STUDY OF THE SYNTHESIS OF GLYCOL MODIFIED EPOXY RESINS IN MICROWAVE FIELD

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Studiul prezintă date experimentale cu privire la obţinerea unor răşini epoxidice modificate prin poliadiţia dietilenglicolului la diglicidileterul bisfenolului-A în câmp de microunde. Conversia reacţiei de poliadiţie a fost urmărită prin spectroscopie FT-IR şi prin analiză chimică. Raşina epoxidică modificată obţinută la final a fost supusă reticulării cu 4,4'-diaminodifenilmetan, pentru acest sistem fiind determinate proprietăţile mecanice şi fizice. S-a observat o îmbunătăţire a elasticităţii şi rezistenţei la şoc pentru raşina epoxidică modificată în comparaţie cu o răşină epoxidică standard.

The study presents experimental data regarding the preparation of modified epoxy resins by polyaddition of diethylene glycol to the diglycidyl ether of bisphenol-A in microwave field. The polyaddition conversion was followed by (FT-IR) spectroscopy and by chemical analysis. The modified epoxy resin was cured to 4,4 '- diaminodiphenylmethane . The mechanical and physical properties of this system have been investigated. Comparison between the properties of a standard epoxy resin and the modified one has shown for the last one an improvement in elasticity and resistance to shock.

Keywords: epoxy resin synthesis, glycols**,** microwaves**,** mechanical properties

1. Introduction

Epoxy resins are a class of polymers with multiple applications related to obtaining materials for the aerospace industry, electronics and automotive electronics. These resins are characterized by an exceptional resistance to chemicals and water, excellent adhesion to most types of substrates (glass, metal, textiles, and wood) and very good mechanical properties.

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Due to their superior mechanical and chemical properties, the modified epoxy resins make possible to obtain materials with a large and diversified range of properties, as well as processing characteristics.

Improvement of the flexibility, elongation and impact strength is achieved by modification of the standard epoxy resins based on the diglycidyl ether of the bisphenol A (DGEBA). The main modification methods used are:

- physical mixing of DGEBA with aliphatic resins containing polyethylene glycol/polypropylene glycol chains;
- chemical reaction of DGEBA with short/long sequences of polyethyleneglycol / polypropyleneglycol.

Such types of materials may be used in a wide variety of applications such as adhesives synthesis for civil building and protecting surfaces which are subjected to aggressive media (sea water, environment etc.) [1, 2].

The classical method of modifying the synthesis of the epoxy chain consists of stirring the glycol-resin mixture, followed by and heating at high temperatures (150^0C -170^0C) in presence of catalysts such as tertiary amines, quaternary ammonium bases, alkali metal halides, etc.

A very good alternative method to classical procedure is the irradiation of the reaction mass with microwaves [4, 5, 6, 7, and 8]. The use of this unconventional method offers several advantages compared with thermal activation, and has enabled the improvement of certain product parameters. Of particular interest are the ones related to the reduction of the reaction time, diminishing the thermal degradation, improving the selectivity of the synthesis process.

The present work concerns the synthesis of new materials based on the modification of DGEBA resins with diethylene glycol (DEG) in a microwave field. The conversion of epoxy groups in the synthesis process has been monitored by quantitative chemical analysis [2] and by FT-IR spectroscopy [8, 9, 10]. The epoxy resin thus obtained was subjected to reticulation with 4,4'-diaminodiphenylmethane (DDM) and the resulting product was characterized in terms of physical-mechanical properties.

2. Experimental part

2.1 Materials

Epoxy resin ROPOXID 501 was furnished by POLICOLOR. The resin characteristics were: dynamic viscosity 14600mPa.s (25^0C); Epoxy Index (IE) = 0.529 equivalents (eq).epoxy/100g, M = 384.15 g/mol.

DEG was used as received from FLUKA and had the following parameters: M = 106.12 g/mol, density=1.118g/cm^3 (20^0C), b.p. = 244^0C-245°C.

The catalyst used for the chemical modification of the epoxy resin was LiCl from MERCK. It was used as a 50% solution in distilled water. An amount of 50 ppm catalyst solution with regard to the ROPOXID 501 resin was used.

