FANICA MUSTATA[*], IOAN BICU

"P. Poni" Institute of Macromolecular Chemistry
Aleea Grigore Ghica Voda
No. 41 A, RO 700487, Iasi, Romania
[*] e-mail: fmustata@icmpp.ro

The effect of some Diels-Alder adducts of resin acids on the process of epoxy resin curing

Summary — Curing reaction of epoxy resins with three Diels-Alder adducts of resin acids in the presence of triethylbenzylammonium chloride as catalyst was examined by differential scanning calorimetry at different heating rates. Using the literature methods (Kissinger and Ozawa) the kinetic parameters of crosslinking reactions were obtained. The activation energies of the curing reactions varied in the range of 44—79 kJ · mol^{-1} depending on epoxy systems and curing agents. The thermal behavior of cured products was also investigated using thermogravimetric analysis. The cured products present good thermal stability — the activation energies of the degradation process have values between 87 to 165 kJ · mol^{-1}.

Key words: epoxy resin, resin acids, Diels-Alder adducts, crosslinking reaction, thermal properties.

WPŁYW WYBRANYCH ADDUKTÓW DIELSA-ALDERA KWASÓW ŻYWICZNYCH NA PRZEBIEG PROCESÓW UTWARDZANIA ŻYWIC EPOKSYDOWYCH

Streszczenie — Metodą skaningowej kalorymetrii różnicowej (DSC) zbadano przebieg reakcji utwardzania czterech związków epoksydowych (diglicydylowego eteru bisfenolu A — DGEBA, diglicydylowego eteru hydrochinonu — DGEHQ, diglicydyloaniliny — DGAN oraz triglicydylo-*p*-aminofenolu — TGAP) za pomocą trzech rodzajów adduktów Dielsa-Aldera z kwasami żywicznymi (trójfunkcyjnego RAMA i dwufunkcyjnych RAAc oraz RAMA*p*ABA, tabela 1) wobec chlorku tribenzyloamoniowego jako katalizatora (rys. 1). Z zastosowaniem metod literaturowych (Kissingera i Ozawy) określono kinetyczne parametry reakcji sieciowania (tabele 2 i 3) i scharakteryzowano wpływ budowy chemicznej badanego układu żywica/utwardzacz na uzyskane wartości. Zmiany budowy chemicznej towarzyszące procesowi utwardzania omówiono na podstawie widm IR (rys. 2). Stabilność termiczną utwardzonych produktów zbadano metodą analizy termograwimetrycznej (tabela 4, rys. 3). Układy sieciowane trójfunkcyjnym adduktem Dielsa-Aldera są bardziej odporne na rozkład termiczny niż układy utwardzane adduktami dwufunkcyjnymi. Próbkę wzorcową w badaniach kinetycznych i stabilności termicznej stanowił układ DGEBA/bezwodnik trimelitowy.

Słowa kluczowe: żywice epoksydowe, kwasy żywiczne, addukty Dielsa-Aldera, kinetyka sieciowania, właściwości cieplne.

In recent years, as a consequence of the frequent oil crises, the prices of petroleum products become very high, and much attention has been attracted to the raw materials obtained from renewable resources (natural rubber, cellulose, vegetable or animal oils, turpentine and rosin, sugar saccharide and so on) as substitutes of them. Particularly, these natural materials have been used for the development of the environmentally friendly chemistry in syntheses of novel polymer-based materials.

Rosin, obtained from oleoresin of conifer trees (principally constituted from resin acids—abietic acid, levopimaric acid, palustric acid, neo-abietic acid *etc.*) has a long history of use as an additive in the formulations of printing inks, paints, lacquers, varnishes, tackifiers for adhesives and alkyd resins, paper sizing agent and so on. In the last decade, the Diels-Alder adducts of resin acids with the dienophile (maleic anhydride, fumaric acid, acrylic acid, diallyl maleate, acrylonitrile, β-propiolactone *etc.*) have been used as raw materials in syntheses of polymers (polyesters, unsaturated polyesters, polyesterimides, polyamides, polyamidimides, alkyd resins, epoxy resins and so on) [1—30]. The presence of hydrophenanthrene moieties onto or in the polymer chain gives to these polymers valuable properties, such as: high solubility in great majority of organic solvents, water repellence, high adhesion and reasonable thermal stability.

There are some reports regarding the use of the resin acids and its derivatives as raw materials in the formulations of epoxy resins syntheses [31—39].

