Pergamon

0014-3057(94)E0018-Y

Eur. Polym. J. Vol. 30, No. 8, pp. 969–973, 1994

0014-3057/94 $7.00 + 0.00

THERMAL DEGRADATION OF *p*-NONYLPHENOL FORMALDEHYDE EPOXY RESINS

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(Received 27 April 1993; accepted 17 September 1993)

Abstract—Epoxy resins synthesized from *p*-nonylphenol formaldehyde novolac resins in reaction with epichlorohydrin have been studied by thermogravimetry, differential thermal analysis and pyrolysis in combination with gas chromatography. The epoxy resins investigated in the range of temperatures between 200 and 600° show a complex degradation mechanism. The complexity of the reaction increases passing from the liquid resins to the solid resins, when the apparent thermal stability increases too. The organic decomposition products analysed include gases and liquids. They consist of C_1–C_4 saturated and unsaturated aliphatic hydrocarbons, carbonylic compounds, ethers, aromatic hydrocarbons, phenol, cresols and higher phenols, respectively. Phenol and cresols are the main decomposition products evolved at temperatures below 350°, while content of aromatic hydrocarbons becomes importantly at temperatures between 400 and 600°.

INTRODUCTION

Both phenol formaldehyde and epoxy resins have wide applications in electronic engineering as insulating, in automobile industry, in adhesive production and as chemical coatings. Although these materials have good chemical and mechanical characteristics, they are not stable enough to oxidation at high temperatures.

The thermal behaviour of epoxy resins has been extensively studied. Most studies refer to epoxy resins based on the diglycidyl ether of bisphenol A, as such, or cured with amines and anhydrides. In the case of these kinds of resins the decomposition products were identified with the aid of pyrolysis-mass spectrometry experimental technique [1], and the quantitative and qualitative composition of the components having low molecular weight have been established [2]. Other experimental techniques have been used for the study of the thermal degradation of epoxy resins, such as: pyrolysis-gas chromatography [3–5], pyrolysis-gas chromatography-mass spectrometry [6, 7], vaporization gas chromatography-mass spectrometry [8, 9], thermogravimetry [10], differential thermal analysis [11] and infrared spectroscopy [12], respectively. The majority of these studies were centred on the identification of the pyrolysis products and on assumptions of some decomposition mechanisms of the thermal reactions.

The pyrolysis of epoxy resins with low molecular weight up to 2000 (liquids and solids) takes place as described below [2, 13]. The light components present in the original resin exhibit evaporation at temperatures between 40 and 200°. Both the side groups and end groups start to detach from the resin in the temperatures range within 200 and 300°, and some light volatile gases are formed. The liquid materials, a low molecular weight epoxide fraction, which are present in the original resin or are formed as a result of the thermal degradation of the resin at temperatures between 200 and 300°, suffer, in, succession, a thermodestruction process at temperature 300°.

In our laboratory new epoxy resins were synthesized starting from *p*-nonylphenol formaldehyde novolac resins with low molecular weight in a reaction with epichlorohydrin. These kinds of epoxy resins, used as pressure-sensitive adhesives, especially, have not yet been analysed by thermal degradation. This paper discusses an investigation into the thermal degradation of an epoxide based on the glycidyl ether of *p*-nonylphenol formaldehyde resins, using the following experimental techniques: thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and pyrolysis in combination with gas chromatography (P–GC).

EXPERIMENTAL PROCEDURES

Resins synthesis

Synthesis of *p*-nonylphenol formaldehyde epoxy resins was carried out starting from *p*-nonylphenol formaldehyde novolac resins. The latter were obtained by acidic catalysis (H_2SO_4), using a reaction mixture with a formaldehyde (F)/*p*-nonylphenol (*p*-NF) molar ratio between 0.32 and 1.0, in cyclohexane [14].

The *p*-nonylphenol formaldehyde novolac resins were transformed into the epoxy resins with the aid of epichlorohydrin, the reaction being performed in basic medium using solutions of NaOH in mixture with dimethyl sulfoxide and water [15]. The epoxy resins synthesized (Table 1) have an epoxy equivalent between 1.111 and 0.250% and a chlorine content around 1%.

The number-average molecular weight of the resins synthesized was evaluated by a cryoscopic method, using hexane as solvent.

