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Fluorescence probe–label methodology for in situ monitoring network forming reactions

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ABSTRACT

The curing of the stoichiometric reaction mixture diglycidyl ether bisphenol A (DGEBA) with *N*-methylethylenediamine (MEDA) and BEPOX 1268 formulation was monitored by FTIR (in the near IR region) and by fluorescence spectroscopy. 5-Dimethylamino-1-naphthalenesulfonamide derivatives and 4-dialkylamino-4′-nitrostilbene structural units were used as labels and/or probes. It has been proved that hardener in BEPOX 1268 formulation consists of amine containing the primary and secondary amino group. The rate constant for the addition reaction of the secondary amino hydrogen to epoxide is approximately two times larger than that of the primary amino group hydrogen in MEDA and several times (∼seven times) lower in the amine component of BEPOX 1268 formulation. The changes in the integrated fluorescence intensity of the label during the epoxy groups conversion indicate the most important changes in chemical transformations of the reaction mixture, i.e. primary reaction of the secondary amino groups, the *gel point* (DGEBA–MEDA) and entry of the system to the glassy state (for DGEBA–MEDA and BEPOX 1268). The change in slope of the fluorescence half bandwidth dependence on the epoxy groups conversion indicates the maximum concentration of the secondary amino groups in the reaction mixture (BEPOX 1268). It has been shown that the dependence of the first moment of the emission band vs. epoxy groups conversion can be used to determine the epoxy groups conversion in situ and in real time.

1. Introduction

The structural properties of epoxide resins are known to strongly depend on the polymerization degree, or extent of cure, and on the physical aging that has taken place after the cure cycle is completed. There exist several physicochemical methods for the characterization of cure and aging phenomena in the epoxides. Among them are such techniques as FTIR spectroscopy, thermal analysis, size exclusion chromatography, microdielectrometry, torsional braid analysis, ^{13}C solid state NMR, thermally stimulated current measurement, fluorescence and ESP spectroscopy. Of these methods, emission spectroscopy became very popular in the last two decades. Literature covering this subject includes in principle intrinsic and extrinsic fluorophore techniques.

The extrinsic fluorophore technique incorporates actually three approaches: (1) a fluorophore molecule-probe is added to the reaction mixture and does not take part in any reaction [1]; (2) the fluorophore moiety-label (at a low concentration) is covalently attached to the already existing prepolymer molecule, but the structure of this fluorophore does not change during the curing process; (3) the added compound contains reactive groups of similar (ideally of the same) reactivity as the main reaction component of a formulation and its fluorescence properties change as the curing reaction proceeds. These changes are caused by modification of the chemical structure of the fluorophore and by the immediate environment [2].

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The intrinsic fluorophore techniques take advantage of emission of the molecules that are components of the epoxide resin formulation and change their emission characteristics with progress of the curing reaction [3]. These changes are caused by chemical modification of the original molecules. Finally, a fluorophore moiety is part of one component of epoxide resin formulation and does not change its chemical structure during the curing process. The curing reaction then creates a polymer labeled with the fluorescent structural units [4].

Sung et al. [2,5] have studied monitoring of the cure reactions of epoxies and other network polymers intensively and extensively; their e.g. azochromophore labeling approach is unique allowing them to compare obtained experimental data with the theoretical prediction.

To the best of our knowledge there has not been any contribution comparing the use of the same fluorophore as a probe and label to monitor the curing process in the epoxies. In our case neither probe nor label change their chemical structure in the course of the cure.

The main objectives of this research in comparison with existing studies carried out in the past can be summarized as follows:

1. To compare behavior of the same fluorophore when used as a probe and label.
2. To analyze chemical composition of reaction mixture for one model reaction mixture and one commercial formulation.
3. To try to correlate the most important changes in chemical transformation of the reaction mixture with the fluorescence parameters.
4. To show that the dependence of the first moment of the emission band, $\langle v\rangle = \sum I_F(v)v / \sum I_F(v)$, on the epoxy groups conversion can be used in situ and in real time for determination of the degree of conversion with very low level of noise.

The curing of the stoichiometric model system diglycidyl ether bisphenol A (DGEBA)–*N*-methylethylenediamine (MEDA) and a commercial epoxide formulation BEPOX 1268 was carried out at 40, 60 and 20, 50 °C, respectively. Curing reaction was monitored by fluorescence of 5-dimethylamino-1-naphthalenesulfonamide (DNS) and 4-dialkyl-4′-nitrostilbene (DAANS) structural units used as a label and/or probe. Determination of the epoxy groups conversion was performed by FTIR in the near IR region.

2. Experimental part

2.1. Low molecular weight compounds—probes and label precursors: 5-dimethylamino-naphthalene-1-sulfonamide derivatives

N-(di-*n*-butyl)-5-dimethylamino-1-naphthalenesulfonamide (DNS-dBu) was prepared by reaction of DNS-Cl with an excess of di-*n*-butylamine according to procedure already described [6].

The product was homogeneous according to TLC; m.p. 67 °C.

$C_{20}H_{30}N_2O_2S$ (362.54 g/mol)
Calc. : C 66.26, H 8.34, N 7.73, S 8.83
Found : C 66.40, H 8.05, N 7.70, S 9.11

N-(2-Aminoethyl)-5-dimethylamino-1-naphthalenesulfonamide (DNS–EDA) was prepared by the reaction of DNS-Cl with ethylenediamine [6]. Colorless crystals were obtained. In comparison with Ref. [7] one hundred molar excess of ethylenediamine over DNS-Cl was used to minimize the amount of the disubstituted derivative. At lower molar ratios ethylenediamine/DNS-Cl, the product always contained a small amount of the disubstituted derivative. The product was homogeneous on TLC; m.p. 155.2 °C.

$C_{14}H_{19}N_3O_2S$ (293.39 g/mol)
Calc. : C 57.31, H 6.53, N 14.32, S 10.93
Found : C 57.32, H 6.56, N 13.99, S 11.03

DNS-Cl (Fluka) was used as received.

2.2. Low molecular weight compounds—probes and label precursors: 4-amino-4′-nitrostilbene derivatives (trans-4-amino-4′-nitrostilbene(trans-4-aminophenyl-4′-nitrophenyl-vinylen) (AmNST))

trans-4,4′-Dinitrostilbene(*trans*-bis-(4-nitrophenyl)-vinylen) was prepared by the reaction of 4-nitrobenzyl chloride with alcoholic sodium hydroxide [8,9]. The product was recrystallized five times from nitrobenzene and sublimated under high vacuum. m.p. 298.5 °C (Ref. [8]: 296–305 °C, Ref. [9]: 280–285 °C). AmNST was prepared by reducing *trans*-4,4′-dinitrostilbene with polysulfide in ethanol [9]. The product was crystallized from nitrobenzene and further sublimation of the product under high vacuum was carried out; m.p. 249 °C (Ref. [9]: 245–245.5 °C); UV (methanol): $\lambda_{max}/nm = 403.3$.

$C_{14}H_{12}N_2O_2$ (240.26 g/mol)
Calc. : C 69.99, H 5.03, N 11.66
Found : C 69.79, H 5.06, N 11.61

2.3. Other low molecular weight compounds

The diglycidyl ether bisphenol A-based epoxy was Aldrich product with a molecular weight 348 g/mol. The main chemical species is pure DGEBA ($M = 340$ g/mol). Aldrich product was purified by recrystallization from acetone and methanol, carefully dried and stored under nitrogen (m.p. 42.5–43.6 °C).

