ELSEVIER

Thermochimica Acta 386 (2002) 143–151

thermochimica acta

www.elsevier.com/locate/tca

Thermal behavior of the epoxy and polyester powder coatings using thermogravimetry/differential thermal analysis coupled gas chromatography/mass spectrometry (TG/DTA–GC/MS) technique: identification of the degradation products

D.F. Parra[a,*], L.P. Mercuri[a], J.R. Matos[a], H.F. Brito[a], R.R. Romano[b]

[a]*Departamento de Química, Fundamental do Instituto de Química da Universidade de São Paulo, C.P. 26077, São Paulo, SP, Brazil*
[b]*Akzo Nobel Coatings S/A R. dos Ciprestes, 130 Guaçu-CEP, 18132-480, S. Roque, SP, Brazil*

Received 9 May 2001; received in revised form 24 September 2001; accepted 25 September 2001

Abstract

Thermal analysis techniques are useful to evaluate physical properties, curing behavior and degradation stability of powder coatings. The composition products of powder coatings were studied by the system composed of the thermogravimetry/differential thermal analysis coupled gas chromatography/mass spectrometry (TG/DTA–GC/MS). The system couples the thermal analysis with a gas chromatography separation and mass spectrometry identification methods. This system improves the analysis of the decomposition products of powder coatings and the identification of toxic products arising from their degradation. The TG curves recorded at different heating rates showed that the epoxy resin-based coating and the polyester-based coating are stable in air around of 210 °C when the degradation is started. The values of the activation energy E_a of the epoxy coating (159.8 ± 11 kJ mol^{-1}) and the polyester coating (162.9 ± 5 kJ mol^{-1}) were determined by Ozawa's method.

Keywords: Epoxy resin; Polyester resin; Powder coating; TG/DTA–GC/MS analysis; Thermal decomposition

1. Introduction

Powder coatings are an important area in the paint industry and they have the advantage of no solvent pollutant emission. However, some health problems were detected from occupational exposure of workers. The powder coatings are solid systems composed mainly of polymers such as: polyesters, epoxy resins, polyacrilates, hybrid systems, epoxy/polyester, and others that are cured using chemical cross-linkers as hardeners or accelerators, for example triglycidylisocyanurate, dicyandiamide, etc [1].

Several cases of allergic eczema caused by occupational exposure of triglycidylisocyanurate (TGIC) have been reported in the literature [2]. It was observed that allergic eczema was followed by asthmatic symptoms. Another case of contact dermatitis and occupational asthma was confirmed by results of patch test and bronchial provocation testing confirming that the TGIC causes contact dermatitis and also respiratory allergy [3].

In the last two decades, new types of toxicologically safe powder coating have been proposed as substitutes for TGIC, considered a potential mutagenic agent. The

---

[*] Corresponding author. Tel.: +55-11-3818-3708; fax: +55-11-3815-5579.
E-mail address: duclercp@iq.usp.br (D.F. Parra).

0040-6031/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(01)00809-7

glycidyl esters are recommended as a TGIC alternative and suitable cross-linker for polyesters [4]. A polyester acrylate hybrid system utilizing carboxylic acid functional polyester resins cured with epoxide-acrylate polymers was evaluated and compared with polyester TGIC systems [5].

Some epoxy allergy cases were described as allergy contact dermatitis caused by diglycidylether ether of bisphenol A (DGEBA) epoxy resins. Occupational asthma was also reported during exposure to heated polyester paint [6]. It was observed that the worker when spraying the paint on metallic surfaces and heating at 200 °C in an oven, after 4 h they had severe respiratory obstruction followed by leucocytosis. Bronchial provocation tests with heated granulated polyester confirmed the symptoms of allergic alveolitis and occupational asthma [7].

Gherloni et al. [8] describe the advantages of thermal analysis, as excellent techniques to evaluate and to characterize the powder coatings. According to Gherloni et al. [8] there is a perfect fit between powder coatings and the differential scanning calorimetry (DSC). This technique permits one to investigate physical events as the glass transition (T_g). The T_g occurs when an amorphous material changes from glassy to a rubbery state. The temperature of T_g is correlated with the stability of the material and it was verified that under storage of 24 h the powder coating exhibits aging with decreasing of the T_g value at about 20–30 °C. In the powder coating preparation steps (premixing, extrusion and grinding processes) the T_g evaluation is a useful tool to control the quality of the process conditions that permits a check on the degree of material dispersion.