The aim of this work is to report the effect of some Diels-Alder adducts of rosin derivatives as curing agents on the kinetics of the epoxy resins' curing. The thermal stability of cured products was also emphasized.

EXPERIMENTAL

Materials

— Maleic anhydride (MA), acrylic acid (AAc), *p*-aminobenzoic acid (*p*-ABA), sodium and potassium hydroxides (NaOH, KOH), triethylbenzylammonium chloride (TEBAC), hydroquinone (HQ), aniline (AN), trimellitic anhydride (TMA) and organic solvents were analytical grade products. Diels-Alder adducts of resin acids in levopimaric form with AAc (RAAc), MA (RAMA) and imidodiacid of RAMA with *p*-aminobenzoic acid (RAMA*p*ABA) were obtained as described in previously published articles [16, 24, 30]. Some physical and chemical properties of Diels-Alder adducts are presented in Table 1.

Table 1. Some physical and chemical properties of Diels-Alder adducts

Diels-Alder adduct	Appearance	Melting point, °C	Acid number mg KOH/g	Nitrogen content, %
RAAc	white	204—205	295	—
RAMA	white grey	223—224	414	—
RAMA*p*ABA	pale yellow	284—285	208	2.71

— Epoxy resins: a) diglycidylether of bisphenol A (DGEBA) (Sintofarm, Bucharest) was a commercial product with an epoxy equivalent weight of 345 g · eq^{-1}; b) diglycidyl ether of hydroquinone (DGEHQ), diglycidylaniline (DGAN), and triglycidyl *p*-aminophenol (TGAP) were synthesized according to the procedure described in our previous article [19, 38, 39] and had an epoxy equivalent weights of 205 g · eq^{-1}, 130 g · eq^{-1} and 118 g · eq^{-1}, respectively.

— Resin acids (RA) (acid number = 180 mg KOH/g) were obtained from commercial rosin by recrystallization from acetone twice.

Methods of testing

— Nitrogen content was determined in accordance with Kjeldahl method [40].

— To determine the acid number, the samples were dissolved in DMF to make a 5 % (*w*/*v*) solution and were directly titrated with 0.1 N ethanolic KOH solution to the phenolphthalein end point.

— The epoxy equivalent weights were obtained according literature method and expressed in g · eq^{-1} [41].

— Infrared spectra (FTIR) were taken using a "Bio-Rad Digi Lab Division" (Portmann Instruments) and KBr pellets.

— The curing thermal data and the glass temperature were obtained by means of a Mettler "DSC-12E" type apparatus. All the experiments were performed in nitrogen under dynamic condition.

For the kinetic characterization, the tests were run at temp. 20 to 300 °C with different heating rates (5, 10 or 15 °C · min^{-1}) in a nitrogen atmosphere (3 l · min^{-1}). For calorimetric calibration, pure indium was used as standard. Kinetic parameters of the curing reactions were calculated from DSC measurements using the variable exothermic peak method of Kissinger, taking in consideration three heating rates [42]. The following equation was used:

$$\ln(\beta/T^2_M) = E_a/R \cdot T_M - \ln(Z \cdot R/E_a) \qquad (1)$$

where: β — *heating rate (deg · min^{-1})*, T_M — *peak exothermic temperature (K)*, E_a — *activation energy of the curing reactions (kJ · mol^{-1})*, R — *gas constant (kJ · kmol^{-1} · K^{-1})*, Z — *frequency factor (min^{-1})*.

From the graph $\ln(\beta/T^2_M)$ *versus* $1/T_M$ the activation energy of curing and frequency factor were obtained. Also, the activation energies for the presented epoxy systems were determined by Ozawa method [equation (2)] [43]:

$$\ln\beta = -0.4567(E_a/RT_M) + const \qquad (2)$$

where the parameters are similar to those in eq. (1). This method is valuable only for curves consisting of single unit process. Ploting ln β *versus* reciprocal absolute temperatures of T_M, one can estimate the activation energies of curing process from the slope of the straight lines.