MEDA (Aldrich) was boiled over potassium hydroxide for 5 h and distilled.

BEPOX 1268 (GAIRESA, SA product, 1551 Lago-Valdoviño, La Coruña, Spain). The epoxide component is a mixture of DGEBA and epoxidized polyol (average functionality ~2.4). An equivalent weight of the epoxy groups equal to 256.4 g/equiv. as determined by acid titration. The amine component is LAROMIN C252 (BASF) (*N*-cyclohexyl-1,3-diaminopropane). The ratio of the epoxide to amine component in formulation equals 3.57/1 by wt.

2.4. Labeling of the epoxide component

Labeling of the epoxide component was performed by the reaction with DNS–EDA and/or AmNST. In a typical labeling experiment BEPOX 1268 (epoxide component) (25 g, ~0.0976 mol epoxy groups) was heated at 60 °C under stirring with DNS–EDA (0.0467 g, 0.159×10^{-3} mol) for 6 h. The efficiency of the labeling reaction was followed by TLC and SEC. At the end of the reaction time, according to TLC and SEC the reaction mixture did not contain any unreacted fluorescent compound. We can expect that the DNS structural unit is attached at the end of an ethylene spacer and this spacer is anchored to an epoxide dimer [6]. Owing to lower reactivity of the aromatic primary amino group in AmNST, reaction was carried out at 160 °C for 16 h. In both cases reaction conditions followed pattern reaction of the label precursors with phenyl glycidyl ether.

2.5. Experimental methods

2.5.1. Differential scanning calorimetry

A Perkin–Elmer DSC-7 (The Perkin–Elmer Corporation, Norwalk, CT, USA) differential scanning calorimeter was used for measurements. The samples of weight 5–15 mg were measured.

Determination of the epoxy groups conversion by FTIR in the near IR region was superior in all cases to DSC, as also reported by Billingham and co-worker [10]. Therefore, the determination of the epoxy and amino groups conversion was carried out by FTIR only.

The glass transition temperatures for the stoichiometric reactions mixtures were determined by DSC. The curing of the DGEBA–MEDA mixture was carried out in DSC equipment (40, 50 and 60 °C). The ultimate conversion was achieved by dynamic scan (30–200 °C) at scanning rate 5 °C/min. DSC thermograms were obtained by temperature scanning at the rate of 10 °C/min. The glass transition temperatures were evaluated by a computer program supplied by PE.

2.5.2. Fourier transform infrared spectroscopy

A Perkin–Elmer GX FTIR (Perkin–Elmer, Ltd., Beaconsfield Bucks, England) spectrometer was used to monitor the rate of disappearance of the epoxy ring and the primary amine group. All spectra were collected in the near IR (7000–4000 cm^{-1}) (FTnIR). Each spectrum was obtained, depending on the rate of the curing reaction, by averaging 4–20 scans at 4 cm^{-1} resolution with scanning rate (OPD) of 0.2 cm/s. Measurements were carried out at 20–60 °C using a temperature controller SPECAC. The epoxide formulations were cured in the disposable cells made from the microscope-glass slide plates with an optical path of 0.7–1.0 mm determined by the thickness of a Teflon spacer.

The main spectral bands of interest in the cure reaction and their assignment are in general agreement with those previously reported [11–13]. The main features in spectra are: (i) a decrease in the epoxy band at around 4530 cm^{-1}; (ii) a decrease in the primary amine groups at 4938 cm^{-1}; (iii) an increase in the hydroxyl bands in the region around 4800 cm^{-1}. The most significant feature is the appearance of the isosbestic point between the epoxy and hydroxyl groups bands. This indicates that Beer's law is obeyed over a wide range of conversion [14]. The integration of the epoxy and amino groups bands was carried out. The values of the integrated absorbance corresponding to ultimate curing were obtained after curing at 150 °C for 3 h. The analysis consists of measuring the integrated absorbance at two specified wave numbers—one corresponding to the changing epoxy and amino groups peak and the other to an invariant band. In each set of spectra, a band appearing invariant was chosen.

2.5.3. UV–VIS spectroscopy

All the spectra were taken on a Perkin–Elmer UV–VIS spectrometer LAMBDA 14P (Perkin–Elmer GmbH, Überlingen, Germany). The spectra of the components and of the epoxide resin formulations were measured in home-made cells from microscope-glass slide plates or spectrometric grade poly(methylmethacrylate). The optical path between 0.6 and 1.0 mm was determined by the thickness of a Teflon spacer. Wavelength cutoff absorption for glass used was 350 nm.

2.5.4. Fluorescence spectroscopy

The steady-state fluorescence spectra were taken on a Perkin–Elmer Luminiscence spectrometer LS 50B (Perkin–Elmer Ltd., Beaconsfield Bucks, England). In the case of the DNS fluorophore (label, probe) samples were excited at 350 nm. For the DAANS structural unit (label) excitation wavelength was the wavelength at maximum absorption 460 nm. In all cases the excitation and emission slits were equal. The samples of the neat epoxide resin formulations either labeled (the probe or label) or non-labeled were measured using the front-face (60°/30°) geometry in the disposable thermostated cells made from microscope-slide glass plates. Time dependent changes in the emission spectra with progress of the

curing reaction were recorded using the same fluorimeter provided with a homemade program. From particular emission spectra the integrated fluorescence intensity, emission maximum, half bandwidth and the first moment, defined by $\langle v \rangle = \sum I_F(v)v / \sum I_F(v)$, of the emission spectrum were obtained using the standard routines for the emission band integration and summation.

2.5.5. Gel point determination

The gel point for the DGEBA–MEDA and BEPOX 1268 resin formulation was determined using sol–gel analysis. The curing reaction took place in sealed Teflon tubing (inner diameter 0.4 cm, LEGRIS, France; ~1 g reaction mixture) allowed to cure at desired temperature. After certain time interval the sample was cooled down to 0 °C, the Teflon tubing was removed by longitudinal cutting in pieces and the reaction mixture was extracted with chloroform in a Soxhlet extractor for 15 h. The content of the gel portion was determined after drying in vacuum at 60 °C for 20 h. In our experiments the addition of acrylonitrile to block the amino groups [15], did not substantially influenced amount of the gel fraction.

2.6. Evaluation of the secondary and tertiary amino groups concentration in the reaction mixture

The concentration of the primary amino and epoxy groups was determined directly by FTIR. For an amine hardener containing both primary and secondary amino groups it is convenient to use the following notation: p_i, is the concentration of primary (p_1), secondary (p_2) or tertiary (p_3) amino groups at a given reaction time which come from the primary amino group of the hardener; s_i, is the concentration of secondary (s_2) and tertiary (s_3) amino groups which come from the secondary amino group of the hardener. For the stoichiometric reaction mixture epoxide–amine containing both the primary and secondary amino groups, the concentration of the secondary and tertiary amino groups can be calculated from the mass balances:

$$e_0 = e + p_2 + 2p_3 + s_3 \tag{1}$$

$$p_{10} = p_1 + p_2 + p_3 \tag{2}$$

$$s_{20} = s_2 + s_3 \tag{3}$$

where e_0, p_{10}, s_{20} are the initial epoxy, primary and secondary amino groups concentrations of the hardener, respectively. e, p_2, p_3, s_2 and s_3 are the corresponding concentrations at reaction time t. Unfortunately, FTnIR analysis of this reaction mixture does not allow simple determination of p_2, s_2, p_3 and s_3. It is necessary to define the overall secondary and tertiary amino groups concentrations.

