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Kinetics of the curing reaction of selected epoxy resin-amine systems

Summary — The paper is a review of authors' research works on curing reaction of some commercial and synthesized by them epoxy resins (among others — with liquid crystalline fragments). As curing agents 5 aromatic diamines differing in chemical structure were used. The results of investigation of curing kinetics by differential scanning calorimetry (DSC) confirm the significant effect of heating rate (up to 20 °C/min) on the process. It was found, for example, that for small heating rate (2—5 °C/min) DSC thermograms of epoxy resins with liquid crystalline fragments show double exothermic peak contrary to the thermograms of typical epoxy resins showing single exothermic peaks. This phenomenon is attributed to the formation of smectic structure during the curing (at temp. 132—162 °C). Usefulness of three various kinetic models (by Barret, Borchardt—Daniels or Kissinger) describing the curing process investigated have been compared.

Key words: epoxy resins, liquid crystalline fragments, amine curing agents, cure, kinetics.

KINETYKA REAKCJI UTWARDZANIA NIEKTÓRYCH UKŁADÓW ŻYWICA EPOKSYDOWA–AMINA

Streszczenie — Artykuł przedstawia przegląd własnych prac dotyczących reakcji utwardzania niektórych handlowych i syntetyzowanych przez autorów żywic epoksydowych [handlowej żywicy epoksydowej typu diglicydylowego eteru bisfenolu A (DGEBA), diglicydylowego eteru 4,4'-bifenolu (DGEBP), trzech różniących się podstawnikiem R we wzorze ogólnym (II) czerofunkcyjnych żywic epoksydowych otrzymanych na podstawie tetraglicydylowych pochodnych różnych diamin, a także związku epoksydowego zawierającego mezogeniczny fragment bifenylowy (DGEBP) bądź naftalenowy (DGEDHN)]. Jako utwardzacze zastosowano 5 różniących się budową chemiczną diamin aromatycznych (tabela 1). Wyniki badania kinetyki utwardzania metodą różnicowej kalorymetrii skaningowej (DSC, rys. 1—3, tabele 4 i 5) świadczą o istotnym wpływie szybkości ogrzewania (do 20 °C/min) na ten proces. Stwierdzono m.in., że w warunkach małej szybkości ogrzewania (2—5 °C) na termogramach DSC żywic epoksydowych z fragmentami ciekłokrystalicznymi (np. DGEBP, rys. 4) występuje podwójny pik egzotermiczny, w przeciwieństwie do termogramów typowych żywic epoksydowych z pojedynczym pikiem egzotermicznym. Zjawisko to przypisano tworzeniu się w trakcie utwardzania (temp. 132—162 °C) struktury smektycznej. Porównano przydatność trzech różnych modeli kinetycznych (Barretta, Borchardta—Danielsa i Kissingera, tabela 5) do opisu badanego procesu utwardzania.

Słowa kluczowe: żywice epoksydowe, fragmenty ciekłokrystaliczne, utwardzacze aminowe, utwardzanie, kinetyka.

Epoxy resins are the most important thermosetting polymers widely used as structural adhesives, composite materials, surface coatings, electronic devices and so on [1, 2]. Generally, epoxy resins show good dimensional stability, thermal stability, chemical resistance and electrical properties, but are brittle and reveal poor resistance to the crack propagation [3—6].

In order to obtain the resins for high performance applications numerous works have been done on the networks obtained by curing reaction of epoxy resins [7—11]. The studies showed that the synthesized materials had outstanding properties when the structures with liquid crystalline (LC) characteristics were incorporated into the networks [12—14].

One way to synthesize LC epoxy resins is the curing reaction of some functionalized potentially mesogenic rigid molecules with a suitable curing agent. Introduction of the mesogenic groups into the structure of the epoxy resins leads to the compounds that combine the properties which are specific to epoxy resins with those which are characteristic to the liquid crystals [15—17].

It is well known that the curing reaction of the epoxy resins is a very complex process, because many chemical reactions occur simultaneously during the cure. The final properties of the crosslinked epoxy resins depend on the kinetics of the curing reaction. Therefore, the kinetical studies contribute to better understanding of the cur-

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ing process and to improve the properties of the final products.