Thermal stability of cured products was evaluated by TGA measurements and was obtained using a MOM-Budapest of Paulik, "Paulik-Erdey" type derivatograph at heating rate of 10 °C · min^{-1} in an air at the temperature range of 25—700 °C. The TG parameters, namely T_{10} (temperature of 10 % weight loss), T_{50} (temperature of 50 % weight loss), WL_{500} (weight loss at 500 °C) and the activation energy of decomposition reaction were used in order to determine the thermal stability of the crosslinked polymers. Kinetic analyses of TG data were performed using the main peak of degradation reaction, by applying Coats—Redfern [44] and Swaminatham—Modhavan [45] methods. The following general equations were used:

$$\log\left[1-(1-c)^{1-n}\right]/(1-n)\cdot T^2 = \log(AR/\beta E_a) - 2.303(E_a/RT) \qquad (3)$$

and

$$d\alpha/dT = A\exp(-E_a/RT)\left[\alpha^m(1-\alpha)^n\right]\left[-\ln(1-\alpha)^p\right] \qquad (4)$$

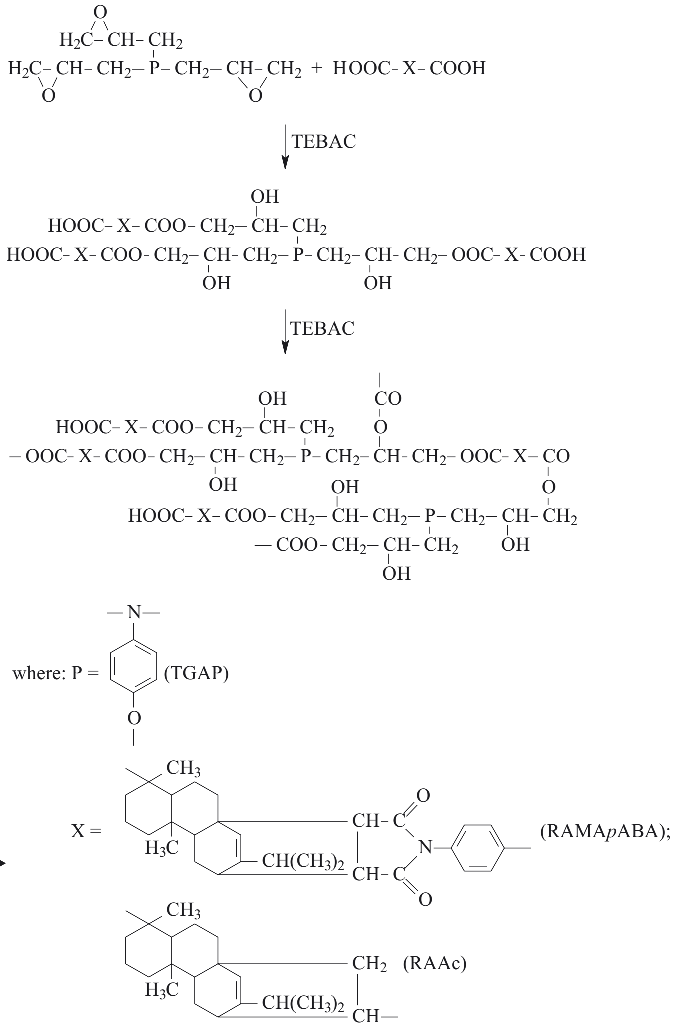
where: α — *conversion degree (ratio of the weight loss at time "t" and at the end of the process)*, A — *pre-exponential factor*, c — *conversion*, n — *reaction order*, m *and* p — *exponents of the conversion function*, T — *temperature [other symbols see eq. (1)]*.