The curing reactions in thermosetting proceed by polyaddition reactions, which are temperature-dependent and determined by kinetic laws. The DSC data of cure time and heat are useful to evaluate the behavior of the thermosetting systems, the efficiency of catalysts or accelerators and the performance of the formulation. Several works [9–12] have described the contribution of the techniques with coupled systems as TG/DTA–FT-IR, TG/DTA–MS and TG/DTA–GC/MS. These coupled techniques provide structural information and elucidate the decomposition processes. The TG/DTA–GC/MS couple system is a powerful technique that is a direct measurement of weight loss, a function of temperature, the separation of products by gas chromatography coupled with a sensitive spectroscopic detector. The identification of volatile products arising from thermal decomposition can be determined by TG/DTA–GC/MS.

The kinetic investigation of polymer degradation can be ascertained from thermogravimetric data by applying Ozawa's method [13,14]. It is based on the determination of the activation energy (E_a) of the decomposition process by the slope of plots of log of heating rate versus $1/T$ [14].

The goal of this article is to indicate the advantages of the thermal analytical techniques and better understand the degradation of powder coatings using a TG/DTA–GC/MS coupled system in the identification of the toxicological degradation products. This study also reports kinetic parameters, for example, the activation energy of thermal decomposition for the epoxy and polyester-based powder coatings.

2. Experimental

The powder coatings used in this work were prepared from the physical mixture of the ingredients. A typical extrusion process followed in a laboratory extruder APV MP 19 of 1 kg capacity operating in zone 1 at 50 °C and zone 2 at 80 °C per 15 min. The formulations based on polyester and epoxy resins are indicated in Table 1.

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained in a thermobalance, Shimadzu model TGA-50, using platinum crucibles under conditions of dynamic nitrogen atmo-

Table 1
Powder coatings formulations used for the polyester coating A and epoxy coating B

Material	Coating A (%)	Coating B (%)
Polyester resin	61.5	–
Epoxy resin (diglycidylether of bisphenol A)	–	52.0
TGIC	4.5	–
Dicyandiamide	–	3.0
TiO_2	31.5	43.0
Antioxidant	1.5	1.0
SiO_2	1.0	1.0
Total	100.0	100.0

sphere (50 ml min^{-1}), sample mass about 5 mg and heating rate at 10 °C min^{-1} in the range from 30 to 900 °C.

DSC curves were obtained in a Shimadzu DSC-50 cell using an aluminum crucible with about 10 mg of sample, in a dynamic nitrogen atmosphere (50 ml min^{-1}) at a heating rate of 10 °C min^{-1}. Thermal transitions at curing conditions were obtained in the temperature interval from 30 to 300 °C. The DSC system was calibrated with indium (mp 156.6 °C; $\Delta H = 28.54$ J g^{-1}).

The DTG–GC/MS system was adjusted to operate at the following conditions: (i) DTG-50H composed by simultaneous TG/DTA modulus-operating under dynamic atmosphere of helium (99.99%) at 50 ml min^{-1} and heating rate of 200 °C min^{-1} from 30 to 900 °C; with sample mass of about 0.8 ± 0.1 mg; (ii) the evolved gaseous material was captured at Tenax 60/80 mesh trap cooled at dry ice temperature. After that the trap was heated until 300 °C and the gaseous material was introduced and separated in the gas chromatograph (GC-14B series) and (iii) GC/MS-QP5000 system is composed by the chromatograph with the MS detector-operating under the helium atmosphere. The injection port was maintained at a constant temperature of 300 °C to introduce all released material into the column. The packed glass column containing 1.1 m × 3.2 mm i.d. and coated with Tenax 60/80 mesh was programmed to heat to the temperature of 80 °C held for 5 min, followed by heating at rate of 20 °C min^{-1} up to 300 °C, holding for 5 min. The Q-MS mass spectrometer was operated in the electron bombardment ionization (70 eV) mode and the *m*/*z* range of 40–300, which enabled the detection of the ions evolved from the sample. Spectral National Institute of Standards (NIST), chemical and structural database were used to assign the mass spectra of unknown evolved compounds.