By combining of Eqs. (1)–(3) and substitution a_3^* and a_2^* for $p_3 + s_3$ and $p_2 + s_2$, respectively, it is possible to obtain a_2^* and a_3^* according to Eqs. (4) and (5)

$$a_2^* = 2\beta p_{10} - \alpha e_0 + s_{20} \tag{4}$$

$$a_3^* = \alpha e_0 - \beta p_{10} \tag{5}$$

where a_2^* and a_3^* are the overall concentrations of the secondary and tertiary amino groups, respectively and α is conversion of the epoxy $(e_0 - e)/e_0$ and β is conversion of primary amine groups $(p_1^0 - p_1)/p_1^0$.

For the stoichiometric (di)epoxide–primary (di)amine systems, concentration of the secondary (a_2) and tertiary amino groups (a_3) was calculated analogously from the mass balances [16] (6) and (7).

$$a_2 = e_0(\beta - \alpha) \tag{6}$$

$$a_3 = e_0(\alpha - \beta/2) \tag{7}$$

2.7. Evaluation of the initial rate of the curing reaction

The apparent second-order reaction rate constants (catalyzed reaction $k_1^{app} = k_1[\mathrm{Cat}]$, $k_2^{app} = k_2[\mathrm{Cat}]$) for addition of the primary and secondary amino groups hydrogen atoms of the amine used for curing, were estimated by the initial reaction rates method. The time dependence of the epoxy and the primary amino groups concentration was fitted by a function and its derivative for $t = 0$ equals the sum of the reaction rates for the reaction of the primary and secondary amino groups and primary amino group, respectively. The apparent second-order reaction rate constants were calculated using the initial concentrations of the epoxy and amino groups.

3. Results and discussion

3.1. Labeling of epoxide component—UV/VIS and fluorescence spectra

Unique reactivity of the primary and secondary amino groups with the epoxy groups justified our effort to prepare fluorescent label precursors that contain the primary amino group. The epoxy groups react readily with the primary and secondary aliphatic amino groups and at higher temperature with the primary and secondary aromatic amino groups as well. At a high molar excess of the epoxy groups over a fluorophore containing the primary amino group, labeled molecule consists of a dimer of the epoxide component(s) containing fluorophore in the side chain [17]. Amino group nitrogen of the label precursor is a part of the epoxide dimer main chain. The structure of the labeled epoxide component

was proved not only by TLC analysis of the model reaction of phenyl glycidyl ether with DNS–EDA or AmNST, but for AmNST also from UV/VIS absorption spectra [17].

To eliminate background emission of the DGEBA–MEDA and BEPOX 1268 reaction mixtures, a relatively high concentration of the DNS fluorophore was used. Then the fraction of light absorbed by the DNS fluorophore is close to unity and the observed emission in the curing experiments represents the emission of the DNS fluorophore only. Details have been discussed elsewhere [18]. The re-absorption of the emitted radiation in spite of rather high optical density did not take place owing to a large Stokes shift of the DNS fluorophore in these reaction media.

The UV/VIS absorption of the DAANS fluorophore in the DGEBA–MEDA and BEPOX 1268 reaction mixtures is shifted farther in the visible region (the absorption maximum is at ~460 nm). In this case the excitation radiation is only absorbed by the DAANS structural units. Possible partial re-absorption of the emitted radiation due to a smaller Stokes shift in this case may distort blue edge of the emission spectrum. However, it has been shown that three times decrease in the concentration of the DAANS fluorophore moiety in this reaction mixture did not affect the course of the dependence of $\langle v \rangle$ on the epoxy groups conversion shown in Fig. 11a.

3.2. Extent of the curing reaction: diglycidyl ether bisphenol A-N-methylethylenediamine

The dependence of the epoxy groups conversion on cure time at 40 and 60 °C is shown in Fig. 1a. It should be pointed out that this reaction mixture in progress contains two types of secondary amino groups, i.e. formed by reaction of the epoxy group with the primary amino group and secondary amino group (R–NH–) in MEDA already present at the beginning of the curing reaction. Similarly, the overall content of the tertiary amino groups consists of the tertiary amino groups formed from the originally present primary amino groups and from secondary methyl amino groups.

The time dependence of the primary, overall secondary and overall tertiary amino groups concentration is shown in Fig. 1b and c for reaction temperature 40 and 60 °C, respectively. The most remarkable difference in comparison with similar dependencies for the DGEBA-primary diamines [6] is immediate and fast increase in the tertiary amino groups concentration at the beginning of the reaction. This observation indicates that the reactivity of the secondary amino group (CH_3–NH–) hydrogen is higher than that of the primary amine in MEDA. Actually the reaction rate constants (for the autocatalyzed reaction of the stoichiometric reaction mixture) determined [6] for *N*,*N*′-dimethylethylenediamine and ethylenediamine with the epoxy groups are $k_2 = 33.1 \times 10^{-4}$ kg^2 mole^{-2} min^{-1} for the former and $k_1 = 16.5 \times 10^{-4}$ kg^2 mole^{-2} min^{-1}, $k_2 = 6.5 \times 10^{-4}$ kg^2 mole^{-2} min^{-1} at 40 °C for the later. The reaction rate constant for the reaction of the secondary amine hydrogen in *N*,*N*′-dimethylethylenediamine with the epoxy groups is two times larger than that of the primary amine hydrogen in ethylenediamine. The dependence of the secondary amine groups concentration on the reaction time does not show a maximum (Fig. 1b, 40 °C) as is usual for the consecutive reactions. Nevertheless,

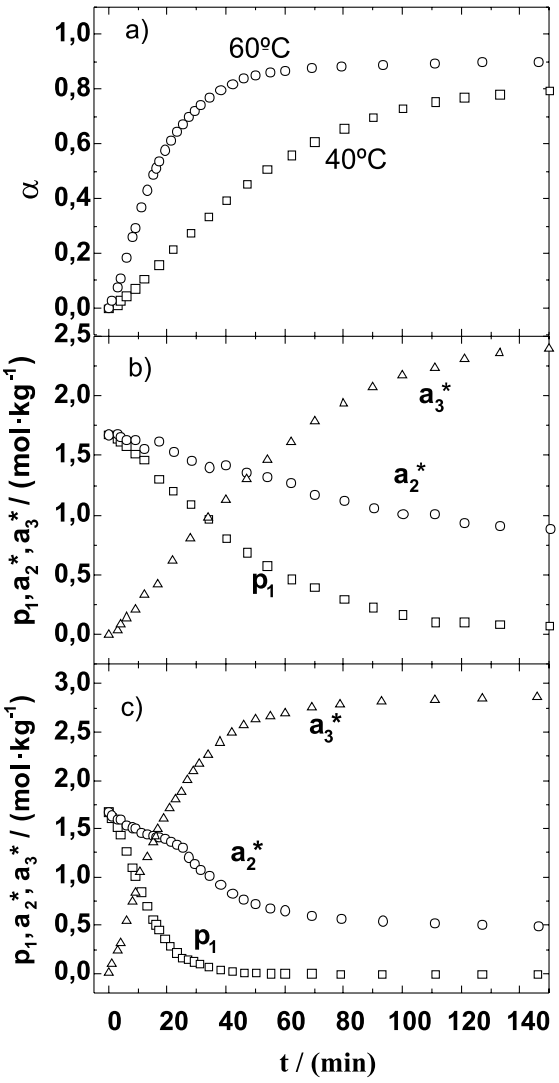

Fig. 1. The dependence of the epoxy groups conversion α (a), and of the primary (p_1), overall secondary (a_2^*), and overall tertiary (a_3^*) amino groups concentrations at 40 (b) and 60 °C (c) on cure time (t) for the stoichiometric reaction mixture DGEBA–MEDA.