Samples preparation for DSC and TGA studies

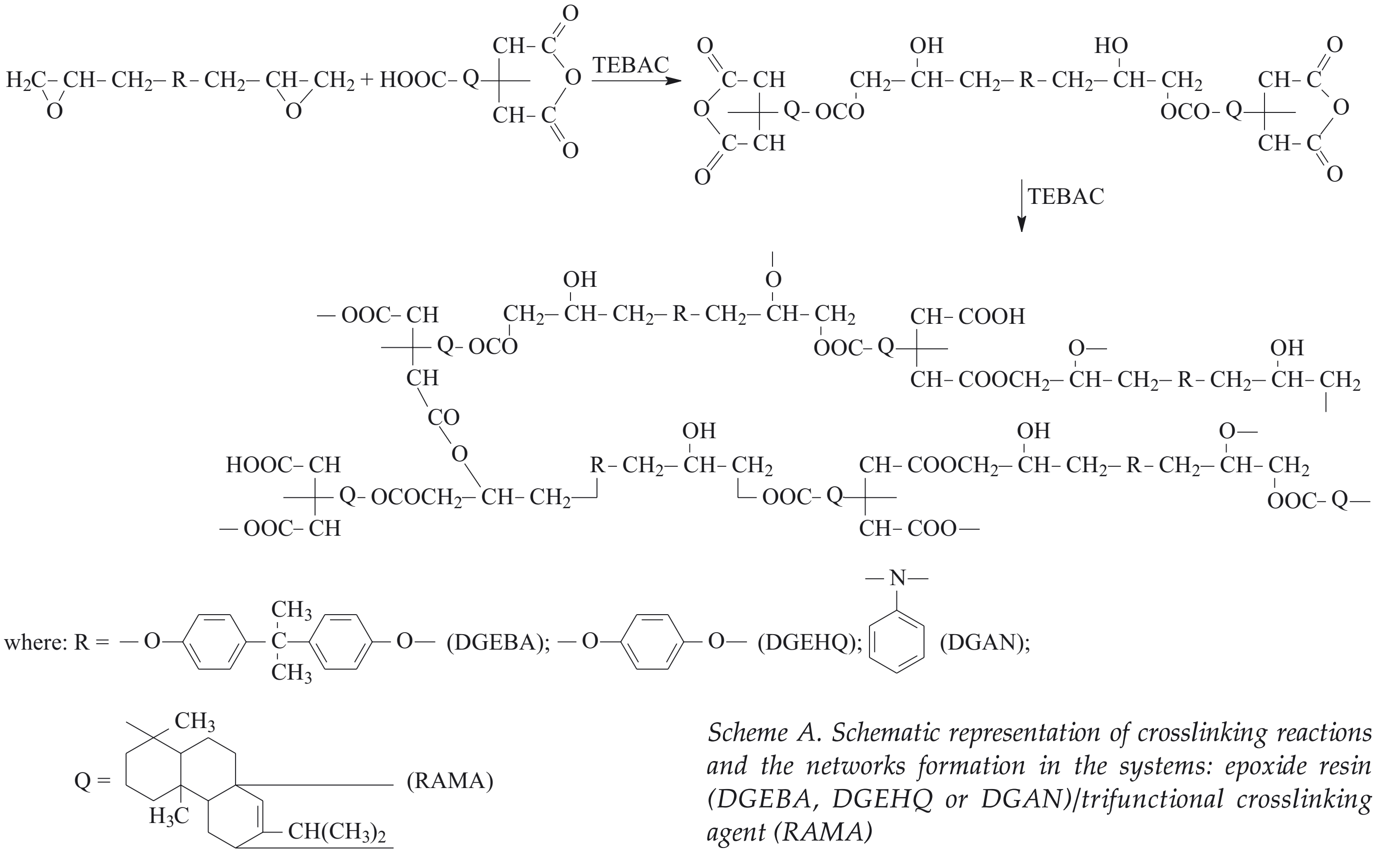
The epoxy resins and Diels-Alder adducts (as fine grains) accurately weighted were vigorously mixed in a proportion corresponding to a ratio *r* = 1 where "*r*" represents the carboxyl group/epoxy ring ratio. A small quantity of a sample, corresponding to each epoxy resin and Diels-Alder adduct mixtures was taken for DSC studies. The remaining quantity of the samples were cured at 120 °C for 1 h, at 140 °C for 1 h and post cured at 180 °C for another 3 h. The cured products were used for TGA studies in the dynamic scan.

RESULTS AND DISCUSSION

It is well known that the oxirane group easy reacts with carboxylic one and carboxylic acid anhydride groups in the presence of catalysts (tertiary amines, phosphines, quaternary ammonium salts, alkali salts) at high temperatures (180 °C) to form crosslinked products [46—55]. The curing behavior and kinetic parameters of these systems were monitored using chemical analysis, IR, and DSC spectroscopy. In our case the networks were obtained by crosslinking of DGEBA, DGEHQ, DGAN,



Scheme B. Schematic representation of crosslinking reactions and the networks formation in the systems: epoxide resins (TGAP)/difunctional crosslinking agents (RAAc or RAMA-pABA)



Scheme A. Schematic representation of crosslinking reactions and the networks formation in the systems: epoxide resin (DGEBA, DGEHQ or DGAN)/trifunctional crosslinking agent (RAMA)

Table 2. Kinetic parameters of epoxy systems from DSC scans (equivalent of carboxyl proton/epoxide group = 1/1) — calculated from first exotherm

Epoxy resin	Curing agent	Heating rate, °C · min^{-1}			Activation energy of curing, kJ · mol^{-1}		Frequency factor min^{-1}	Glass transition temperature T_g, °C
		5	10	15	Ozawa	Kissinger		
		T_M	T_M	T_M				
DGEBA	RAMA	197	212	227	72.37	63.90	17.90	103.62
DGEHQ	RAMA	185	193	204	79.05	71.30	19.10	119.56
DGAN	RAMA	140	165	178	44.35	40.84	12.20	96.10
DGEBA/DGAN (1/1)	RAMA	187	202	214	76.04	68.26	19.20	100.34
DGEHQ/DGAN (1/1)	RAMA	184	190	207	78.02	70.55	20.05	108.78
TGAP	RAAc	164	172	191	63.10	55.60	16.86	113.49
TGAP	RAMApABA	170	186	195	75.28	67.75	19.78	120.09
DGEBA[a)]	TMA	169	187	196	75.06	66.51	19.71	126.92

[a)] blank test.