Dynamic differential scanning calorimetry (DSC) is one of the most useful techniques used for analysis of the curing process. Different curing characteristics like the temperature at which curing reaction is initiated and/or is finished, cure range, cure time, degree of cure, heat of reaction of the exothermic transition, can be evaluated by DSC. For LC epoxy resins other important techniques used to put in evidence LC character of the cured epoxy resins are both optical microscopy and X-ray diffraction.

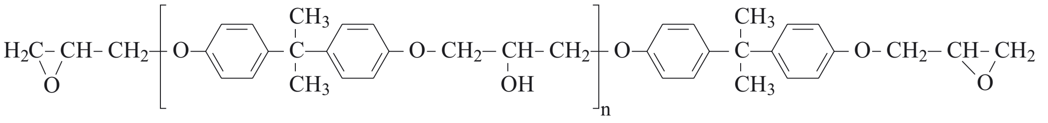
The present paper is a review containing our proper results regarding the curing reaction of some commercial and in laboratory synthesized epoxy resins, as well as of the epoxy resins displaying LC structure.

EXPERIMENTAL

Materials

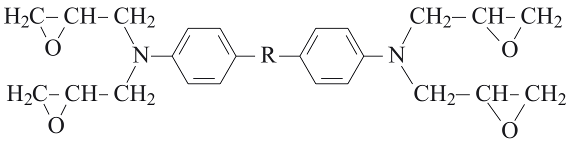
Some of the epoxy resins used in our works are as follows:

— DGEBA epoxy resin [formula (I)] is a commercial product (Sintofarm SA-Bucharest, Romania) obtained by the reaction between bisphenol A and epichlorohydrin (EPI). It has an epoxy equivalent of 0.54 and a number-average molecular weight of 500.


(I)

Diglycidyl ether of bisphenol A (DGEBA)

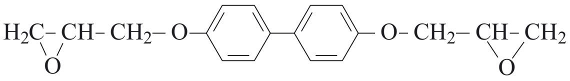
— The three tetrafunctional epoxy resins [general formula (II)] were prepared starting from the proper amines in the presence of an excess of EPI, as was reported elsewhere [18, 19].


(II)

where:

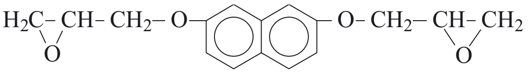
R = -O- : tetraglycidyl of diaminodiphenyl ether (TGDDE),
-CH_2-: tetraglycidyl of diaminodiphenyl methane (TGDDM),
-CH_2-CH_2-: tetraglycidyl of diaminodibenzyl (TGDDBZ)

— DGEBP [formula (III)] is a mesogenic containing biphenyl epoxy compound obtained according to the method reported previously, by a base-catalyzed reaction of EPI with the precursor dihydrobiphenyl [20].


(III)

Diglycidyl ether of 4,4'-biphenol (DGEBP)

— 2,7-DGEDHN mesogenic monomer [formula (IV)] was synthesized starting from 2,7-dihydroxy naphthalene (2,7-DHN), EPI and NaOH [21].


(IV)

Diglycidyl ether of 2,7-dihydroxy naphthalene (2,7-DGEDHN)

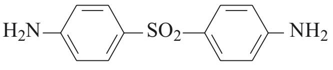
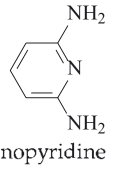
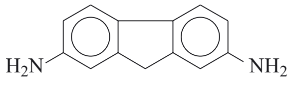
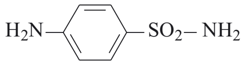
Curing

The curing reactions of the studied epoxy resins took place in the presence of various amines, used as the curing agents, which structures are shown in Table 1.

Kinetics analysis

The extent of the curing reaction was evaluated using DSC technique (Mettler 12E type differential scanning calorimeter) as well as size exclusion chromatography (SEC). The SEC analysis were performed using Waters chromatograph equipped with Styragel columns (HR5E and HR4E) and differential refractrometer R410.