Fig. 1c (curing at 60 °C) clearly shows that the addition of the primary amine hydrogen to the epoxide ring takes place simultaneously with reaction of the secondary amine group hydrogen of MEDA. The shoulder on the secondary amine concentration curve demonstrates superposition of a decaying concentration of the *N*-methylamino groups with increasing concentration of the secondary amine formed by reaction of the primary amino groups with the epoxide groups. This secondary amino groups are further consumed in the consecutive reactions with the epoxy groups giving tertiary amino groups.

3.3. Extent of the curing reaction: BEPOX 1268 epoxide formulation

On the basis of FTIR spectra we can guess that BEPOX 1268 formulation is the stoichiometric reaction mixture of the epoxide and amine components. In spite of the fact that the composition of particular components of BEPOX 1268 is not exactly defined, analysis of the experimental data clearly showed the presence of an amine containing the primary and secondary amino group. The time dependence of the primary (p_1) and calculated overall secondary (a_2^*) and overall tertiary (a_3^*) amino groups concentration (according to Eqs. (4) and (5)) is shown in Figs. 2 and 3 for 20 and 50 °C, respectively. In comparison with the DGEBA–MEDA system, the rate constant of the addition of the primary amino group of *N*-cyclohexyl-1,3-diaminopropane (amine component of the BEPOX 1268 formulation) to the epoxide is much larger than that of the secondary amino group. The maximum on the a_2^* time dependence is clearly seen at both temperatures. The determined apparent second-order rate constants for addition of the primary (k_1^{app}) and secondary (k_2^{app}) amine hydrogens to the epoxide are summarized for the stoichiometric DGEBA–MEDA mixture and BEPOX 1268 formulation in Table 1 and support the aforementioned observations. It is quite obvious that the experimental data for BEPOX 1268 do not obey reaction scheme for the stoichiometric mixture (di)epoxide-primary (di)amine (Eqs. (6) and (7)). A large systematic deviation leading to the negative values in the tertiary amino groups concentration at the beginning of the curing process was observed (Fig. 4).

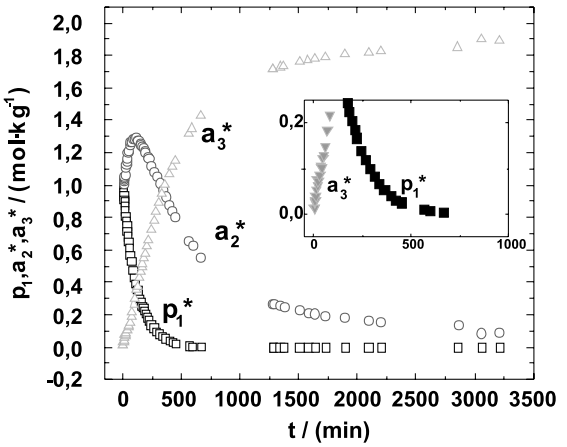

Fig. 2. The dependence of the primary (p_1), overall secondary (a_2^*), and overall tertiary (a_3^*) amino groups concentration on cure time (t) for BEPOX 1268 formulation at cure temperature 20 °C.

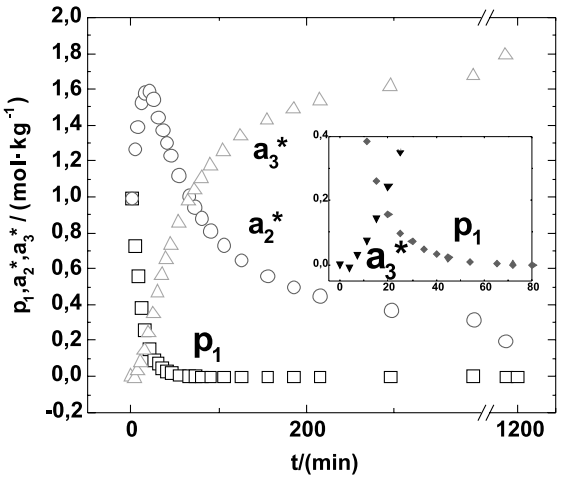

Fig. 3. The dependence of the primary (p_1), overall secondary (a_2^*), and overall tertiary (a_3^*) amino groups concentrations on cure time (t) for BEPOX 1268 formulation at cure temperature 50 °C.

Table 1
The apparent reaction rate constants for addition of the primary (k_1^{app}) and secondary (k_2^{app}) amino groups to the epoxy group in diglycidyl ether bisphenol A (DGEBA)–*N*-methylethylenediamine (MEDA) reaction mixture and in BEPOX 1268 formulation

Reaction mixture	Curing temperature (°C)	$10^3 \cdot k_1^{app}/(kg \cdot mol^{-1} \cdot min^{-1})$	$10^3 \cdot k_2^{app}/(kg \cdot mol^{-1} \cdot min^{-1})$
DGEBA–N-MEDA	40	2.5	3.5
	60	7.8	13.4
BEPOX 1268	20	3.3	0.23
	50	22.7	3.6

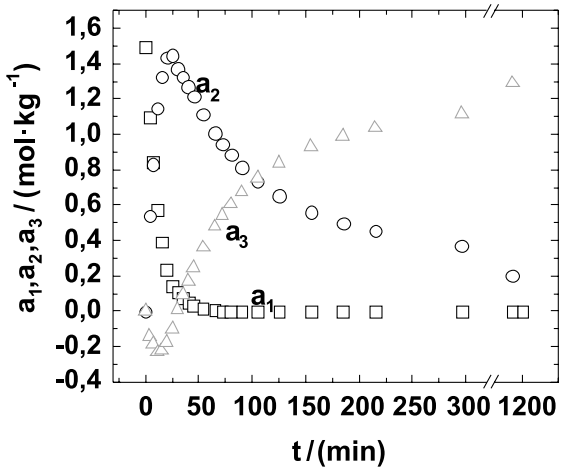

Fig. 4. The dependence of the primary (a_1), secondary (a_2), and tertiary (a_3) amino groups concentrations on cure time (t) for BEPOX 1268 formulation at cure temperature 50 °C (calculated using Eqs. (6) and (7) supposing that reaction mixture consists of diepoxide and primary diamine).

