 50% (T$_{50}$) weight loss (°C)		Weight loss at 500 °C (%)	Reaction order (Coats and Redfern method)	Moisture absorption (%) a)	Decomposition activation energy (kJ/mol)	
	T$_{10}$	T$_{50}$				Coats and Redfern method	Swaminathan and Modhavan method
1/1/2	337	470	58	1.1	1.47	73.2	70.1
2/1/3	327	490	55	1.05	1.09	66.7	58.9
1/2/3	318	510	48	1.6	1.89	60.1	54.3

a) cured polymer

Table 4. The main thermal parameters of DGEBA crosslinked with formaldehyde resins.

Sample	Molar ratio (p-BA /CH$_x$ /p-FA)	Temperature coressponding to 10%(T$_{10}$) and 50% (T$_{50}$) weight loss (°C)		Weight loss at 500 °C (%)	Reaction order (Coats and Redfern method)	Decomposition activation energy (kJ/mol)	
		T$_{10}$	T$_{50}$			Coats and Redfern method	Swaminathan and Modhavan method
1	1/1/2	337	470	58	1.1	73.2	70.1
2	2/1/3	327	490	55	1.05	66.7	58.9
3	1/2/3	320	510	48	1.6	60.1	54.3

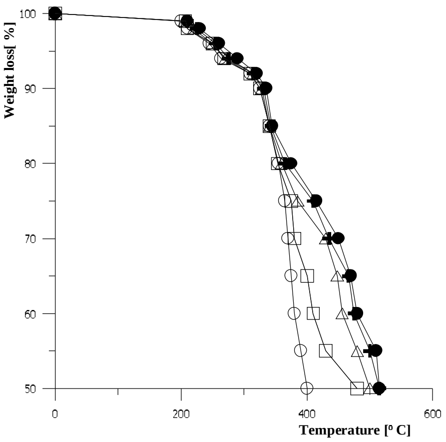


Fig. 5. The main thermal parameters of formaldehyde resins: (●) *p-ABA/CH_x/p-FA 1/0/1;* (O) *p-ABA/CH_x, 0/1/1;* (△) *p-ABA/CH_x/p-FA,1/1/2;* (✚) *p-ABA/CH_x/ p-FA,2/1/3;* (☐) *p-ABA/CHx/p-FA,1/2/3.*

The activation energy and the kinetic parameters of degradation process were calculated using Coats and Redfern and V.Swaminathan, N.S. Modhavan, equations. Accepting T_{10} (temperature for 10% weight loss), T_{50} (temperature for 50 % weight loss) weight loss at 500 ^{o}C and the activation energy of the degradation process as the criteria of the relative thermal stability, we can consider that the crosslinked product with formaldehyde resin with high content of CH_x are more stable in comparison with the product obtain by crosslinking with formaldehyde resin with p-ABA in structure. The ordering by thermal stability is Sample 3>Sample 2> Sample 3. The activation energy of degradation process of formaldehyde resin and crosslinked products are situated in the range of 29-35 kJ/mol and between 60-73 kJ/mol. The moisture absorption of cured multifunctional formaldehyde resins are presented in Table 3. The crosslinking reaction between formaldehyde resins and epoxy resin produced by ring opening a large number of OH groups. The resins that contain a low content of p-ABA exhibited little moisture absorption as a consequence of the fact that the polymer with low p-ABA content has a little amount of OH groups and are thus less hydrophilic in nature.

4. Conclusions

The formaldehyde resins, which contain NH_2 and COOH groups on polymeric chain, were obtained in acid catalysis. Using these resins as hardner for epoxy resins, the obtained crosslinking products present high glass temperature transition and low moisture absorption. These values suggest that the croslinked products can be used in the field of advanced materials. The apparent energy for crosslinking process was situated in the range 54-62 kJ/mol and is similar with the values presented in literature data [26-29]. The crosslinked products have good thermal stability and the apparent energy of degradation process have value situated in the range 60-73 kJ/mol.

References

[1] H. Lee, K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York (1972).
[2] C. D. Wright, J. M. Muggee, "Epoxy Structural Adhesives" in: "Structural Adhesives, Chemistry and Technology", S. R. Hartson Ed., Plenum Press, NewYork (1986).
[3] H. Lee, K. Neville, Encyclopedia of Polymer Science and Technology, Interscience Publishers, John Willey & Sons, New York (1968).
[4] M. Kaji, K. Nakahara, K. Ojima, T. Endo, J. Appl. Polym. Sci. **75,** 528 (2000).
[5] EP 0220133 (1987), invs.: K. Amsler, W. Scheinder.
[6] Jpn Kokai Tokkyo Kohu, JP 01, 259 457(1989) invs,: K. Yamaguchi, Y. Tanabe, T. Urgami, T. Yamaguchi; Chem. Abstr. **1990**, 112, 159836.
[7] R. L. Bindu, C. P. Reghunadhan, K. N. Ninan, J. Polym. Sci.: Part A, Polym. Chem. **38**, 641 (2000).
[8] F. Mustata, I. Bicu, J. Polym. Eng. **22,** 369 (2002).
[9] F. Mustata, I. Bicu, Mat. Plast. (Bucharest) **42,** 17 (2005).
[10] Jpn Kokai Tokkyo Koho, JP 01, 275,618 (1989), invs.: K. Yamagachi, Y. Tanabe, T. Urgami, T. Yamaguchi; Chem. Abstr. **112**, 180724 (1990).
[11] F. Mustata, I. Bicu, Macromol. Mater. Eng. **289**, 800 (2004).
[12] F. Mustata, I. Bicu, Polimery **7/8**, 534 (2001).
[13] F. Mustata, I. Bicu, Polimery **11/12,** 817 (2002).
[14] S. K. Chatterjee, S. Ghosh, D. Yadav, B. V. Farahany, Angew. Makromol. Chem. **180**, 1 (1990).
[15] F. Mustata, Rev. Chem. **53**, 239 (2002).
[16] F Must-Mat. Plast. **41,** (2004).
[17] Jpn Kokai Tokkyo Koho, JP 07,150008 (1995) invs.:Y. C. Tomatsu, M. Sumaya, CA 1995, 123 Ab230290.
[18] N. D. Cheronis, T. S. Ma, "Organic Functional Group Analysis by Micro and Semimicro Methods", Interscience Publishers, Wiley & Son, New York 1964.
[19] C. N. Cascaval, F. Mustata, D. Rosu, Angew. Makromol. Chem. **209,** 157 (1993).
[20] A. W. Coats, J. R. Redfern, Nature **201,** 68 (1964).
[21] V. Swaminathan, N. S. Modhavan, J. Anal. Appl. Pyrolysis **3,** 131(1981).
[22] T. Ozawa, J. Thermal. Anal. **9,** 364 (1976).
[23] H. F. Kissinger, Anal. Chem. **29**, 1702 (1957).
[24] K. C. Cole, Macromolecules **24,** 3093 (1991).
[25] K. C. Cole, Macromolecules **24,** 3098 (1991).
[26] D. Rosu, F. Mustata, C. N. Cascaval, Thermochemical acta **370**, 105 (2001).
[27] R. D. Patel, R. G. Patel, V. S. Patel, British Polymer **19,** 37 (1987).
[28] D. Feldman, D. Banu, J. Polym. Sci.: Part A: Polym. Chem. **26**, 973 (1988).
[29] F. Mustata, I. Bicu, J. Polym. Eng. **22**, 369 (2002).

---

* Corresponding author: fmustata@mail.icmpp.ro