Table 1. Amines used as the curing agents

a)	H_2N-$(CH_2)_2$-NH-$(CH_2)_2$-NH-$(CH_2)_2$-NH_2 Triethylenetetramine (TETA)
b)	 4,4'-Diaminodiphenylsulfone (4,4'-DDS)
c)	 2,6-Diaminopyridine (2,6-DAP)
d)	 2,7-Diaminofluorene (2,7-DAF)
e)	 Sulfanilylamide (SAA)

The basic assumption for the application of DSC technique to the cure of the thermoset polymers is that the rate of the kinetic process (dα/dt) is a function of conversion (α), and can be described by Eq. (1):

$$d\alpha/dt = K(T)f(\alpha) \tag{1}$$

The rate constant $K(T)$ of the curing reaction was estimated from variation of α *versus* time (t) using Barrett's relation [22] (2):

$$K(T) = \frac{d\alpha/dt}{A-a} = \frac{dH/dt}{A-a} \tag{2}$$

where: Z — *pre-exponential factor*, A — *total area of the peaks in DSC thermogram*, a — *partial area at a particular temperature (T)*, dH/dt — *heat flow (J/mol)*.

There is an Arrhenius type dependence between $K(T)$ and temperature according to Eq. (3):

$$K(T) = Ze^{-E_a/RT} \tag{3}$$

where: E_a — *activation energy*, R — *gas constant*, T — *absolute temperature*.

The kinetic parameters of the curing reaction were evaluated by Borchardt—Daniels method [23], using Eq. (4):

$$d\alpha/dt = K(T)(1-\alpha)^n \tag{4}$$

where: α — *fractional conversion*, $K(T)$ — *specific rate constant* (s^{-1}), n — *reaction order*, t — *time*.

E_a value determined taking into consideration all the used heating rates in the DSC experiments was evaluated by means of the Kissinger method [24] [Eq. (5)]:

$$\ln\beta/T_p^2 = \ln\frac{K_0}{\beta} - \frac{\beta}{T_p} \tag{5}$$

where: β — *scan rate* ($^oC/s$), T_p — *peak temperature in DSC trace*, K_0 — *Arrhenius pre-exponential factor* (s^{-1}), $\beta = E_a/R$.

The experimentally evaluated values of E_a were used to find the appropriate kinetic model which best describes the conversion fraction of the studied process.

The kinetic parameters of the curing process were determined too by isoconversional method given by Málek [25, 26] for the kinetic analysis of the data obtained by the thermal treatment. A two-parameter (n, m) autocatalytic model (Šesták—Berggren equation [27]) was found to be the most adequate selected to describe the cure kinetics of the analyzed epoxy resins. Once the kinetic model has been determined using the value of E_a, other kinetic parameters can be evaluated, such as pre-exponential factor and the kinetic exponents.

RESULTS AND DISCUSSION

Curing reaction of DGEBA

DGEBA epoxy resin was mixed with diglycidyl aniline (DGA), as a reactive diluent, and TETA, as the curing agent, at the weight ratios shown in Table 2.

The cure kinetics of the analyzed samples was studied by non-isothermal DSC technique, using different heating rates [6]. Figure 1 shows the DSC thermograms of DGEBA/TETA mixture (sample 1) recorded at 5, 10 and 20 ^oC/min.

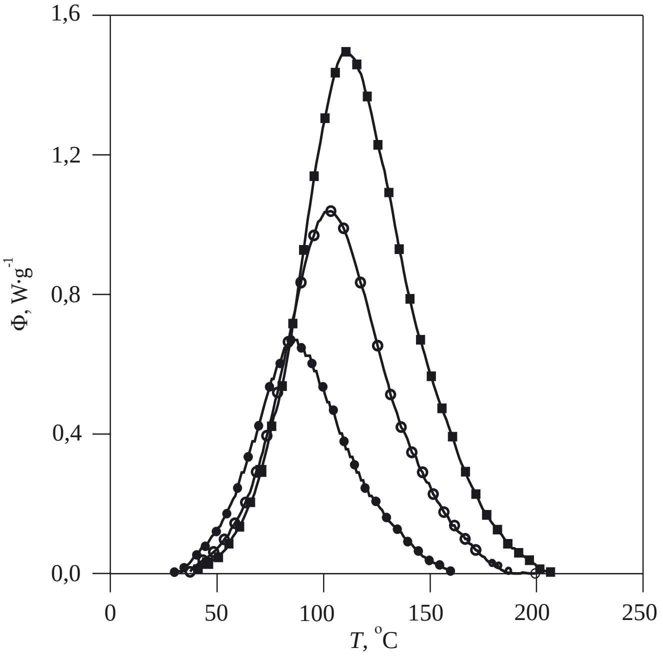


Fig. 1. Typical DSC curves recorded for DGEBA/DGA/TETA system at different heating rates: (●) 5 ^oC/min; (o) 10 ^oC/min; (■) 20 ^oC/min