3.4. Fluorescence monitoring of curing reaction: DGEBA–N-methylethylenediamine

Fig. 5 illustrates the time evolution of the emission spectrum for the aforementioned system. The initial fast increase in the emission intensity of the DNS label is primarily due to the fast reaction of the secondary amino group of MEDA with epoxy groups followed by a decrease in the emission intensity at the maximum, but at the same time by an enormous increase in the half bandwidth (Fig. 6).

The change in the integrated fluorescence intensity characterizing the curing process for the stoichiometric

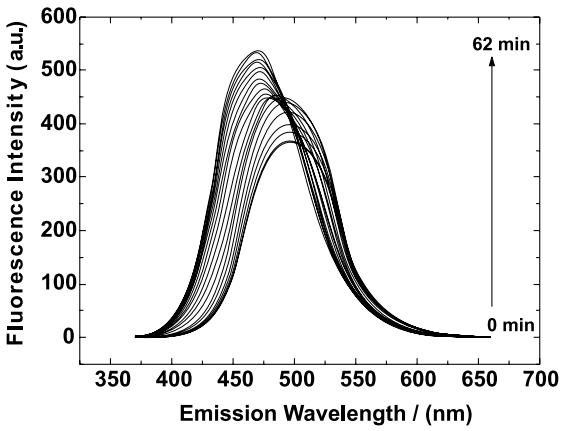

Fig. 5. Time evolution of the fluorescence emission spectrum for the DNS labeled stoichiometric reaction mixture DGEBA–MEDA at reaction temperature 40 °C. Concentration of the DNS label 5.39×10^{-3} mol kg^{-1} of reaction mixture.

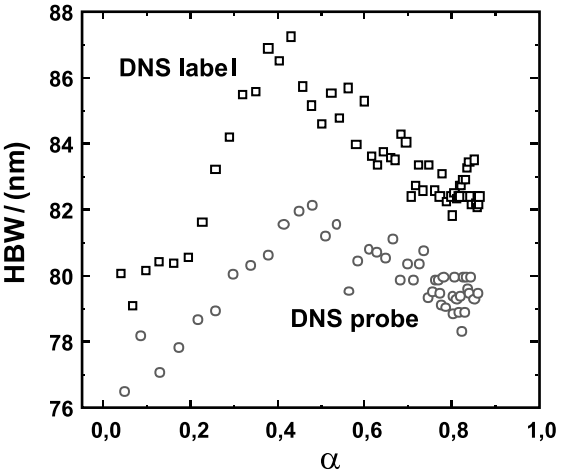

Fig. 6. The dependence of the half bandwidth (HBW) of the DNS label and probe on the epoxy groups conversion (α) for the stoichiometric reaction mixture DGEBA–MEDA at cure temperature 40 °C. Concentration of the DNS label and/or probe 5.39×10^{-3} mol kg^{-1} of reaction mixture.

reaction mixture DGEBA–MEDA with the DNS label and/or DNS probe together with the dependence of the glass transition temperature on the epoxy groups conversion is shown in Fig. 7.

In the dependence of the integrated fluorescence intensity on the epoxy groups conversion for the DNS label (Fig. 7b) one can observe several regions as in the system DGEBA-ethylenediamine [6]:

Region 1. The reaction of the epoxy groups primarily with the secondary amino groups of MEDA is accompanied by an increase in the viscosity of the medium and a corresponding increase in the fluorescence quantum yield of the DNS fluorophore. At the beginning of the curing the tertiary amino groups are formed mostly by reaction of the secondary amino groups of MEDA with the epoxy groups. Primarily linear low molecular weight compounds are being formed in accordance with the low T_g values obtained for $\alpha < 0.3$. At the same time a moderate increase in the half bandwidth of the emission band can be observed (Fig. 6).

Region 2. An abrupt increase in the half bandwidth with conversion takes place. We can assume that large increase in the half bandwidth of the emission band is caused by the onset of the tertiary amino groups concentration—the actual branching points formed by reaction of the secondary amino groups with epoxide oligomers.

Region 3. A monotonous increase in the integrated fluorescence intensity takes place, caused by increasing viscosity of the system, molecular weight and branching reactions. At the epoxy groups conversion $\alpha \sim 0.63$ (Fig. 7a) the glass transition temperature reaches the cure temperature ($T_{cure} = T_g = 40$ °C). The entry of the

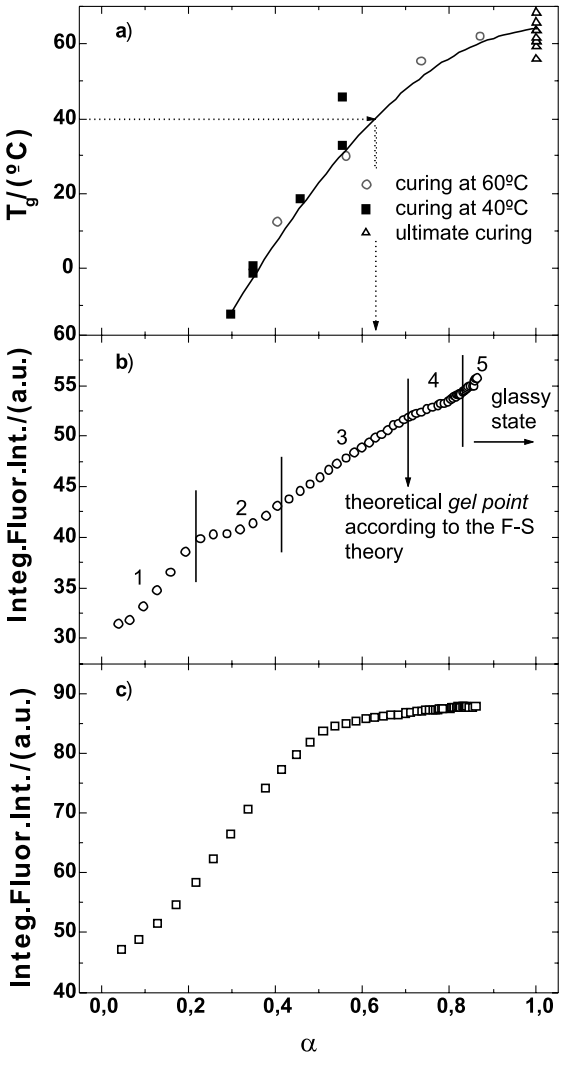

Fig. 7. The dependence of the glass transition temperature (T_g) (a), the integrated fluorescence intensity (Integ. Fluor. Int) for the DNS label (b) and DNS probe (c) on the epoxy groups conversion (α) for the stoichiometric reaction mixture DGEBA–MEDA at cure temperature 40 °C. Concentration of the DNS label and/or probe 5.39×10^{-3} mol kg^{-1} of reaction mixture.

system to vitrification region [19] is monitored neither by label nor probe.

Region 4. The onset of this part of the curve is characterized by a change in slope. At conversions around the gel point conversion (according to the Flory–Stockmayer theory conversion of epoxy groups at the *gel point* for this system is 0.707) it can be observed that the linear trend of fluorescence intensity decreases its slope in about 40%. The increasing fraction of the gel in this region is accompanied by a moderate decrease in the mobility of the DNS label and thereby an increase in its fluorescence quantum yield.