Thermal characterization techniques

The TG experiments were carried out with a MOM-Budapest derivatograph, under the following conditions: sample weight 50 mg, heating rate 12°/min, the reference

Table 1. *p*-Nonylphenol formaldehyde epoxy resins analysed by TG and P–GC

Sample No.	Molar ratio F/*p*-NF used at synthesis	$\bar{M}_n$ of *p*-nonylphenol formaldehyde novolac resins	$\bar{M}_n$ of *p*-nonylphenol formaldehyde epoxy resins
1	0.32	500	640
2	0.50	580	810
3	0.67	620	1170
4	0.75	740	2020
5	1.00	1400	3150

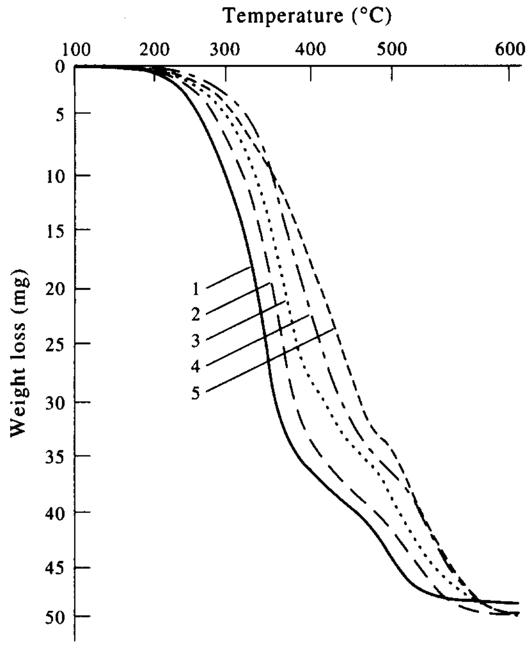


Fig. 1. TG curves for decomposition in air of *p*-nonylphenol formaldehyde epoxy resins.

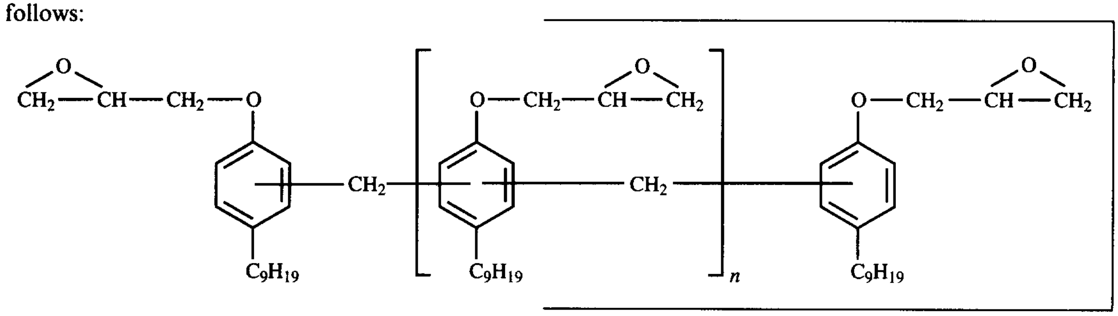
material α-Al_2O_3 and decompositions took place in a current of air with a rate of 30 ml/min.

The P—GC experiments were performed by means of a filament type pyrolysis unit described elsewhere [16]. The separation and the analysis of the thermal decomposition products were carried out with a Siemens L-400 gas chromatograph, under the following operating parameters: the stainless steel chromatographic column (2 x 3 mm i.d.) was packed with Chromosorb W (60–80 mesh) acid washed and coated with 5% carbowax 20 M; the column temperature was programmed from 60 to 200° at a rate of 7°/min and then operated isothermally at 200°; carrier gas was argon with a rate of 12 ml/min.

The resins weighed in small platinum boats were pyrolysed at temperatures between 200 and 600°. The identification of the thermal decomposition products was made by calibration vs the pure substances.

RESULTS AND DISCUSSION

The structure of *p*-nonylphenol formaldehyde epoxy resins synthesized here can be written as follows:



where, $n = 2$–10.

Thermogravimetric analysis

Figures 1 and 2 show dynamic TG and DTG curves recorded for *p*-nonylphenol formaldehyde epoxy resins, respectively.

