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Synthesis of elevated-molecular-weight epoxy resins with aid of microwaves

RAPID COMMUNICATION

Summary — A new method of synthesis of elevated-molecular-weight (E-M) epoxy resins with desired epoxy-groups content, based on polyaddition of bisphenol A to a lower-molecular-weight (L-M) epoxy resin (epoxy value *EV* = 0.57 mol/100 g) under microwave irradiation in the presence of 2-methylimidazole, as a catalyst, was described. Syntheses were carried out in a multimode microwave reactor "Plazmatronika" (Poland) of microwave frequency 2.45 GHz and maximal microwave power 300 W. Analogical syntheses have been done using conventional heating for the comparison of the methods. Values of *EV*, M_n, M_w and M_w/M_n of the products obtained were determined. The main advantage of the process is twofold reduction of reaction time of the processes carried at microwave reactors in comparison to the conventional heating.

Key words: microwave irradiation, epoxy resins, polyaddition, reaction time.

Epoxy resins based on bisphenol A are about 85% of the world's epoxy resins production. More than 60% of the global production is used in the coatings industry [1—2]. In that group [elevated-molecular-weight (E-M) epoxy resins, epoxy value (*EV*) *EV* = 0.11—0.02 mol/ 100 g, M_n = 1000—4000], that are mostly used in baking varnishes and powder coatings amount to almost 26%. They have appropriate properties like high chemical and thermal resistance, very good adhesion to various substrates, hardness and elasticity.

E-M epoxy resins are produced according to two different methods:

— polycondensation of bisphenol A and epichlorohydrin carried out in solution in the presence of sodium hydroxide [3—5] (purification of the product is needed),

— polyaddition of bisphenol A with lower-molecular-weight (L-M) epoxy resins [6—10] (*EV* = 0.58—0.35 mol/100 g, M_n = 370—500) or medium molecular-weight (M-M) epoxy resins (*EV* = 0.30—0.15 mol/100 g, M_n = 500—1000) in the presence of a catalyst (pure product is obtained so all the costly procedures of purification are avoided).

In the industry, these two reactions are generally provided under conventional heating and E-M epoxy resins are manufactured by the melt process wherein liquid epoxy resins and bisphenol A are heated in a batch reactor for a couple of hours. The reaction is carried out in the temperature range of 140—180°C with nitrogen "blanket" to minimize oxidative degradation reactions [11—12]. In the reaction, the known catalysts such as tertiary amines or phosphines (*e.g.* triphenylphosphine), quaternary ammonium or phosphonium salts, and imidazole derivatives are applied. The reaction mixture needs an excess of epoxy groups in relation to active hydrogen atoms in bisphenol A [13].

Recently there is a growing interest in the new method of chemical synthesis using microwaves to induce the reactions. Microwave irradiation can interact with polar substances because of the inability to instant reorientation of dipoles according to the changes in the electromagnetic field. Microwave energy can be converted into heat directly inside the material. Therefore, it is possible to achieve rapid and uniform heating even in the materials showing low thermal conductivity (*e.g.* epoxy resins), because transfer of energy does not rely on heat diffusion. The advantage consists in much higher heating rates and shortening of the reaction time [14—17].

The aim of present work was to check the possibility of using of microwave irradiation for E-M epoxy resins syntheses.

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EXPERIMENTAL

Materials

Bisphenol A and 2-methylimidazole were obtained from Fluka. L-M epoxy resin Rütapox 0162 (high content of bisphenol A diglycidyl ether, EV = 0.57 mol/100 g) was obtained from Bakelite AG.

Synthesis of epoxy resins

E-M epoxy resins were prepared by mixing of 2-methylimidazole (the amounts given in Table 1) and bisphenol A (11.649 g) with L-M epoxy resin (25.0 g). Constant molar ratio of bisphenol A to the epoxy resin (3:4) was calculated according to the equation:

$$m_B = \frac{m_E \cdot M_B \cdot (EV_1 - EV_2)}{EV_2 \cdot M_B + 200} \qquad (1)$$

where: m_B — *amount of bisphenol A (g),* m_E — *amount of the L-M epoxy resin (g),* M_B — *molecular weight of bisphenol A,* EV_1 — *epoxy value of the L-M epoxy resin,* EV_2 — *epoxy value of the desired E-M epoxy resin (0.11 mol/100 g).*

Then the mixture was irradiated and stirred under nitrogen at three different temperatures: 140, 160 and 180°C, in a multi-mode microwave reactor "Plazmatronika" (Poland) of microwave frequency 2.45 GHz. The reaction was continued until epoxy value of the resin dropped to 0.11 mol/100 g. In majority of cases, 30% of full microwave power was applied (*i.e.* 100 W) to reach the desired reaction temperature. After the reaction, E-M epoxy resin was cooled down and pulverized.

Measurements

Epoxy values of the synthesized resins were determined according to the Polish Standard PN-87/C-89085/13.

All GPC analyses of the final products were performed using GPC chromatograph ("Knauer"). A system of three columns was used: 2 x PL-gel (300x7.5 mm; dimension of grains 3 mm and type of pore Mixed-E) with one precolumn; conditions of measurements: flow rate 0.8 mL/min, temperature 30°C, solvent — tetrahydrofuran (THF).