Region 5. A further steep increase in the integrated fluorescence intensity at the epoxy groups conversion $\alpha \sim 0.83$ was observed. According to analogy with the other systems studied (kinetics and fluorescence study on the curing of the DGEBA-ethylenediamine and/or *N*,*N*′-dimethylethylenediamine systems) [6] we can interpret this change as a consequence of entry of the system to the boundary between vitrifying and vitrified regions. On the threshold of the glassy state, strongly limited mobility of the polymer molecule segments imposes further mobility restriction on the fluorophore attached to the polymer molecule and an increase in the fluorescence quantum yield occurred.

The "wavy" course of the fluorescence intensity is only observed when the fluorophore is attached to the polymer chain. The gel point and the last stage of curing reaction, which is characterized by entry of the system to the glassy state, are not sensed if the fluorophore is a probe (Fig. 7c).

The emission of the DNS label in the DGEBA–MEDA occurs from less relaxed fluorophore in comparison with the DNS probe. The DNS label is attached at the end of a short ethylene spacer in the microenvironment of the polymer chain. In comparison with the DNS probe translational and rotational diffusion of the DNS label is partially hindered. Dissipation of the excitation energy is therefore less efficient during the excited life time of the fluorophore and emission takes place from a higher energy state. The half bandwidth indicates less homogeneous microenvironment of the DNS label than probe (Fig. 6). With increasing epoxy groups conversion, the emission of the DNS label takes place from progressively less relaxed state and the steady-state spectra show a larger half-width, irrespective of whether the relaxation is continuous or two-state. The half bandwidth attains its maximum at $\alpha \sim 0.4$. Owing to increasing viscosity of the medium at higher epoxy groups conversion than 0.4, emission proceeds primarily from the less relaxed state. This process is characterized by a decrease in the half bandwidth. The reorientation ability of the DNS probe in comparison with the DNS label may be at high epoxy groups conversions still higher. As a consequence, the DNS probe emits still from partially relaxed fluorophore. Therefore, the difference between half bandwidth at the maximum and half bandwidth at the highest conversion is larger for the DNS label than for DNS probe.

3.5. Fluorescence monitoring of curing reaction: BEPOX 1268 epoxide formulation

In comparison with the DNS labeled DGEBA–MEDA system, DNS labeled BEPOX 1268 does not show a "wavy" dependence of the integrated fluores-

cence intensity on the epoxy groups conversion. Owing to the fact that the fluorescence properties of the fluorophores are generally influenced by the polarity and viscosity of the (micro)surrounding, in the case of the epoxide multicomponent mixture one cannot expect distinct changes in the viscosity of the reaction mixture even for the initial stage of curing (for BEPOX 1268—basically reaction of the primary amino groups takes place at the early stage of the curing only). The features of the dependence of the integrated fluorescence intensity on the epoxy groups conversion such as sharp changes in the slope are "washed out" owing to polydispersity in the chemical composition and in the distribution of the epoxy groups in the epoxide component. Nevertheless, derivative of this dependence for cure temperature 50 °C shows pronounced discontinuity at $\alpha \sim 0.64$. This value is in a good agreement with the experimentally determined conversion at the gel point ($\alpha_{gel} = 0.63$) (the sol–gel analysis). The DNS probe in BEPOX 1268 formulation at cure temperature 50 °C senses neither the gel point. At the epoxy groups conversion $\alpha \sim 0.80$ (Fig. 8a) the glass transition temperature reaches the cure temperature ($T_{cure} = T_g = 20$ °C). Entry of the system at cure temperature 20 °C to vitrification region is monitored neither by label nor probe. Analogous to the other systems [6], an abrupt increase in the integrated fluorescence intensity at $\alpha \sim 0.91$ (Fig. 8b) is caused by entry of the system to the glassy state. This change is not sensed by the DNS probe in the same system.

The emission of the DNS label in BEPOX 1268 occurs from less relaxed fluorophore in comparison with the DNS probe and the half bandwidth indicates less homogeneous microenvironment of the DNS label (Fig. 9b) in comparison with the DNS probe. Similar behavior was observed for the DGEBA–MEDA reaction mixture. At higher temperature (50 °C) these differences become smaller.

The curing experiments for the DAANS labeled BEPOX 1268 were performed at 50 °C. The integrated fluorescence intensity increases monotonously with increasing epoxy groups conversion. No dominant changes characterizing the important stages of the curing process were observed. The dependences of the primary, overall secondary and overall tertiary amino groups concentration on the epoxy groups conversion together with the dependence of the half bandwidth for DAANS and DNS label are depicted in Fig. 9a and b, respectively. Discontinuity in the half bandwidth dependence occurs in both cases at the epoxy groups conversion $\alpha \sim 0.33$. This value of α is coincident with the maximum of the dependence of the overall concentration of the secondary amine groups on the epoxy groups conversion. In the region of conversions 0–0.33 primarily addition reaction of the primary amino groups to epoxy groups take place, as can be deduced from Fig. 9a.

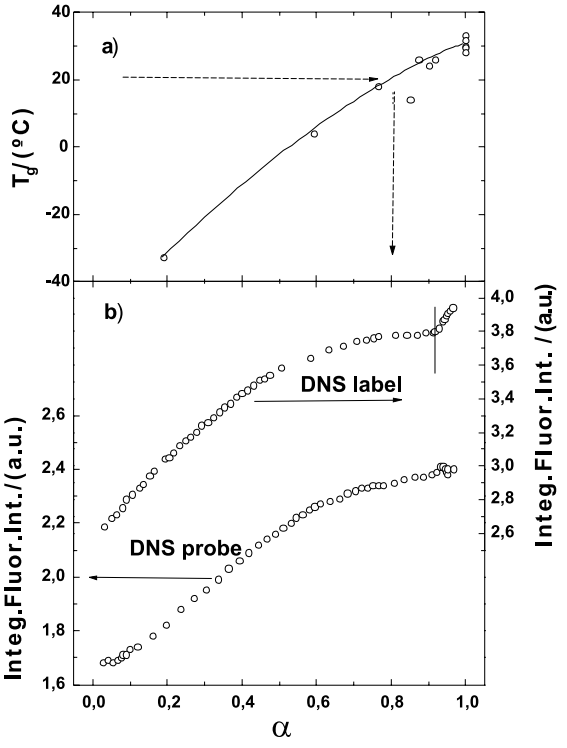

Fig. 8. The dependence of the glass transition temperature (T_g) (a) and the integrated fluorescence intensity (Integ. Fluor. Int.) (b) for DNS label and DNS probe on the epoxy groups conversion (α) for BEPOX 1268 formulation at cure temperature 20 °C. Concentration of the DNS label and/or probe 4.96×10^{-3} mol kg^{-1} of reaction mixture.

Further addition reaction of the secondary amino groups to the epoxy group gives rise to fast increase in the concentration of the tertiary amino groups characterized by a change in slope of the dependence of the half bandwidth on the epoxy groups conversion.

3.6. Determination of the conversion degree—treatment of experimental data

Changes in the fluorescence parameters of some fluorophores that accompany polymerization reactions have been utilized for monitoring of polymerization processes. According to aforementioned results the most significant features of some fluorophores is that they display a fluorescence wavelength shift and change in the magnitude of the fluorescence intensity as the polyaddition reaction proceeds.