The kinetic investigation was performed in different heating rates (2.5, 5.0, 10, 15 and 20 °C min^{-1}) under a dynamic oxidant atmosphere of air:nitrogen in the ratio 60:40, respectively, at 50 ml min^{-1}.

3. Results and discussion

The TG/DTG curves (omitted figure) revealed that the epoxy and polyester resins used in the coating formulations were thermally stable around 210 °C, with subsequent mass loss starting above this temperature. The TG data showed that the coatings are more thermal stable than the resins with a weight loss beginning at 300 °C (Table 2).

As can be seen in Table 2, the polyester, TGIC and epoxy resins have thermal decomposition in three events, under inert atmosphere of nitrogen. It is observed that the polyester and epoxy coatings degraded in two steps at the same atmosphere and heating rate conditions. Furthermore, a slightly oxidant atmosphere of air:nitrogen was used in ratio 60:40, respectively, to promote the thermal decomposition. For the last condition it was verified that the epoxy and polyester resins decompose only in two steps, similar to the coatings, according to Table 3. This slightly oxidant condition also presents a similar decomposition curve profiles when performed at lower heating rates. Consequently, it was optimized to obtain the kinetic analysis.

Table 2 presents the elevated residual mass content of the coatings above the temperature of 600 °C, which is related to the residue of inorganic material, typical of the coating formulation.

Table 2
TG results obtained for materials in non-isothermal temperature range of 30–900 °C, at N_2 atmosphere (50 ml min^{-1})[a]

Material	First event		Second event		Third event		Residual mass Δres. (%)
	$T_{ons} - T_f$ (°C)	Δm (%)	$T_{ons} - T_f$ (°C)	Δm (%)	$T_{ons} - T_f$ (°C)	Δm (%)	
TGIC	273.3 – 302.7	21.6	326.9 – 474.0	62.4	474.0 – 600	16.0	–
Polyester resin	264.2 – 380.0	8.8	455.7 – 519.3	83.9	629.9 – 693.8	4.47	2.8
Epoxy resin	307.7 – 344.3	6.7	444.6 – 493.5	83.4	646.1 – 847.1	8.40	1.4
Coating A	415.4 – 452.8	61.8	599.3 – 687.0	5.6	–	–	32.5
Coating B	394.8 – 444.7	47.4	553.8 – 699.4	12.3	–	–	40.3

[a] T_{ons}: temperature onset of weight loss; T_f: temperature final of event; Δm: mass loss.