As can be seen in Fig. 1, the TG curves indicate a decomposition of the resins analysed very close to each other. However, it is observed that the resins with low molecular weight (up to 1200) degrade faster than the resins with higher molecular weight. This behaviour, which was remarked and reported and for *p*-nonylphenol formaldehyde novolac resins [17], could be due to the presence of a liquid resinous material (*p*-nonylphenol glycidyl ether, for instance) in the low molecular weight resins (samples 1, 2 and 3) in a quantity larger than in the resins with higher molecular weight (samples 4 and 5). In accordance with other data reported for some epoxy resins with low molecular weight [1, 2, 13] the high molecular weight liquid products suffer a degradation starting with temperatures >200° and lead to organic and inorganic gases. The presence of epoxy fragments, non-volatile at temperatures up to 300°, and their decomposition at temperatures >200° could be the explanation and the line of TG curves recorded for samples 4 and 5. From Fig. 3, it can be presumed that sample 5 has such liquid epoxy materials in a ratio larger vs sample 4 and hence an advanced decomposition is remarked for resin 5 at the temperatures placed between 200 and 350°.

The TG curves in Fig. 2 show an increase in the complexity of the thermal degradation mechanism passing from the liquid resins (samples 1 and 2) to the semi-solid resins (samples 3 and 4) and to the solid resin (sample 5). This is evidenced by the increase of the number of thermodegradation stages, as is shown in Table 2. Thus, while sample 1 shows two decomposition stages and sample 2 presents three decomposition stages, samples 3, 4 and 5 degrade after four thermal decomposition stages.

A common degradation stage is observed for all samples analysed; the first stage of decomposition, when significant mass losses (*W*%) were recorded. Table 3 shows some kinetic data evaluated by means of the method of Coats and Redfern [18], e.g. the

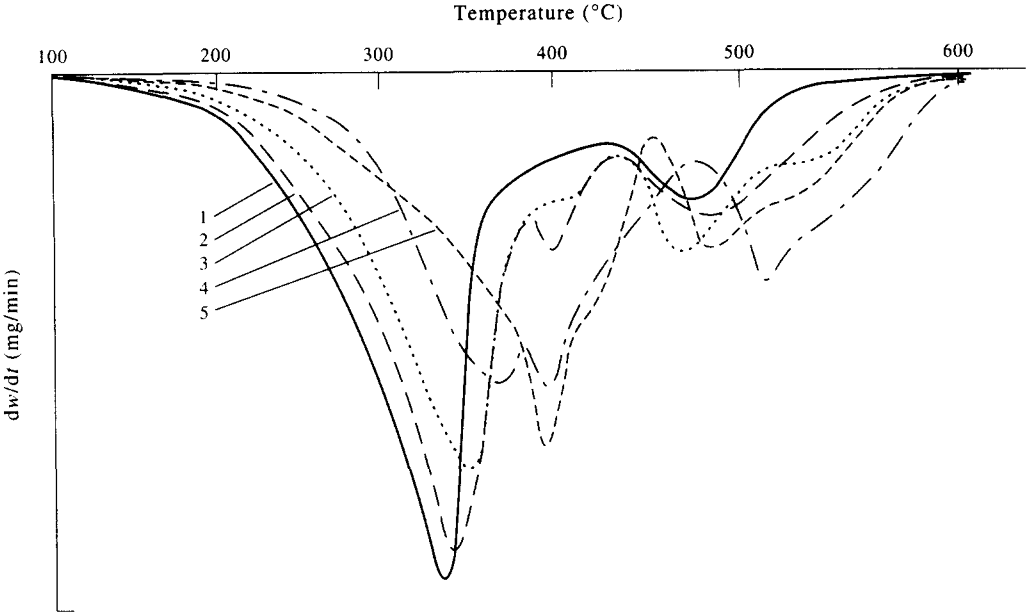


Fig. 2. DTG curves for decomposition in air of *p*-nonylphenol formaldehyde epoxy resins.

activation energy (E_a), the reaction order (n) and the temperature corresponding to the medium decomposition rate (T_m).

The experimental data listed both in Tables 2 and 3 show that the epoxy resins analysed degrade statistically, with E_a ranging within 16.0 and 20.0 kcal/mol and a reaction order around 1. The values of the all kinetic parameters are close and this suggests the fact that differentiations in the thermal behaviour of the resins analysed could be made only by the conversion intervals. The T_m shifting from the value of 330 (resin 1) up to 400° (resin 5) suggests an increase of the apparent thermal stability of the solid resins vs the liquid resins.

The important information regarding the thermoxidative destruction of epoxy resins could be obtained and from the DTA technique. Figure 3 shows the DTA curves recorded for three resins analysed in the range of temperatures between 0 and 600°.