The cross-linking agent for the modified epoxy resin was 4.4'-diaminodiphenylmethane (DDM), purchased from ACROS ORGANICS and with the following characteristics: M = 198 g/mol, m.p = 89^0C-91^0C; b.p = 398^0C.

2.2 Apparatus and procedure

The synthesis reaction has been conducted in the microwave field of an oven using an EG 1031 Hyundai INP-DK-1 (P = 1000W, frequency 2.45 Hz; Volume- 31L (multimode cavity); the microwave power has been adjusted by modification of the irradiation time.

The low molecular weight epoxy resin (ROPOXID 501) has been stirred in a porcelain dish, with diethylene glycol in a 2:1 molar ratio; an aqueous solution of 50 ppm 50% LiCl, used as catalyst, has been added to the system. After mixing, the reaction mass has been subjected to microwave irradiation for 26 min at a power of 300W.

Samples have been taken at different intervals for tracking the reaction progress.

Chemical analysis (ISO 3001) was used to measure the time variation of epoxy groups concentration. The possibility to use spectrophotometric methods (FT-IR) for quantitative measurements of epoxy groups has been also examined. FT-IR spectra were recorded with a JASCO FT- IR 6300 spectrometer equipped with an ATR Specac Golden Gate (sapphire/diamond) accessory.

3. Results and discussions

In order to obtain the conversion rate, the samples were characterized by epoxy index measured by chemical analysis and FT-IR spectrometry.

Mass reaction irradiation was stopped to limit the secondary reactions of polyaddition of epoxy groups at an epoxy index IE = 0.280 eq. /100g.

Fig. 1 presents the decreasing value of the epoxy index the reaction.

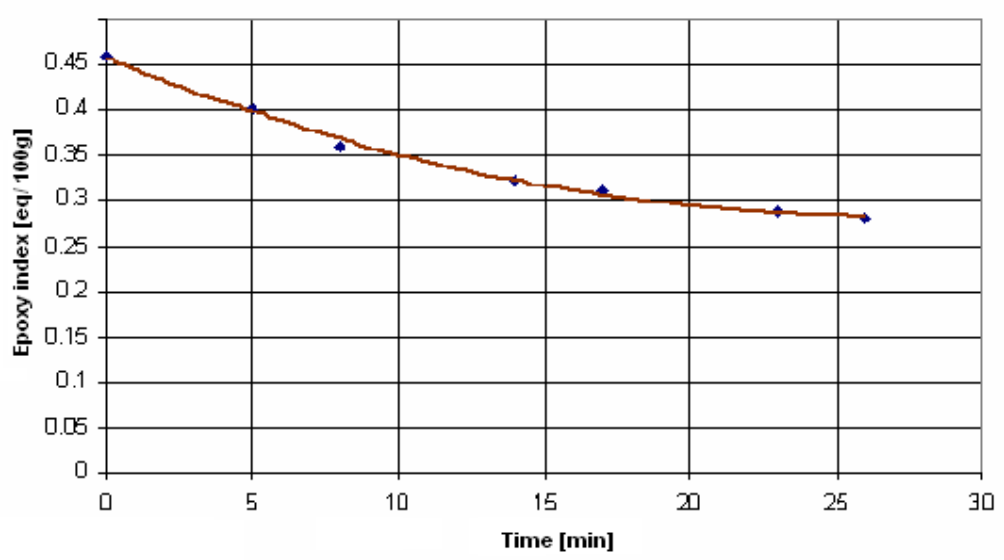

Fig.1. Variation of the epoxy index in time; 50 ppm LiCl 50%; 150^{0}C; [DGEBA]/[DEG] = 2:1

During the synthesis the conversion of the epoxy groups was also measured using the FT-IR method. Several absorption bands have been examined: 913 cm^{-1}(corresponding to the vibration of epoxy cycle) and 828 cm^{-1} (corresponding to the vibration of the C-H bond from the aromatic ring). The absorption spectra (IR) were also recorder for the initial resin-glycol mixture, final reaction mass, samples extracted during the reaction (Fig. 2).