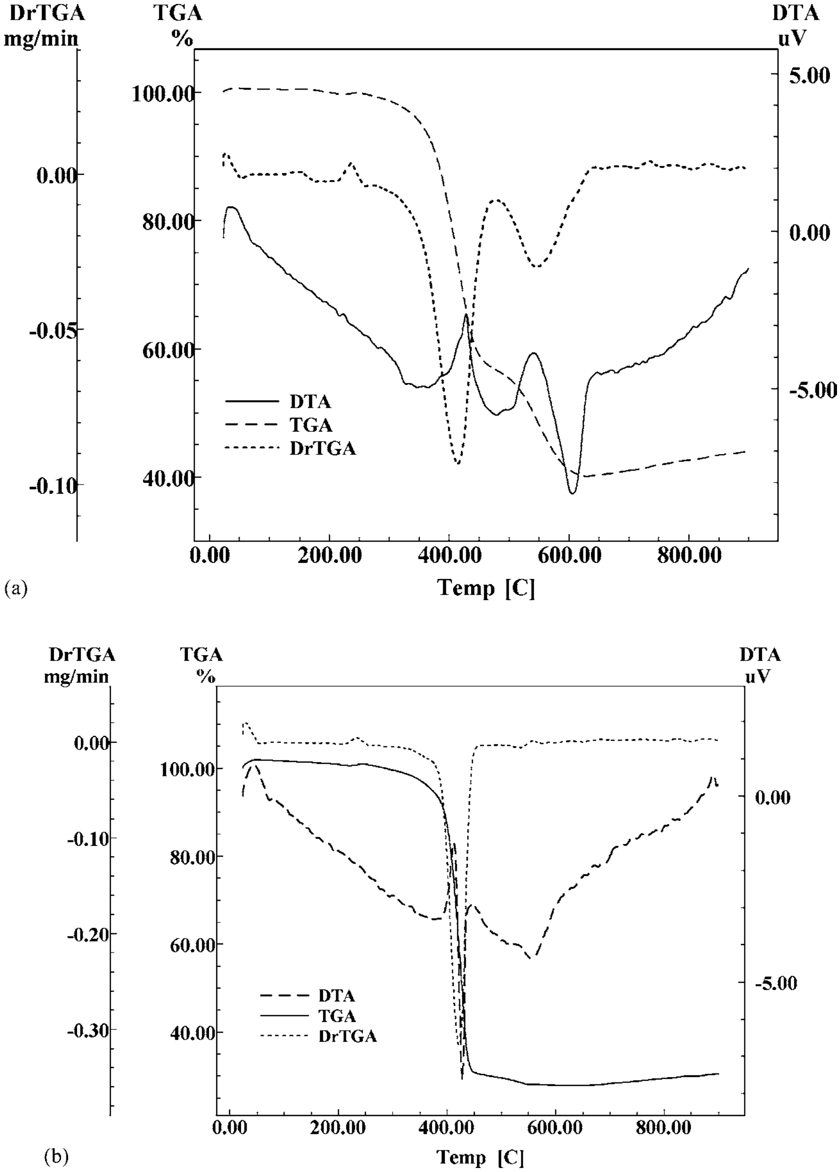

Fig. 1. TG and DSC curves obtained from the TG/DTA–GC/MS coupled system. (a) Coating A; (b) coating B.

Table 3
TG results obtained for materials in non-isothermal temperature range of 30–900 °C, at air atmosphere (50 ml min^{-1})[a]

Material	First event		Second event		Residual mass Δres. (%)
	$T_{ons} - T_f$ (°C)	Δ*m* (%)	$T_{ons} - T_f$ (°C)	Δ*m* (%)	
Epoxy resin	377.1–445.7	63.3	530.4–580.3	35.9	0.8
Polyester resin	350.0–450.0	64.0	540.0–600.0	35.0	1.0
Coating A	405.0–429.5	60.2	504.0–526.5	6.28	33.3
Coating B	417.0–474.4	43.6	543.5–591.1	15.4	41.0

[a] T_{ons}: temperature onset of weight loss; T_f: temperature final of event; Δ*m*: mass loss.

Table 4
DSC measurements of glass transition (T_g) and temperatures related to the exothermic reaction of the coatings cure[a]

Sample	T_g (°C)	T_{ons} of cure (°C)	T_f of cure (°C)	$T_{R\ max}$ (°C)	ΔE cure (J mol^{-1})
Polyester resin	61.8	–	–	–	–
Epoxy resin	50.0	–	–	–	–
Coating A	61.8	138.8	242.6	184.6	17.5
Coating B	53.7	117.1	207.9	165.6	63.4

[a] T_g: glass transition; T_{ons}: temperature onset of cure; $T_{R\ max}$: temperature relative of maximum reaction.

The DTA curves recorded for the epoxy and polyester coatings using a coupled system have no cure reaction on reticulation in the range from 30 to 300 °C, Fig. 1. In these analysis is used a low quantity of the sample (about 1 mg) which hampers the register of a typical exothermic cure event.

On the other hand, the DSC data (Table 4) were obtained with a sample quantity about 10 times higher than in the coupled systems. In this case the exothermic event of cure was clearly verified for the complete cure reaction of the coatings in the range of 120–300 °C, at conditions of heating rate of 10 °C min^{-1}. Based on DSC analysis it is evident that the reaction of cure of polyester-based coating (A) occurs in temperature interval of 138–243 °C, whereas the epoxy-based coating (B) is observed in the range of 117–208 °C (see Table 4).

The kinetic investigation of coatings thermal degradation (polyester or epoxy resins) was achieved from thermogravimetric data by the application of Ozawa's method [13,14]. The slope of plots of log of heating rate versus $1/T$ gives the activation energy (E_a) of the process. The oxidative atmosphere of air:nitrogen was used for this propose.

The activation energy for the beginning of the decomposition step was calculated by the application of the Ozawa's method considering the main decomposition step, the event of loss mass in the range of 350–480 °C. The kinetic calculations were made with the TG data recorded in the following heating rates: 2.5, 5.0, 10.0, 15.0 and 20 °C min^{-1}. As can be seen in Fig. 2a, the plots obtained for coating (A) present a very good correlation at the five heating rates due to similarity of the angular coefficients. Whereas, Ozawa's plot of the coating (B) presented in Fig. 2b, shows fairly good correlation. The activation energy (E_a) values determined for the coatings (A) and (B) were 162 ± 5 and 159 ± 11 kJ mol^{-1}, respectively, considering the main decomposition step.