Table 3. Kinetic parameters of epoxy systems from DSC scans (equivalent of carboxyl proton/epoxide group = 1/1) — calculated from the second exotherm

Epoxy resin	Curing agent	Heating rate, °C · min^{-1}			Activation energy of curing, kJ · mol^{-1}		Frequency factor, min^{-1}
		5	10	15	Ozawa	Kissinger	
		T_M	T_M	T_M			
DGEBA	RAMA	266	296	312	62.83	52.80	13.28
DGEHQ	RAMA	248	262	272	107.08	98.66	24.21
DGAN	RAMA	191	230	243	40.35	37.56	9.92
DGEBA/DGAN (1/1)	RAMA	255	280	295	67.12	59.23	14.97
DGEHQ/DGAN (1/1)	RAMA	245	278	290	50.75	42.45	11.21

DGEBA/DGAN and DGEHQ/DGAN with RAMA and by crosslinking of TGAP with RAAc and RAMA*p*ABA; these processes were studied using DSC technique. Schemes A and B show a schematic representation of crosslinking reactions and the networks formation with using trifunctional and difunctional crosslinking agents, respectively. The dynamic DSC scans of the systems presented above were registered at different heating rates and the curing exotherms were recorded. The obtained data are presented in Table 2 and 3. Figure 1 shows the typical DSC thermograms for DGEBA/RAMA and DGEBA/TMA systems obtained at 10 °C/min heating rate. It may be observed from curve (a) that the systems, which contain RAMA as crosslinking agent, present three exotherms. The first exotherm may be due to the opening of maleic anhydride moieties, which are converted into ester group and a new carboxylic group. The second peak can be due to the reaction of the new appeared carboxylic group with epoxy ring which leads to the crosslinked structure. The third exotherm can be at-

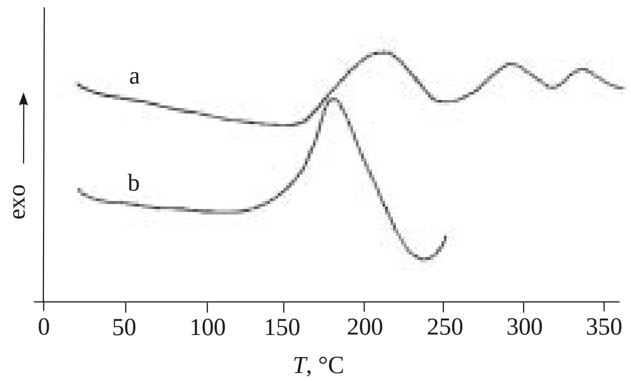


Fig. 1. DSC scans at 10 °C · min^{-1} for: (a) DGEBA/RAMA, (b) DGEBA/TMA

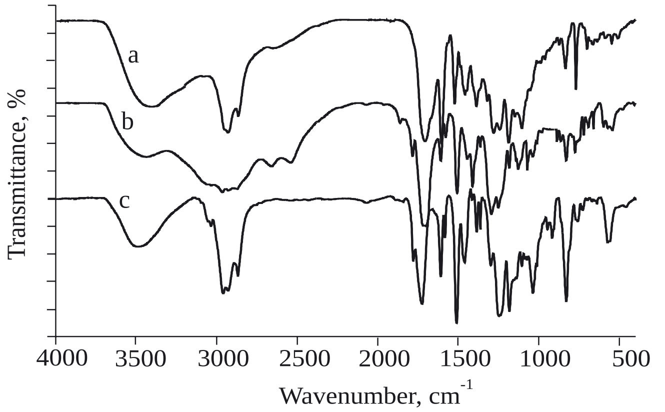


Fig. 2. IR spectra of crosslinked products: (a) TGAP crosslinked with RAAc, (b) DGEBA crosslinked with TMA, (c) DGEBA crosslinked with RAMA

tributed to the chemical reaction of esterification type, appeared between the third carboxylic group bonded to the hydrophenanthrene moieties (which is steric hindrance) and epoxy ring or carboxylic groups with new tertiary OH groups. The second and the third reaction induce the formation of crosslinked structures.