A decrease of the area of the absorption band at 913 cm^{-1} was noticed during the reaction. The epoxy index variation has been evaluated from the change in the (A_{913}/A_{828}) ratio during synthesis according to equation (1), in which η is the conversion (%), and (A_{913} /A_{828})$_t$ is the ratio of the areas of the absorption peaks at 913 cm^{-1}and 828 cm^{-1}at time t, and (A_{913}/A_{828})$_0$ is the initial ratio (at time t = 0) of the areas of the absorption peaks at 913 cm^{-1}and 828 cm^{-1}.

$$\eta = \left[1 - \frac{\left(A_{913} / A_{828} \right)_t}{\left(A_{913} / A_{828} \right)_0} \right] \cdot 100 \qquad (1)$$

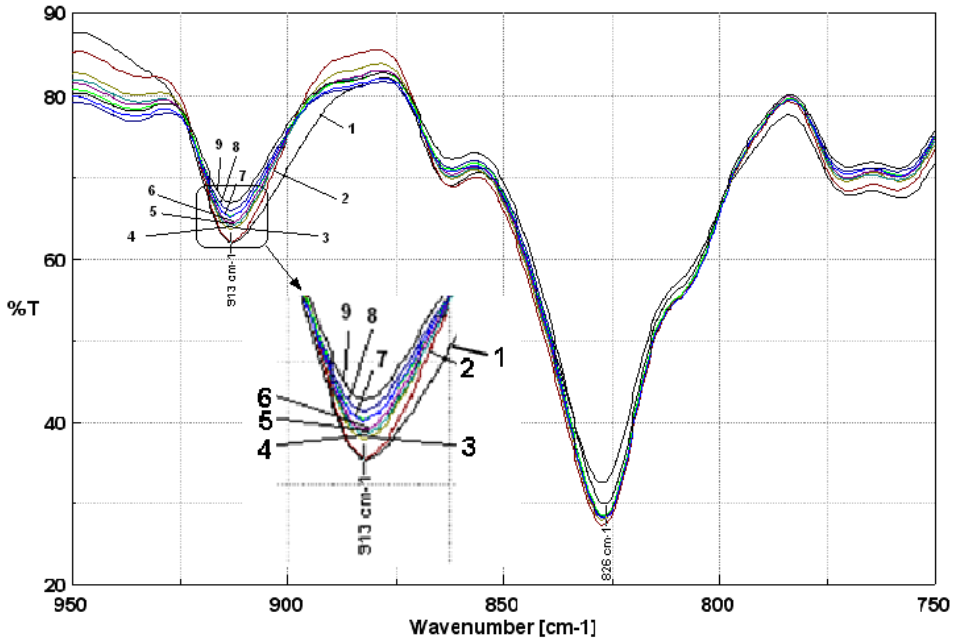

Fig.2. IR absorption bands at different reaction times (minutes): 0 (1); 5 (2); 8 (3); 11 (4); 14 (5); 17 (6); 21 (7); 23 (8); 26 (9); inset: detail of the bands between 875 and 925 nm

Fig. 3 shows a very good agreement between the two methods used for the quantitative analysis of the epoxy groups (chemical analysis, respectively FT-IR method).

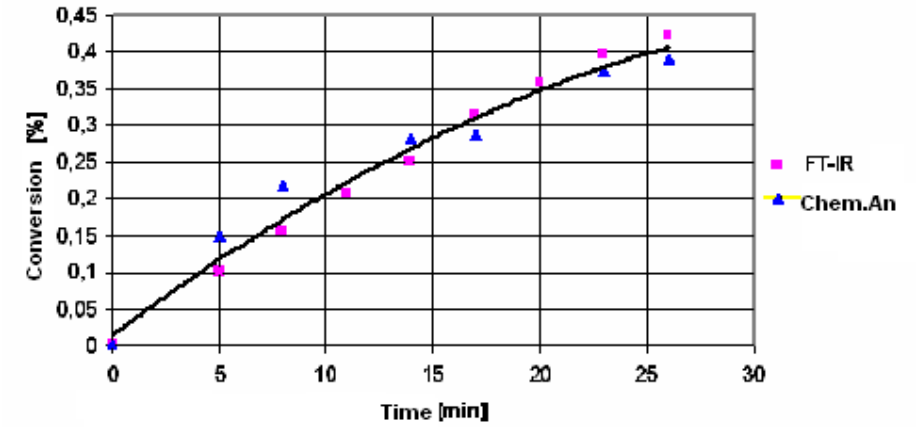

Fig. 3. Epoxy group conversion determination by chemical analysis (Chem. An) and FT-IR