The TG/DTG and DTA curves of the polyester and epoxy coatings recorded by the coupled system are showed in Fig. 1. The data corroborate to the weight

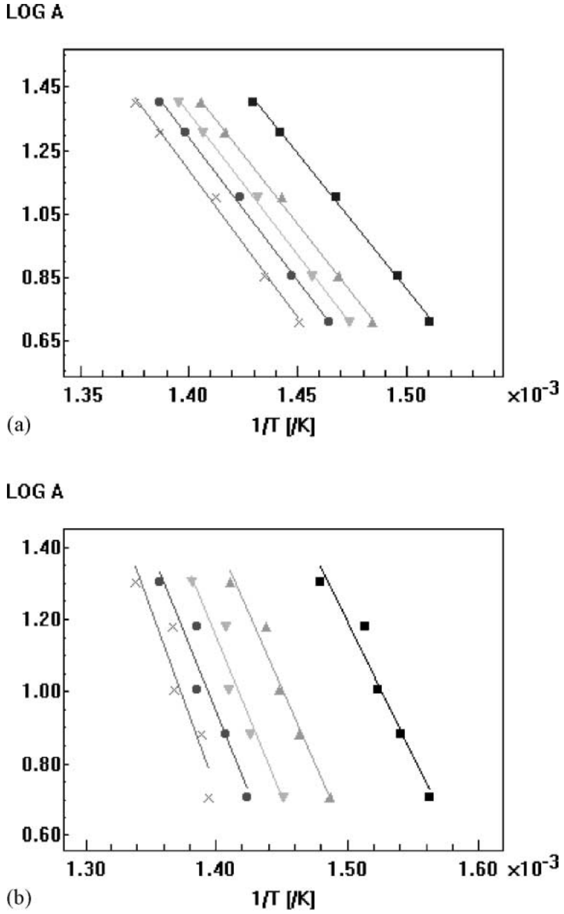

Fig. 2. Ozawa's plot of the coatings. (a) Coating A; (b) coating B. The E_a values obtained for coating A is 162.9 ± 5 kJ mol^{-1} and coating B is 159.8 ± 11 kJ mol^{-1}.

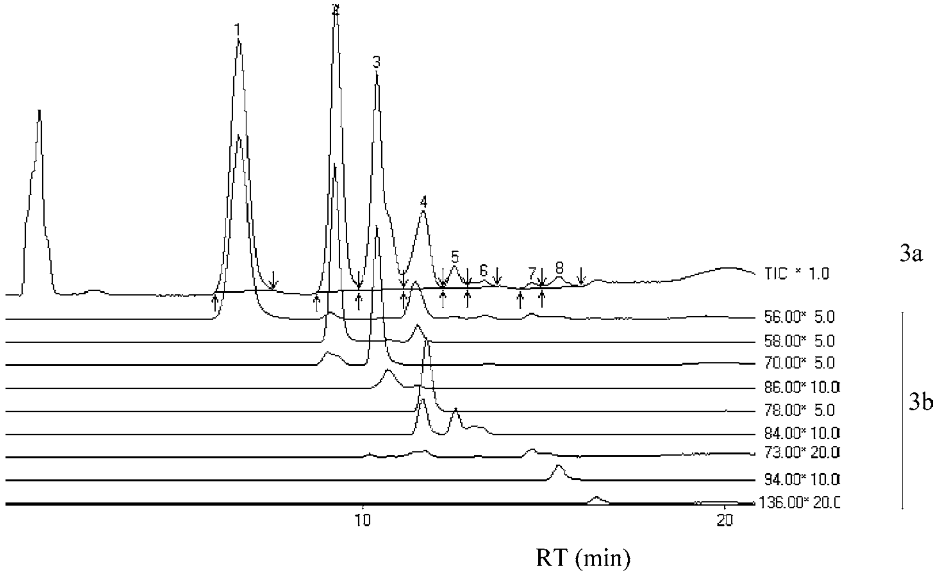

Fig. 3. Total ion chromatogram obtained from decomposition of polyester resin. (1) 1-Butene; (2) acetone; (3) 2-methyl-2-propenal; (4) benzene; (5) 2-ethylacrolein; (6) cyclopentanone; (7) 2-ethyl-1,3-hexanodiol; (8) phenol, and (9) methylbenzoate.