Generally, on DTA curves in Fig. 3, a common endothermic stage is distinguished in the range of

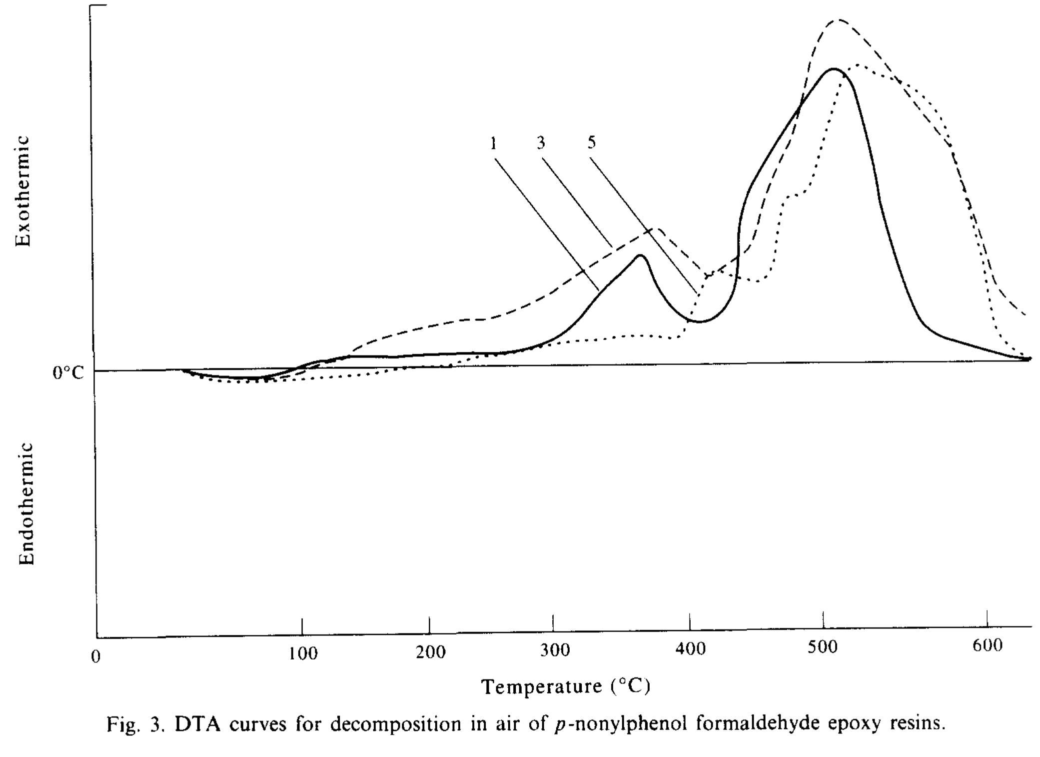


Fig. 3. DTA curves for decomposition in air of *p*-nonylphenol formaldehyde epoxy resins.

Table 2. Some thermogravimetric data of the epoxy resins analysed

Sample No.	First stage		Second stage		Third stage		Fourth stage	
	T (°C)	W (%)	T (°C)	W (%)	T (°C)	W (%)	T (°C)	W (%)
1	180–480	75	480–580	25	—	—	—	—
2	190–390	72	390–480	9	480–590	19	—	—
3	200–380	64	380–440	8	440–540	16	540–590	12
4	210–375	52	375–480	39	480–530	7	530–590	2
5	210–420	48	420–460	28	460–510	14	510–590	10

temperatures between 30 and 200° which could be assigned to the volatilization of undesirable components, which are present in the starting materials (water, solvent and other low molecular weight compounds).

The exothermic effects recorded at temperatures between 350 and 360°, respective 500 and 520°, are in connection with proper thermodestruction of the epoxy resins analysed. The maximum observed in Fig. 3 at temperatures around 350°, more pronounced for the resins 1 and 3 and less pronounced for the resin 5 (this is in favour of the higher thermostability of the solid resin), is due to the decomposition of the products obtained by rupture of the larger fragments existing in the original resin, or formed during the thermal degradation of the resins at lower temperatures (*p*-nonylphenol glycidyl ether or phenol glycidyl ether). The decomposition of the carbonization products takes place with char formation at temperatures >500°.