T a b l e 2. Samples of DGEBA analyzed by DSC technique

Sample	Weight ratio of the components DGEBA/DGA/TETA
1	1/0/0.75
2	1/1/1.5
3	0/1/0.75

From DSC thermograms the following information on the curring reaction was obtained: initial curing temperature (T_i), peak temperature (T_p), final temperature (T_f) and curing range of the systems studied. Some data on the curing reaction of DGEB are summarized in Table 3.

T a b l e 3. Curing characteristics of DGEBA/TETA samples evaluated from DSC thermograms recorded at 10 ^oC/min heating rate

Sample*)	T_i, °C	T_p, °C	T_f, °C	Cure range °C	Cure duration min	ΔH, J/g
1	28	92	150	122	12.0	373
2	37	104	187	150	15.0	680
3	49	110	158	109	11.0	718

*) See Table 2.

Arrhenius plots from DSC scans recorded for the cured samples using Eq. (3) and the same α value were straight lines, the slope of which gave the value of E_a.

Table 4. Kinetic parameters of DGEBA curing reaction

Sample	Heating rate °C/min	E_a kJ/mol	ln$A$	Mean ln$A$ value	m	Mean m value	n	Mean n value
DGEBA/TETA	5	69.5	17.973	17.953	0.0147	0.0284	1.948	1.755
	10		18.061		0.0259		1.770	
	20		17.837		0.0447		1.549	
DGEBA/DGA/TETA	5	59.1	13.842	13.783	0.194	0.155	1.880	1.826
	10		13.727		0.156		1.732	
	20		13.779		0.114		1.865	

The kinetic parameters evaluated for the curing reaction of DGEBA led to observation that the studied curing processes can be described using the two-parameter autocatalytic kinetic model Šesták—Berggren [Eq. (6)].

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{6}$$

where: *m and n — kinetic exponents.*

Table 4 lists some kinetic parameters evaluated for the proposed Šesták—Berggren kinetic model.

As can be noted, the variation of the kinetic parameter values with the heating rate is placed in the experimental errors limit (within 10 % of the average value). The value of E_a determined by isoconversional method was 69.5 kJ/mol. The presence of the reactive diluent leads to decrease in E_a.

The kinetic parameters experimentally determined were used to calculate the theoretical DSC curves.

Curing reaction of multifunctional epoxy resins

Multifunctional epoxy resins are widely used in the manufacture of fibre-reinforced structures for high performance military and aerospace applications [28, 29]. The curing reaction of multifunctional epoxy resins is a complex process, due to the high functionality of the epoxy compounds, especially.

Curing reaction of three tetrafunctional epoxy resins, in the presence of TETA, was examined by DSC at different heating rates [15]. The chemical reactions involved in the curing reaction of the tested epoxy resins are shown in Scheme A.