These chemical reactions can be evidenced from IR spectra of crosslinked products (Fig. 2). The peaks specific to epoxy ring located in the range of 915 cm^{-1} disappeared and the new obtained groups (tertiary OH and ester one) give peaks located in the ranges of 3450—3500 cm^{-1}, 1710—1730 cm^{-1} and 1100—1280 cm^{-1}.

The exothermic temperature peaks are specific to each epoxy/curing agent systems and have minimum values for DGAN/RAMA system (Tables 2 and 3). This fact can be explained by small viscosity of DGAN, which gives to the system an increase in the mobility of molecules. On the other hand, this behavior concerns also the mixed systems, DGEBA/DGAN and DGEHQ/DGAN. It was noted that with the increasing heating rate, the tested samples showed a continuous increase in maximum peak temperatures. This behavior can be related to the instrumental, structural and kinetic factors.

The kinetic data (activation energy of crosslinking and frequency factor) listed in Tables 2 and 3 showed differences in the values E_a of each systems, as a consequence of different chemical structures of epoxy resins and curing agents. The activation energy of curing process obtained from the first and second exotherms have different values but the pre-exponential factor (ln*A*) does not very significantly with the exception of the systems containing DGAN.

Generally the pre-exponential factor reflects the frequency of the collisions between the molecules and directly depends on the temperature. The systems with DGAN in composition cross-link at lower temperature in comparison with the other systems, and as a consequence, their pre-exponential factors get the smallest values.

The systems which contain DGEHQ in compositions present high values of the activation energy of curing process. This fact may be due to high rigidity of DGEHQ, being solid at room temperature, in comparison with DGEBA, DGAN or TGAP. The activation energy of curing process has values in the range 41—79 kJ · mol^{-1} and depends on the chemical structures of epoxy resins and curing agents. The activation energies for third peaks were not calculated because in the range of the third peak temperatures the sample weight loss is higher than 3 % and the energies were composed as a sum of crosslinking energies and degradation energies.

The DGEBA/TMA system was cured in the same conditions as all experiments and was used as control sample. This system, oppositely to the systems cured with RAMA, presents a single exotherm [Fig. 1, curve (b)], which suggests that the activation energies of polymerization and crosslinking reactions are equal.

The influence of the structure of the crosslinking agent on the thermal and physical properties of the crosslinked resin was also examined by measuring the glass transition temperatures and thermal behaviors. The glass transition temperatures were measured by DSC scans at heating rate of 20 °C · min^{-1}. T_g of the cured resins has different values as a consequence of chemical structures of epoxy resins and of crosslinking agents. As can be seen in Table 2, T_g of DGEBA/TMA system is enhanced in comparison with all crosslinked epoxy resins. This can be attributed to the fact that DGEBA crosslinked with TMA is more rigid, as a consequence of TMA structure (it has only aromatic ring), in comparison with the systems cured with all Diels-Alder adducts. In this second case the enhancement of glass transition temperatures arises from the rigidity of epoxy resin (DGEHQ and TGAP) and of adducts (RAMA and RAMA*p*ABA); they have T_g values of *circa* 120 °C.

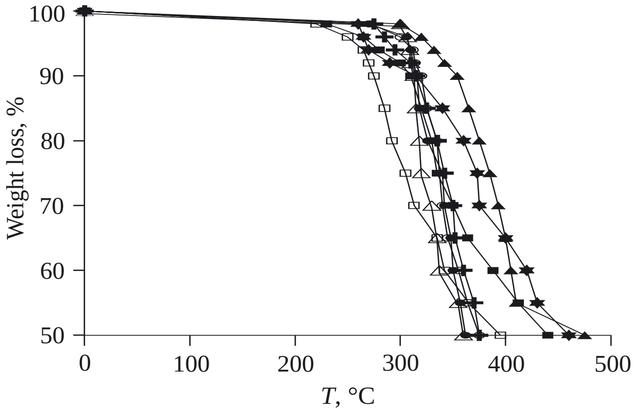


Fig. 3. Weight loss versus temperature for: (▲)DGEBA crosslinked with RAMA; (△)DGEHQ crosslinked with RAMA; (+)DGAN crosslinked with RAMA; (O)DGEBA/DGAN crosslinked with RAMA, (●)DGEHQ/DGAN crosslinked with RAMA, (□)TGAP crosslinked with RAAc, (■)TGAP crosslinked with RAMApABA, (✱)DGEBA crosslinked with RAMA