RESULTS AND DISCUSSION

Reaction conditions and results of all the analyses are given in Table 1. The catalyst was applied in the ratio of 0.0005, 0.001 and 0.005 mol N/mol OH in bisphenol A (*i.e.* the ratio of nitrogen atoms in 2-methylimidazole to hydroxyl groups in bisphenol A). As it was expected, at given temperature the longest reaction time was observed in the presence of the lowest catalyst content (0.0005). Reaction time always exceeded 1 h within the investigated temperature range. However, at 140°C and 160°C, reaction time necessary to achieve the desired epoxy value equal to 0.11 mol/100 g was reduced almost twice in comparison to the process under conventional heating. In the next stage, for reaction time reducing to less than one hour, a higher concentration of the catalyst in the reaction mixture was applied (0.001). On the other hand, when the concentration of the catalyst is too high, the reaction is difficult to control since it is accompanied

T a b l e 1. **Parameters of E-M epoxy resins syntheses and properties of the products obtained**

Reaction heating	Temperature °C	Optimum time min	Concentration of catalyst mol N/mol OH bisphenol A · 10^3	EV mol/100 g	GPC analysis		
					M_n	M_w	M_w/M_n
Microwave (Conventional)	180	65 (80)	0.5	0.109 (0.101)	2380 (2180)	4340 (4000)	1.85 (1.89)
Microwave (Conventional)	160	65 (120)	0.5	0.110 (0.106)	2140 (1790)	3780 (3130)	1.77 (1.75)
Microwave (Conventional)	140	150 (280)	0.5	0.114 (0.114)	1810 (1380)	3260 (2860)	1.80 (2.08)
Microwave (Conventional)	180	30 (50)	1	0.109 (0.105)	2180 (2250)	3990 (4250)	1.83 (1.89)
Microwave (Conventional)	**160**	**40** (80)	**1**	**0.113** (0.111)	**2150** (2180)	**3930** (4000)	**1.83** (1.84)
Microwave (Conventional)	140	90 (150)	1	0.112 (0.114)	1470 (2020)	2580 (3760)	1.75 (1.84)
Microwave (Conventional)	180	16 (35)	5	0.105 (0.100)	2420 (2320)	4580 (4420)	1.89 (1.91)
Microwave (Conventional)	160	20 (35)	5	0.104 (0.100)	2470 (2380)	3390 (5010)	1.83 (2.10)
Microwave (Conventional)	140	25 (55)	5	0.110 (0.113)	1950 (2170)	3780 (3640)	1.94 (1.68)

by a strong exothermic effect. It was found that the catalyst concentration above 0.005 mol N/mol OH bisphenol A caused a rapid gelation of the reaction mixture. The reaction temperature range from 140°C to 180°C was chosen because below 140°C the viscosity of the reaction mixture, which grew during the reaction, was so high that stirring was impossible, while above 180°C the degradation of the resin caused a strong darkening of the reaction mixture. Eventually, the optimum reaction conditions for the microwave processes: 40 min at 160°C, the catalyst content 0.001 mol N/mol OH bisphenol A, and 30% of microwave irradiation power (100 W) were applied (see Table 1, bold-faced type). Shortening of reaction time for all processes carried out in microwave reactor, in comparison to conventional heating, was observed.

The characterization of the final products shows that the resins prepared by the microwave and conventional methods have comparable properties. Particulary, GPC analyses showed that all E-M epoxy resins prepared have a similar molecular weight distribution.

CONCLUSIONS

It was demonstrated that it was possible to obtain E-M epoxy resins with a desired epoxy groups content applying microwave irradiation (2.45 GHz) to heat up the reaction mixtures of bisphenol-A with L-M epoxy resins in the presence of a catalyst. The main advantage of such a process carried out in the microwave reactor is the reaction time reduction.

ACKNOWLEDGMENT

The Polish State Committee for Scientific Research supported the research by Grant No 7T09B06521.

REFERENCES

1. Brojer Z., Hertz Z.: *Polimery* 1974, **19**, 569.
2. Kielska B.: *Polimery* 1980, **25**, 265.
3. Brojer Z., Hertz Z., Penczek P.: "Żywice epoksydowe", WNT, Warszawa 1982.
4. *US Patent* 2 992 239 (1961).
5. *US Patent* 2 694 694 (1954).
6. Brojer Z.: *Polimery* 1980, **25**, 205.
7. Csillag L., Antal I., Dolp H. R.: *Polimery* 1974, **19**, 578.
8. Penczek P., Rejdych J.: *Polimery* 1986, **31**, 81.
9. Rejdych J., Szczepaniak B.: *Polimery* 1982, **27**, 236.
10. Alvey F. B.: *J. Appl. Polym. Sci.* 1969, **13**, 1473.
11. Penczek P., Szczepaniak B.: *Acta Polymerica* 1991, **42**, 112.
12. Szczepaniak B., Penczek P., Rejdych J.: *Polimery* 1998, **43**, 732.
13. Bryan E.: "Chemistry and technology of Epoxy Resins", Chapman and Hall, London 1994.
14. Varma R. S.: "Microwave-Assisted Reactions under Solvent-Free Dry Conditions" in "Microwaves: Theory and Application in Material Processing IV" (Eds. Clark D., Sutton W., Lewis D.), American Ceramic Society (*Ceramic Trans.* 1997, **80**, 375).
15. Loupy A., *et al.*: *Synthesis* 1998, 1213.
16. Bogdał D.: *Wiad. Chem.* 1999, **53**, 66.
17. Deshayes S., Liagre M., Loupy A., Luche J. L., Petit A.: *Tetrahedron* 1999, **55**, 10851.

Received 16 VII 2002.