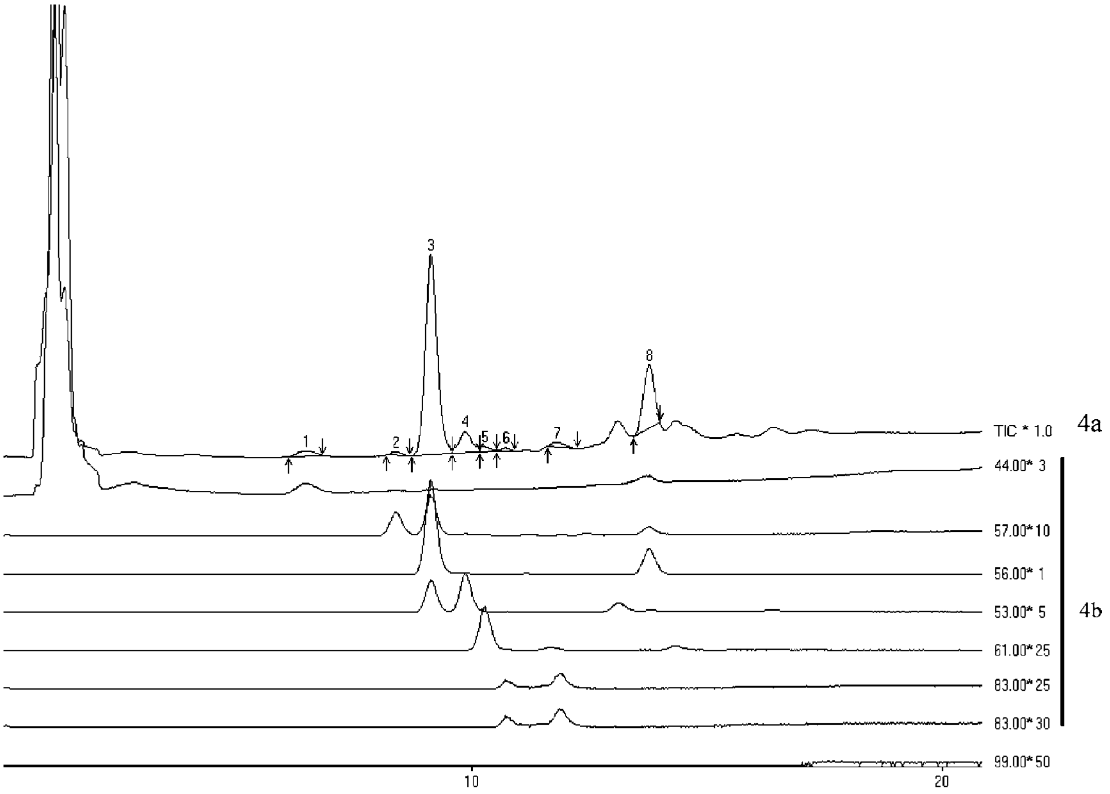

Fig. 4. Total ion chromatogram obtained from decomposition of TGIC. (1) Acetaldehyde; (2) methane isocyanate; (3) 2-propenal; (4) 2-propenenitrile; (5) *N*-methoxy methanamine; (6) pentanenitrile; (7) 2,2-dimethyl propanenitrile and (8) pivalolactam.

loss data obtained from TG/DTG conventional. In addition, this coupled system created the total ion chromatogram (TIC) of the volatile products formed during thermal decomposition (Figs. 3a–6a). Furthermore, the mass chromatograms (MC) obtained, indicating each peak at proper retention time (RT), refers to individual abundance of molecular ion (Figs. 3b–6b).