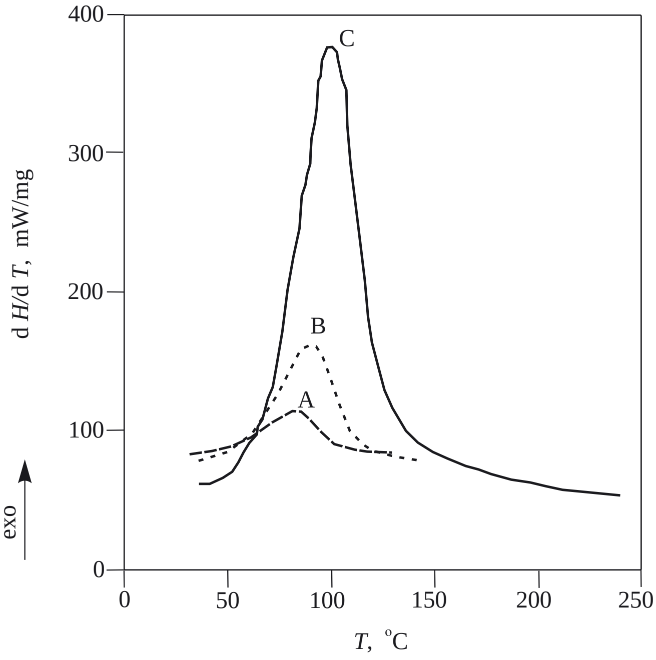
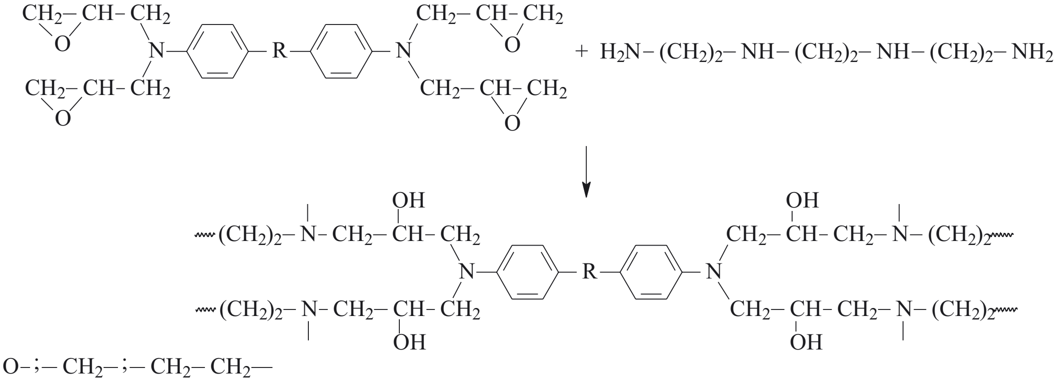


Fig. 2. Typical DSC curves for TGDDM/TETA system at different heating rates: (A) 5 °C/min; (B) 10 °C/min; (C) 20 °C/min

Figure 2 shows a typical example of DSC thermograms recorded for TGDDM/TETA mixture, at different heating rates, in the temperature range 40—250 °C. The kinetic parameters of the curing process were determined for all the synthesized tetrafunctional epoxy resins (Table 5).



where: R = – O–; – CH2–; – CH2– CH2—

Scheme A. Curing reaction of tetrafunctional epoxy resins/TETA systems

T a b l e 5. DSC kinetic parameters of the studied tetrafunctional epoxy resin/TETA mixture

System	Heating rate °C/min	Method								
		Barrett			Borchardt—Daniels			Kissinger		
		E_a kJ/mol	ln*A* min^{-1}	regression coefficient	E_a kJ/mol	ln*A* min^{-1}	*n*	E_a kJ/mol	ln*A* min^{-1}	regression coefficient
TGDDM/TETA	5	60.1	12.0	0.983	58.9	17.6	0.86	74.5	9.2	0.996
	10	77.8	14.9	0.962	72.3	22.3	1.04			
	20	72.6	12.5	0.952	76.0	24.4	1.06			
TGDDE/TETA	5	46.9	6.7	0.975	77.5	23.7	1.39	78.1	19.8	0.997
	10	45.1	2.3	0.964	78.1	26.1	1.98			
	20	43.5	1.9	0.995	76.2	25.0	2.02			
TGDBBZ/TETA	5	60.8	10.3	0.982	80.4	26.2	1.18	71.1	17.8	0.969
	10	59.4	13.5	0.916	64.3	17.3	1.26			
	20	67.9	25.7	0.974	76.8	45.4	1.28			

The kinetic data listed in Table 5 show important differences in E_a value, in function of both the used calculation method and the curing rate. The evaluated kinetic parameters support the assumption of the presence of the different reaction mechanisms, involving several steps, and hence the kinetics may be rather complex. The kinetic parameters (E_a, ln$A$ and n), determined using three different computational methods, show the great influence of the heating rate on the curing process. E_a determined at three heating rates (5, 10 and 20 °C/min) shows the values between 43 and 80 kJ/mol, which are in good agreement with the values reported for various epoxy-amine systems [30, 31].

Curing reaction of DGEBP

The phase transformation of DGEBP isotropic monomer was carried out by reaction of the rigid monomer with four tetrafunctional aromatic amines (see Table 1). Generally, the reactions which take place between DGEBP and the amines are shown in Scheme B.