The thermal study of the crosslinking products is based on thermogravimetric analysis (TGA). Typical TGA curves for the cured products in an air atmosphere are shown in Fig. 3. The main parameters characterizing the decomposition process (T_{10}, T_{50} and WL_{500}), pre-exponential factor (ln*A*) and activation energy of degradation process (estimated with Coats—Redfern and Swaminathan—Modhavan equations) are collected in Table 4. It can observed, that the thermal stability of the cured products depends on the nature of epoxy resin and crosslinking agents. The 5 % weight loss temperature in an air of these crosslinked resins is in the range of 290—325 °C for the resins cured with trifunctional derivatives of Diels-Alder adducts and in the range of 270—300 °C for the resins cured with difunctional ad-

T a b l e 4. Thermal parameters of cured epoxy resins

Epoxy resin	Curing agent	T_{10}, °C	T_{50}, °C	WL_{500}, %	Decomposition activation energy, kJ · mol^{-1}		Order of reaction	Frequency factor min^{-1}
					Coats—Redfern	Swaminathan—Modhavan		
DGEBA	RAMA	354	475	40	119.6	107.92	1.41	18.26
DGEHQ	RAMA	313	360	37	164.3	178.91	2.02	27.55
DGAN	RAMA	315	375	20	111.8	109.54	2.05	12.62
DGEBA/DGAN (1/1)	RAMA	320	375	27	118.0	123.12	1.83	29.03
DGEHQ/DGAN (1/1)	RAMA	316	362	32	146.0	172.21	2.17	33.11
TGAP	RAAc	275	395	40	93.0	86.43	1.22	16.45
TGAP	RAMA*p*ABA	310	440	42	87.0	84.23	0.85	14.76
DGEBA[a)]	TMA	340	400	38	165.9	157.89	2.12	16.78

[a)] blank test.

ducts (Fig. 3). The cured resins containing difunctional adducts exhibit the poorest thermal stability in the range under 10 % weight loss as compared with epoxy resin crosslinked with trifunctional crosslinking agents, and weight loss is rather rapid in the range of 300—400 °C. This fact can be explained as a consequence of poor crosslinking induced by difunctional crosslinking agents. Accepting the above parameters as criteria for thermal stability, we can conclude that the cured products of DGEBA/RAMA and DGEBA/TMA are more thermally stable in comparison with all other systems. This observation may be explained on the basis of chemical structures of crosslinking agents which give a high rigidity to the cured resin.

CONCLUSIONS

Three Diels-Alder rosin derivatives (RAAc, RAMA, RAMA*p*ABA) were successfully used as crosslinking agents for epoxy resins. Cured resins showing moderate glass temperatures and good thermal stability were obtained. The prepared systems, after crosslinking, show similar properties, which suggest potential applications in the field of electrical and electronic industries especially as environmentally friendly materials obtained from renewable resources.

REFERENCES

[1] Stonecipher W. D., Turner R. W.: "Encyclopedia of Polymer Science and Technology", Interscience Publishers, John Wiley & Sons, New York 1970, vol. 12, p. 145. [2] Roy S. S., Kundu A., Maiti S.: *Eur. Polym. J.* 1990, **26**, 471. [3] Hoa L. T. N., Pascault J. P., My L. T., Son C. P. N.: *Eur. Polym. J.* 1993, **29**, 491. [4] Halbrook N. J., Lawrence R. V., Dalluge M. D., Stein G. A.: *I&EC Prod. Res. Develop.* 1963, **2**, 183. [5] *Jap. Pat.* 35 655 (2004), cf. *CA* 2004, **140**, 129 841. [6] *Pat. US* 2 973 332 (1961). [7] *Pat. US* 2 938 006 (1960). [8] Maiti M., Adhikari B., Maiti S.: *J. Polym. Mater.* 1988, **5**, 201. [9] Ray S. S., Kundu A., Maiti S.: *J. Appl. Polym. Sci.* 1988, **36**, 1283. [10] Das S., Maiti S., Maiti M.: *J. Macromol. Sci.-Chem.* A 1982, **17**, 1177.