The run-to-run reproducibility of the profile shape of the fluorescence intensity signal is generally good; however, the reproducibility of the absolute intensity values when measuring samples in front-face geometry is in most cases unsatisfactory. For this reason an intensity

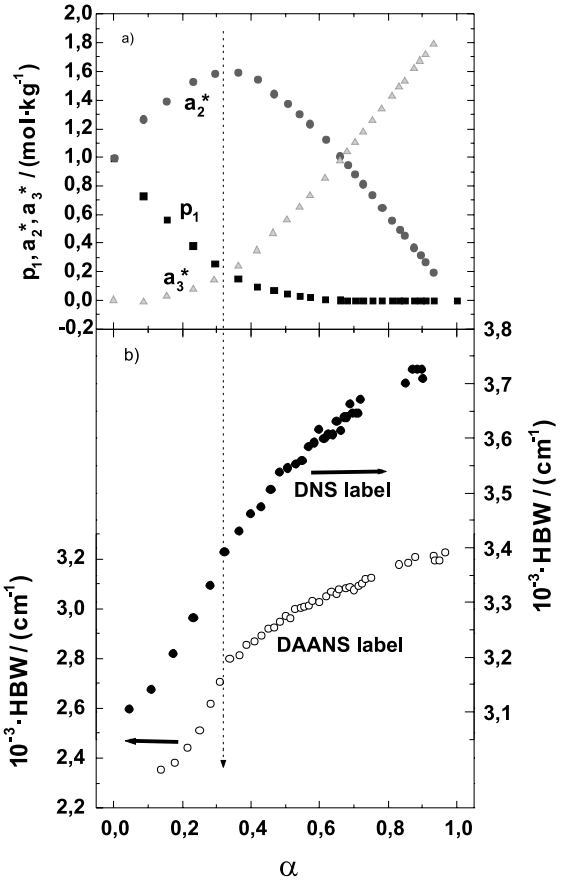

Fig. 9. The dependence of the primary (p_1), overall secondary (a_2^*), overall tertiary (a_3^*) amino groups concentration (a) and the half bandwidth (HBW) (b) for the DNS label and DAANS label on the epoxy groups conversion (α) for BEPOX 1268 at cure temperature 50 °C. Concentration of the DNS and DAANS label is 4.96×10^{-3} mol kg^{-1} and 1.11×10^{-3} mol kg^{-1} of reaction mixture, respectively.

ratio method using fluorophores for monitoring polymerization processes has been reported [20,21].

Changes in the fluorescence maximum wavelength as a function of cure degree produce a highly characteristic signal profile which is reproducible and also reveals sometimes the main chemorheological events with a distinct change in slope [6]. However, the determination of the emission maximum for broad emission bands (e.g. for the DNS fluorophore) is not very accurate and suffers from a large scatter. We have proposed to evaluate the first moment (the center of gravity) of the emission band ($\langle \nu \rangle$) defined by Eq. (8).

$$\langle \nu \rangle = \sum I_F(\nu)\nu / \sum I_F(\nu) \tag{8}$$

where $I_F(\nu)$ is the intensity of fluorescence at wavenumber ν. To compare this method with the ratio intensity method a brief analysis of data has been carried out for BEPOX 1268 labeled with the DNS and/or DAANS fluorophore at cure temperature 20 and 50 °C, respectively. Generally, the shape of the dependence of the fluorescence intensity ratio on the epoxy groups conversion depends on the pair of emission wavelengths used for the evaluation of this ratio. In Fig. 10a is shown for illustration the emission spectrum of the DAANS label in BEPOX 1268 formulation at the beginning and at the end of the curing process. The wavelength corre-

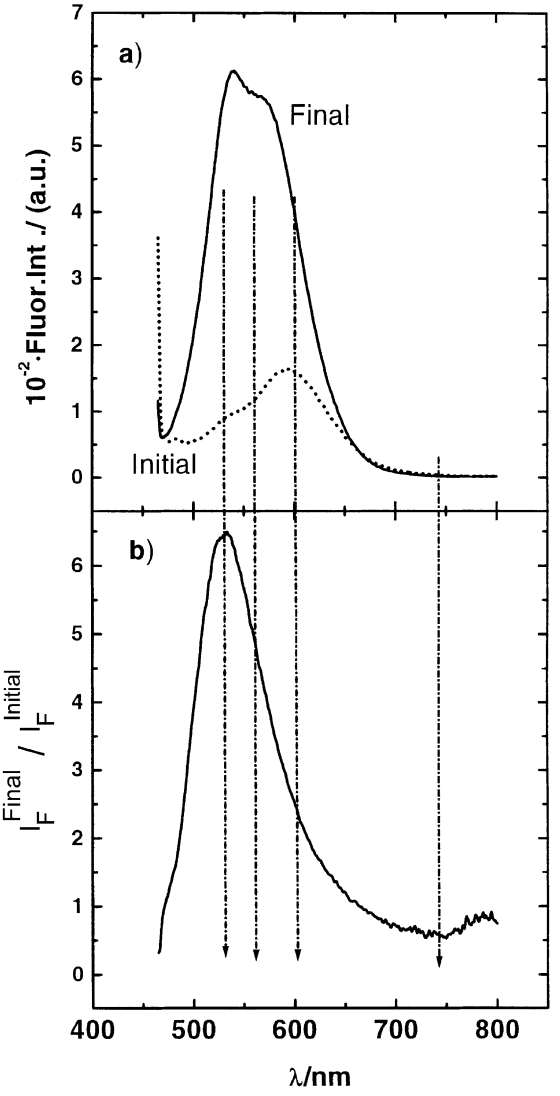

Fig. 10. The emission spectra (a) of the DAANS label for the initial (MIK11) and final (MIK36) stage of the curing and the dependence of the fluorescence intensity ratio (I_F^{MIK36}/I_F^{MIK11}) (b) on emission wavelength (λ) for BEPOX 1268 at cure temperature 50 °C. Concentration of the DAANS label 1.11×10^{-3} mol kg^{-1} of reaction mixture.