The curing kinetics of DGEBP epoxy mesogenic resin, in presence of SAA, was studied by non-isothermal DSC technique, at different heating rates [32]. At low heating rates (2—5 °C/min) the curing reaction takes place by two processes evidenced by the presence of a double peak at DSC thermogram, while at higher heating rates (10 °C/min, for example) the processes are superposed in a single exothermal signal (Fig. 3).

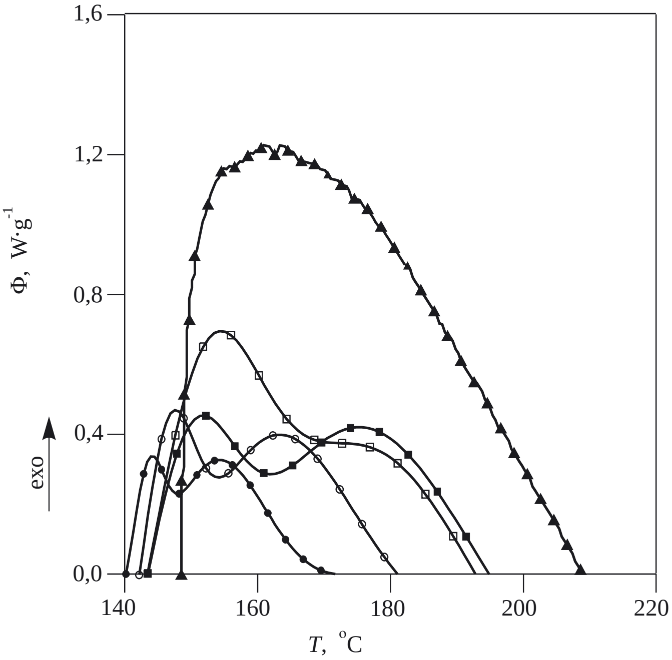
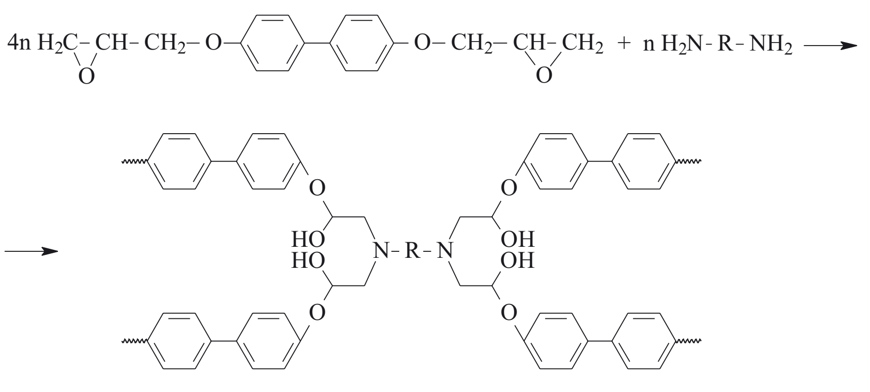


Fig. 3. Typical exothermal peaks recorded for DGEBP/SAA system at different heating rates: (●) 2 °C/min; (o) 3 °C/min; (■) 4 °C/min; (□) 5 °C/min; (▲) 10 °C/min [32]



Scheme B. Curing reactions of DGEBP with aromatic amines (DDS, SAA, DAP, DAF; for R see Table 1)

The curing reaction starts immediately after the melting of the two components of the mixture. The first process can be attributed to the nucleophilic attack of the primary amine onto the epoxy resin, while the second process corresponds to the formation of three-dimensional network structure showing LC properties — by the attack of previously formed secondary amine onto the epoxy groups, unreacted in totality in the first stage.

The curing studies carried out with DGEBP/SAA system show that the kinetics of the first process is complex: E_a decreases in function of conversion. The second process proceeds by a constant E_a (E_a = 59 kJ/mol) in the conversion interval α = 0.3—0.6. An autocatalytic kinetic model (Šesták—Berggren equation) was proposed to describe better the cure kinetics of the system studied.