The reaction rate v_r (given by equation (2)) depends both on the time (t) and temperature (T). At constant temperature (T=150^{0}C) the time dependency of the conversion α follows a polynomial dependency (3).

$$v_r = \left(\frac{d\alpha}{dt}\right) \tag{2}$$

$$\alpha = F(t,T) \tag{3}$$

Conversion values were used to calculate the reaction rate and, respectively, the reduced reaction rate α_0, evaluated from modified epoxy resin samples analysis during the process using the equation (4). The results obtained by chemical analysis and FT-IR for α, v_r, α_0, are shown in Tables 1 and 2, respectively.There is a good agreement of the calculated parameters.

$$\alpha_0 = \frac{\left(\frac{d\alpha}{dt}\right)}{(1-\alpha)^2} \tag{4}$$

Table 1

Variation of the reaction rate v_r (min^{-1}), conversion α , and reduced reaction rate **α_0 during the modification of the epoxy resin with DEG; data obtained from chemical analysis***

Time (min)	α. x 10^2	v_rx 10^2	α_0x 10^2
0	0	2,97	3,15
5	15	2,56	2,85
8	22	2,32	2,43
11	-	-	-
14	28	1,83	1,90
17	29	1,58	1,63
21	-	-	-
23	37	1,09	1,11
26	39	0,85	0,87

*Conditions: (constant temperature, 150^{0}C); [epoxy resin]/[DEG]=2/1)

Table 2

Variation of the reaction rate v_r (min^{-1}), conversion α, and reduced reaction rate **α_0 during the modification of the epoxy resin with DEG; data obtained from FT-IR***

Time (min)	α x 10^2	v_r x 10^2	α_0x 10^2
0	0	1,31	1,34
5	10	1,23	1,26
8	15	1,19	1,21
11	21	1,14	1,17
14	25	1,09	1,11
17	31	1,04	1,06
21	36	0,98	0,98
23	40	0,95	0,96
26	42	0,90	0,91

*Conditions:(constant temperature, 150^{0}C); [epoxy resin]/[DEG]=2/1)

The final epoxy resin has been further cured with 4.4'-diaminodiphenylmethane by heating up 60^0C for 18 hours, followed by a post-curing at 120^0C for 6 hours. The specimen bar obtained after the complete reticulation was then characterized in comparison with those for a standard resin. The physical-mechanical of the modified resin presented in Table 3.

Table 3

Phsico-mechanical properties of modified cured epoxy resine

Caracteristics	units	Method of analysis	DEG epoxy resin	Standard epoxy resin
Specific weight, 25 °C	g/cm^3	SR EN ISO 1183-1:2004	1,20	1.16-1.20
Tensile Strenght	MPa	ISO 527	60	40-70
Ultimate Elongation	%	ISO 527	7	4-6
Flexural Strenght	MPa	ISO 178	151	110-140
Charpy Impact Strenght	KJ/mm^2	ISO 179	14	8-12
Hardness, Shore D	grd	ISO 868	37	56
Dinamic Modulus (at 1MHz ultrasonic frequency)	MPa	ASTM 494	8528	8470

By analysing the data presented in Table 3, it can be noticed that the properties of flexibility and impact strength are superior for the modified epoxy resin as compared with the standard resins.

4. Conclusions

Modified epoxy resins with low molecular mass DEG were obtained by reaction of standard epoxy resin with glycol. The use of microwave irradiation reduces the reaction time and consequently improves the synthesis process.

Physical and mechanical determinations on specimens obtained by curing the resin with 4.4'-diaminodiphenylmetane have shown that the modified product has better flexibility and impact strength, as compared with the standard epoxy resin.

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