The experimental data recorded in the GC/MS of the coupled system, Figs. 3–6, permitted the identification of the following products separated at respective retention time (RT):

- *Polyester resin* (Fig. 3): (1) 1-butene at RT (min), 6.599; (2) acetone, 9.281; (3) 2-methyl-2-propenal, 10.419; (4) benzene, 11.698; (5) 2-ethylacrolein, 12.557; (6) cyclopentanone, 13.361; (7) 2-ethyl-1,3-hexanodiol, 14.687; (8) phenol, 15.44; (9) methylbenzoate, 16.478.
- *TGIC* (Fig. 4): (1) acetaldehyde at RT (min), 6.503; (2) methane isocyanate, 8.388; (3) 2-propenal, 9.131; (4) 2-propenenitrile, 9.857; (5) *N*-methoxy methanamine, 10.283; (6) pentanenitrile, 10.734; (7) 2,2-dimethyl propanenitrile, 11.827; (8) oxanamide, 13.775.
- *Polyester coating* A (Fig. 5): (1) 1-butene at RT (min), 6.587; (2) 1,3-pentadiene, 9.381; (3) 2-methyl-2-propenal, 10.420; (4) 2-butenone, 10.762; (5) benzene, 11.557; (6) 2-ethylacrolein, 12.570; (7) oxanamide, 13.329; (8) phenol, 15.509; (9) 2-amino-1-(*O*-methoxyphenyl)propane, 16.058.
- *Epoxy coating* B (Fig. 6): (1) acetaldehyde at RT (min), 6.471; (2) acetone, 9.269; (3) butanal, 10.762; (4) butanone, 11.142; (5) benzene, 11.825; (6) toluene, 13.067; (7) phenol, 15.636; (8) phenylurea, 17.072; (9) 2-ethyl-6-methyl-*O*-cresol, 18.533; (10) 1-(2-methylphenyl) ethanone, 20.00.

Some volatile products of degradation are compounds formed during thermal decomposition arising from the polyester resin and the coating A, according to the TIC identification obtained from

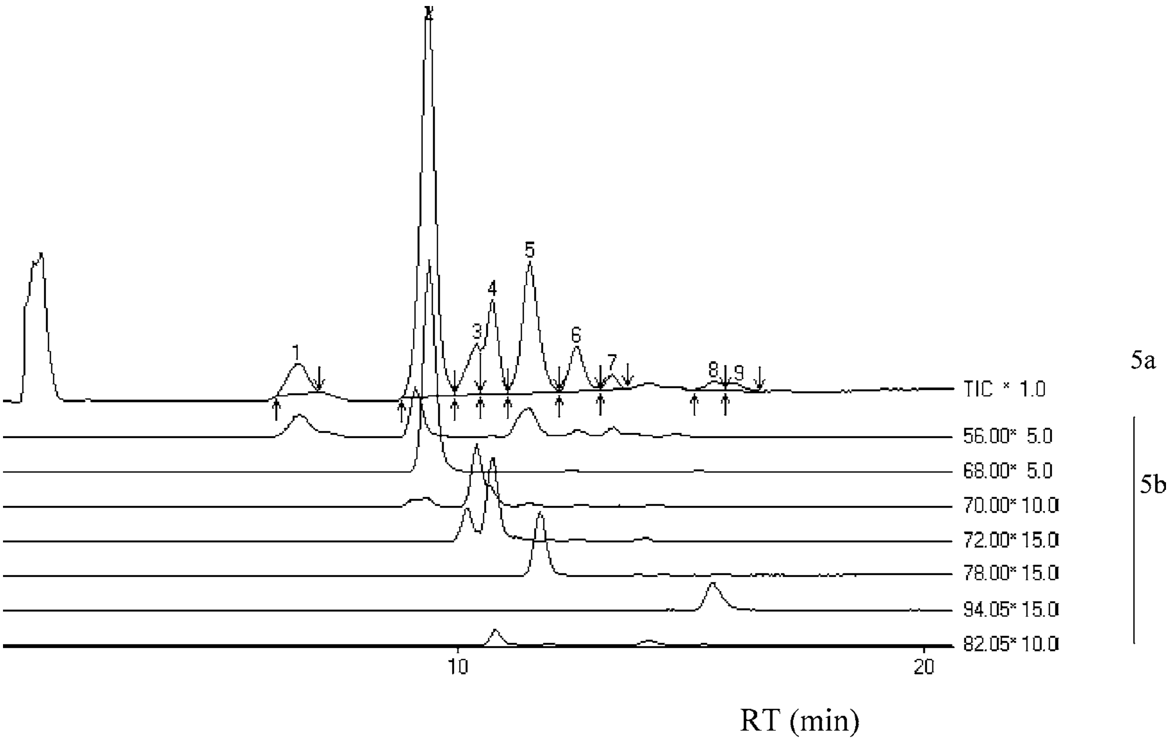

Fig. 5. Total ion chromatogram obtained for the decomposition of coating A. (1) 1-Butene; (2) 1,3-pentadiene; (3) 2-methyl-2-propenal; (4) 2-butenone; (5) benzene; (6) 2-ethylacrolein; (7) oxanamide; (8) phenol and (9) 2-amino-1-(methoxyphenyl)propane.