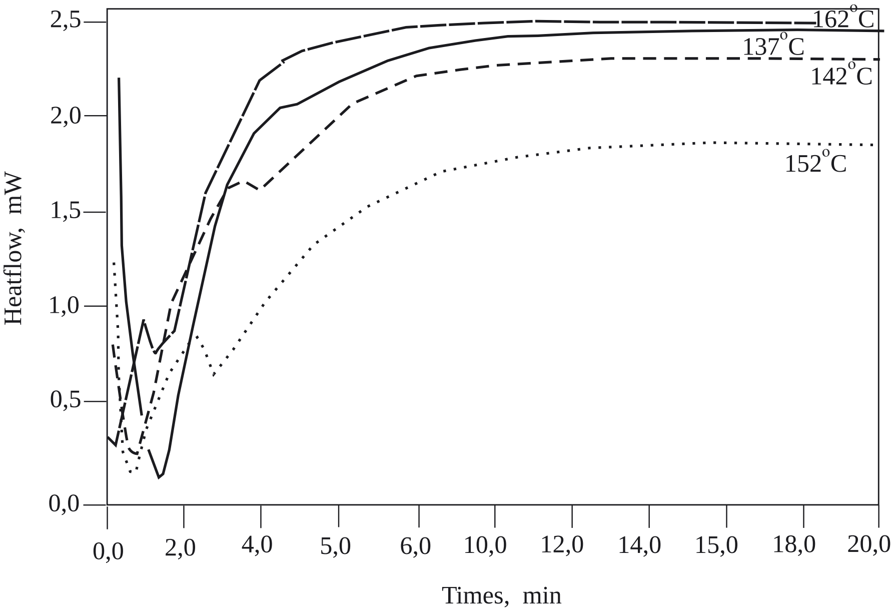


Fig. 4. Curing isotherms for DGEBP/DAF mixture obtained at various temperatures

The curing kinetics of DGEBP in the presence of DDS was investigated using SEC in the range of 155—175 °C above the melting temperature [20]. It was found that the ratio $r = k_2/k_1$ of secondary and primary amine hydrogen rate constants displayed unusually values higher than unity, and decreased with increasing temperature. This unusual higher reactivity of the secondary amine in the curing reaction of the mesogenic DGEBP monomer can be interpreted by an increased mobility of the functional groups in the nematic phase [33, 34].

The curing kinetics of DGEBP, as compared to DGEBA, in the presence of 2,6-DAP, has been studied by polarized light microscopy (PLM) and DSC techniques [35]. PLM in combination with wide-angle X-ray diffraction (WAXD) proved the formation of LC structure with the smectic type texture. For DGEBP/2,6-DAP mixture a great influence of the heating rate on the final morphology of the cured product was observed.

DGEBP monomer has not LC properties. The curing reaction of DGEBP with 2,7-DAF leads to a smectic type structure, in the temperature range 132 and 162 °C [36]. DSC technique evidences the complexity of the curing reaction, confirmed by the presence of a second peak (Fig. 4), in contrast with the traditional epoxy resins, when a single exothermal peak is remarked.

For the system studied the first peak is due to the reaction between the epoxy monomer and the curing agent. The presence of the second peak suggests a modification of the reaction mechanism, with formation of a smectic-type mesophase, which was evidenced by optical microscopy and X-ray diffraction.

Curing reaction of DGEDHN

The curing reaction of 2,7-DGEDHN mesogenic epoxy resin, in the presence of SAA, DAP or DDS amines as curing agents, was studied by DSC, OM and X-ray diffraction techniques [37].

Curing reaction of 2,7-DGEDHN/SAA mixtures led to a texture of nematic-like structure. The mixture of 2,7-DGEDHN/DAP, heated at 150 °C, presented a smectic-like structure of Schlieren type of high density. The curing reaction of 2,7-DGEDHN/DDS mixtures led to a network without LC properties.

The curing reaction of 2,7-DGEDHN in the presence of 4,4'-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA), 2,7-diaminofluorene (DAF) or 2-aminobiphenyl (2-ABP) was also studied [38]. The curing reaction of 2,7-DGEDHN/MCDEA mixture led to a product without liquid crystalline properties. The product obtained by the curing reaction of 2,7-DGEDHN/DAF mixture is characterized by a texture of smectic-like structure, while the mixture of 2,7-DGEDHN/2-ABP, when cured, formed an isotropic non-crosslinked product.

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