Pyrolysis–gas chromatography

Thermogravimetrical analysis alone does not give a full picture of the thermal degradation of the epoxy resins. As a complementary tool, the pyrolysis technique in combination with gas chromatography is needed for evaluation of the thermal behaviour of the epoxy resins, by identification of the decomposition products.

The P–GC technique was used to analyse the thermal degradation products, which were identified in the range of temperatures between 200 and 600°. The organic decomposition products analysed include gases and liquids. They consist of C_1–C_4 saturated and unsaturated volatile aliphatic hydrocarbons, carbonilyc compounds, ethers, aromatic hydrocarbons, phenol, cresols and higher phenols, respectively. As an illustration of this, Fig. 4 shows a typical pyrogram for one of the resins analysed, recorded at 580°.

The primary chain scission products result from breakdown of the nonylphenolic segment and from initial stages of breakdown of the aromatic and epoxy segments. Qualitatively, the pyrolysis of *p*-nonylphenol formaldehyde epoxy resins with various molecular weights leads to the same decomposition products, but their amount varies from one resin to another one. The decomposition of the liquid resins takes place with release of low-molecular volatile products in a large amount vs both the semi-solid and solid resins. Simultaneously, the content in compounds with low-boiling points increases pronounced with increase of the pyrolysis temperature.

The main pyrolysis products evolved at temperatures below 350° are phenol and cresols, while at temperatures between 400 and 600° the content in aromatic hydrocarbons becomes important. Among the pyrolysis products which were not identified by us, water is one of the main decomposition products of the epoxy resins [3]. The large quantity of water found in the pyrolysis products indicated that the epoxy resins were thermally degraded and dehydration of the hydroxyl linkage to olephinic ether is preferred for the formation of the phenol and higher phenols. The aromatic compounds found on the

Table 3. Kinetic and thermogravimetric characteristics of epoxy resins analysed

Sample No.	Kinetic characteristics		
	n	E_a (kcal/mol)	T_m (°C)
1	1.2	17.0	330
2	1.3	16.4	338
3	1.0	17.5	350
4	1.3	20.0	370
5	1.0	16.1	400

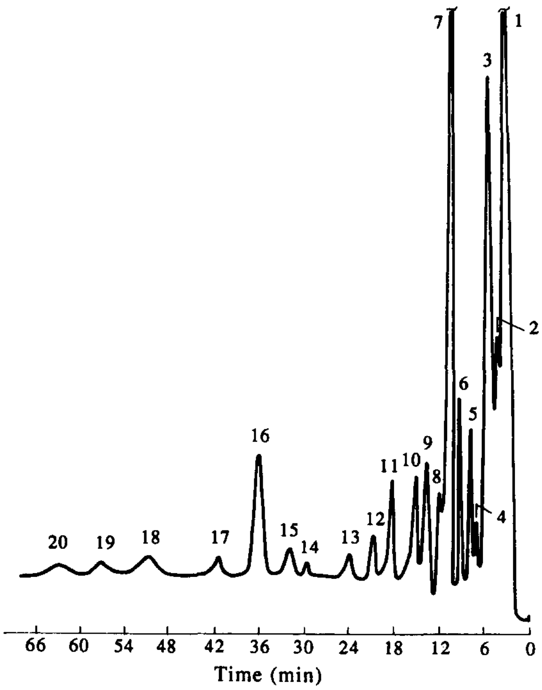


Fig. 4. Typical pyrogram for the resin 4, recorded at 580°. Peaks: 1, C_1–C_4 high volatile aliphatic hydrocarbons + acetaldehyde; 2, acrolein; 3, acetone; 4, benzene; 5, toluene; 6, ethylbenzene; 7, xylenes; 8, unknown; 9, isopropylbenzene; 10, anisole; 11, ethyltoluene; 12, unknown; 13, unknown; 14, 1.2.4-trimethylbenzene; 15, 1.3.5-trimethylbenzene; 16, phenol; 17, *m*,*p*-cresols; 18–20, higher phenols.

pyrolysis of *p*-nonylphenol formaldehyde resins in a large amount, could originate from both the rupture of the main chain with formation of the aromatic ring with various substitution degrees, and from the aliphatic part of the resin, when some competing reactions of cyclization, hydrogenation, dehydrogenation and rearrangement take place.

It can be concluded that the thermal degradation of epoxide resins based on *p*-nonylphenol formaldehyde novolac epoxy resins is a complex process, which is mainly influenced by temperature.

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