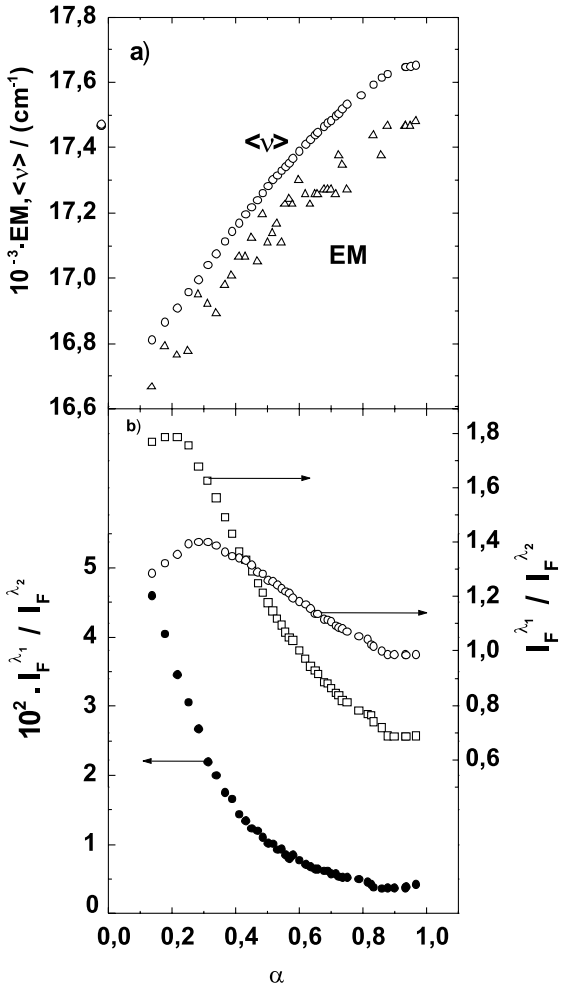

Fig. 11. The dependence of the emission maximum (EM), the first moment of emission band ($\langle \nu \rangle$) (a) and the fluorescence intensity ratio ($I_F^{\lambda 1}/I_F^{\lambda 2}$) (b) at emission wavelengths λ_1 and λ_2 on the epoxy groups conversion (α) for the DAANS labeled BEPOX 1268 formulation at cure temperature 50 °C. (b) λ_1: (•) 740, (□) 600, (○) 560 nm; λ_2 : (•, □, ○) 532 nm. Concentration of the DAANS label 1.11×10^{-3} mol kg^{-1} reaction mixture.

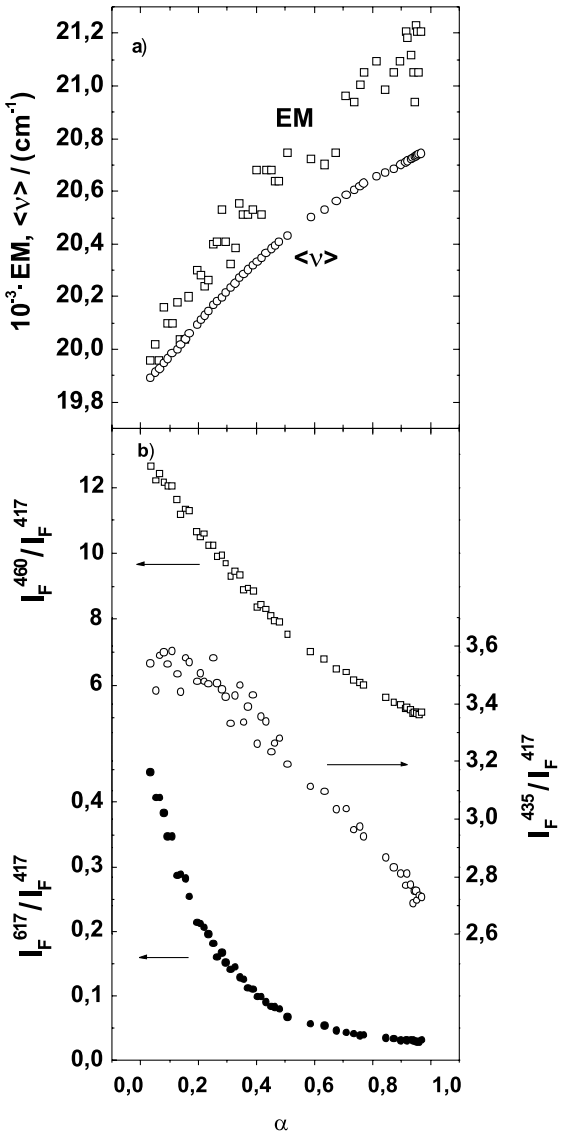

Fig. 12. The dependence of the emission maximum (EM), the first moment of emission band ($\langle \nu \rangle$) (a) and the fluorescence intensity ratio($I_F^{\lambda}1/I_F^{\lambda}2$) (b) at emission wavelengths λ_1, λ_2 on the epoxy groups conversion (α) for the DNS labeled BEPOX 1268 formulation at cure temperature 20 °C. Concentration of the DNS label 4.96×10^{-3} mol kg^{-1} of reaction mixture.

sponding to the lowest and highest intensity change is 740 and 532 nm, respectively. As can be seen from Fig. 11b the ratio of the fluorescence intensities at these wavelengths is not sufficiently sensitive to the changes in the high epoxy groups conversion region. Similar behavior was observed for all systems studied. For BEPOX 1268 formulation labeled with the DNS fluorophore at cure temperature 20 °C (see Fig. 12). The dependencies of the fluorescence intensity ratio for other pairs of wavelengths are generally more sensitive to changes in the high conversion region; these dependencies may be more or less smooth depending on the quality of the fluorescence data and on the absolute fluorescence intensity values. Correlation of the first moment of the emission band with the epoxy groups conversion is straightforward and does not require any preliminary treatment of data. Limitations of the intensity ratio method and the dependence of $\langle \nu \rangle$ on the epoxy groups conversion for determination of the epoxy groups conversion were discussed elsewhere [16]. A smooth correlation was found between the first moment of the emission band $\langle \nu \rangle$ and the degree of the epoxy

groups conversion in comparison with analogous dependence for the emission maximum (Figs. 11a and 12a). The results show that correlation between $\langle v \rangle$ and conversion degree provides a method for monitoring the curing of epoxide systems.

4. Conclusions

The determination of the epoxy and primary amino groups concentrations by FTnIR analysis and evaluation of the overall secondary and overall tertiary amino groups from the mass balances for the model stoichiometric reaction mixture DGEBA–MEDA allowed us to confirm the type of the diamine used in BEPOX 1268 resin formulation. It has been shown that the secondary amino group in MEDA is approximately two times more reactive than the primary amino group and several times less reactive in *N*-cyclohexyl-1,3-diaminopropane in reaction with the epoxy groups.

The DNS labeled DGEBA in the reaction mixture with MEDA senses (the integrated fluorescence intensity, the half bandwidth vs. the epoxy groups conversion) the initial addition reaction of the secondary amino groups to the epoxy group, the gel point and at cure temperature 40 °C, entry of the system to the glassy state (the integrated fluorescence intensity vs. the epoxy groups conversion).

The DNS labeled BEPOX 1268 senses at 50 °C not very distinctly the gel point and at 20 °C entry of the system to the glassy state.

The DNS and/or DAANS labeled BEPOX 1268 sense at 50 °C maximum concentration of the secondary amino groups in the system (the half bandwidth vs. epoxy groups conversion).

Owing to a number of factors that influence fluorescence properties of the fluorophores used as probes or labels, features of the data such as the onset of the tertiary amino groups concentration [6], the maximum concentration of the secondary amino groups [18], the gel point [6] and entry of the system to the glassy state [6,18] can be sensed under certain conditions:

1. The systems have to be as far as possible monodisperse in the chemical composition and in distribution of the epoxy and amino functionalities, that is to say, single chemical individuals with unique reactivity.
2. The amine component should possess amino groups that differ substantially in the reactivity toward the epoxy groups.
3. Distinct changes in features of the data can be observed at certain temperatures only.

The conversion degree of the epoxy groups can be determined from the plot $\langle v \rangle$ vs. epoxy groups conversion (determined by an absolute method e.g. FTnIR) with a lower level of noise than previously reported by other methods.

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