[11] Schuller W. H., Lawrence R. V., Culbertson B. M.: *J. Polym. Sci., Part A* 1967, **5**, 2204. [12] *Jap. Pat.* 7 615 004 (1976), cf. *CA* 1976, **85**, 34 916. [13] *Pat. U.R.S.S.* 519 435 (1976), cf. *CA* 1976, **85**, 144 853. [14] *Pat. U.R.S.S.* 489 765 (1975) cf. *CA* 1976, **84**, 75 895. [15] Kundu A. K., Ray S. S., Adhikari B., Maiti S.: *Eur. Polym. J.* 1986, **22**, 369. [16] Bicu I., Mustata F.: *Angew. Makromol. Chem.* 1996, **234**, 91. [17] Bicu I., Mustata F.: *Angew. Makromol. Chem.* 1997, **246**, 11. [18] Bicu I., Mustata F.: *Angew. Makromol. Chem.* 1999, **264**, 21. [19] Mustata F., Bicu I.: *Polimery* 2000, **45**, 258. [20] Mustata F., Bicu I.: *Design. Monom. Polym.* 2000, **3**, 489.

[21] Bicu I., Mustata F.: *Macromol. Mater. Eng.* 2000, **280—281**, 47. [22] Mustata F., Bicu I.: *J. Polym. Eng.* 2001, **21**, 389. [23] Bicu I., Mustata F.: *J. Appl. Polym. Sci.* 2004, **92**, 2240. [24] Mustata F., Bicu I.: *Polimery* 2005, **50**, 176. [25] Mustata F., Bicu I.: *J. Polym. Eng.* 2005, **25**, 217. [26] Bicu I., Mustata F.: *J. Polym. Sci. Part A: Polym. Chem.* 2005, **43**, 6308. [27] *Pat. US* 5 021 538 (1991). [28] *Pat. US* 6 734 280 (2004). [29] *Pat. US* 5 120 781 (1992). [30] Mustata F., Bicu I.: *J. Polym. Eng.* 2007, **27**(1), 75.

[31] MatyniaT.: *Polimery* 1975, **20**, 7. [32] Penczek P., Matynia T.: *Polimery* 1974, **19**, 609. [33] Penczek P., Kicko-Walczak E., Smolovik E.: *Plast. Massy* 1977, No 6, 11. [34] *Pat. Pol.* 78 841 (1975), cf. *CA* 1976, **85**, 47 549. [35] Atta A. M., Mansour R., Abdou M. I., El-Sayed A. M.: *J. Polym. Res.* 2005, **12**, 127. [36] Atta A. M., Mansour R., Abdou M. I., El-Sayed A. M.: *Polym. Advan. Technol.* 2004, **15**, 514. [37] Mustata F., Bicu I.: *J. Polym. Eng.* 2003, **23**, 191. [38] Mustata F., Bicu I.: *Polym. Test.* 2001, **20**, 533. [39] Mustata F., Bicu I.: *Polimery* 2002, **47**, 717. [40] Cheronis N. D., Ma T. S.: "Organic functional group analysis by micro and semimicro methods", Wiley & Son, Interscience Publishers, New York 1964.

[41] Cascaval C. N., Mustata F., Rosu D.: *Angew. Makromol. Chem.* 1993, **209**, 157. [42] Kissinger H. F.: *Anal. Chem.* 1957, **29**, 1702. [43] Ozawa T.: *J. Thermal. Anal.* 1976, **9**, 364. [44] Coats A. W., Redfern J. R.: *Nature* 1964,

68, 201. [45] Swaminathan V., Modhavan N. S.: *J. Anal. Appl. Pyrolysis* 1981, **3**, 131. [46] Matejka L., Pokorny S., Dusek K.: *Polym. Bull.* 1982, **7**, 123. [47] Madek P. J., Marechal E.: *Adv. Polym. Sci.* 1985, **71**, 53. [48] Boutevin B., Parisi J. P., Robin J. J., Roume C.: *J. Appl. Polym. Sci.* 1993, **50**, 265. [49] Crandall E., Mih W.: "Chemorheology of Thermosetting Polymers", Am. Chem. Soc. Symp. Ser., No. 227, p. 113, ACS, Washington, D. C. 1983. [50] Fedke M., Domaratius F.: *Plaste Kautsch* 1983, **30**, 36.

[51] Roks J., Halter M., George G., Vohwinkel F.: *Polym. Int.* 2003, **52**, 1749. [52] Sadner B., Schreiber R.: *Makromol. Chem.* 1992, **193**, 2763. [53] *Pat. US* 3 637 618 (1972). [54] Lundsford D., Banthia A. K., McGrath J. E.: *Polym. Prep.* 1981, **22**, No 1, 194. [55] Pendyala V. N. S., Banthia A. K.: *Polym. Prep.* 1988, **29**, No 1, 256.

Received 28 XII 2006.