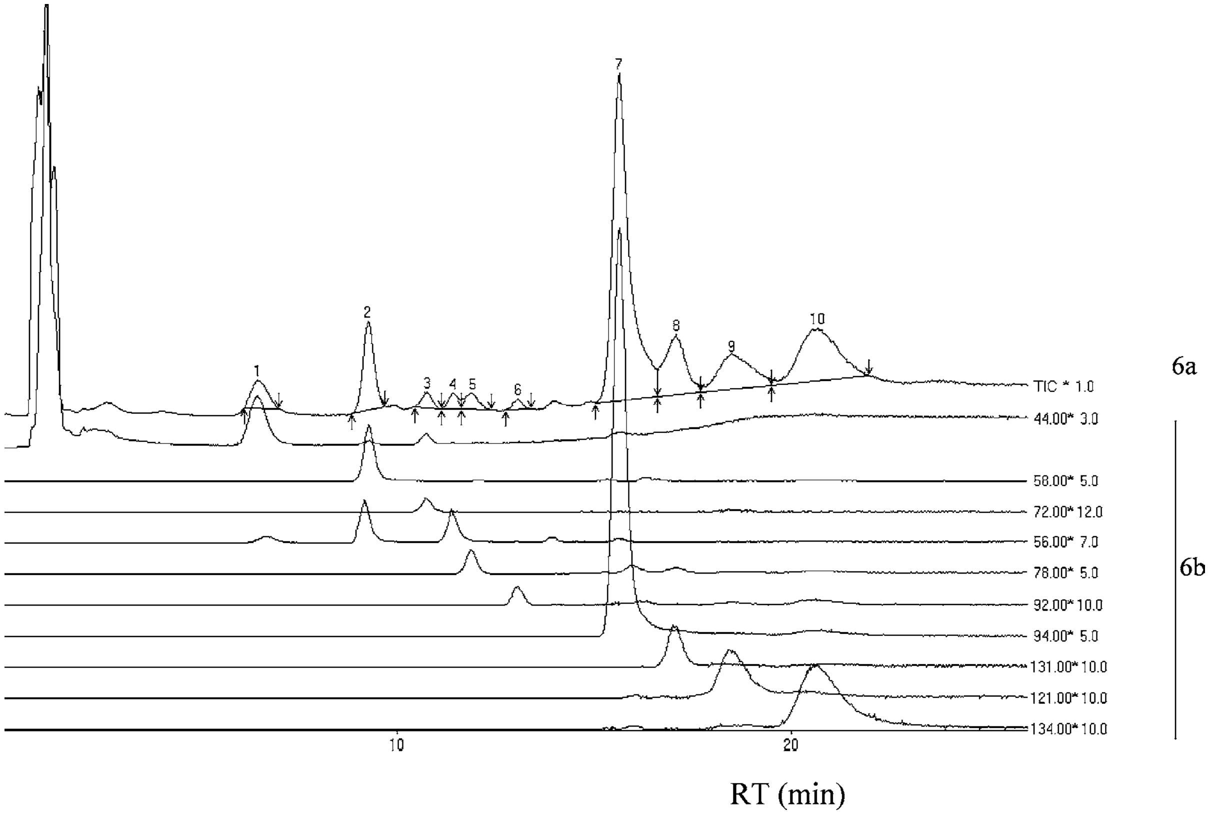

Fig. 6. Total ion chromatogram obtained for the decomposition of coating B. (1) Acetaldehyde; (2) acetone; (3) butanal; (4) butanone; (5) benzene; (6) toluene; (7) phenol; (8) phenylurea; (9) 2-ethyl-6-methyl-*O*-cresol and (10) 1-(2-methylphenyl) ethanone.

the thermal decomposition under the same analytical conditions. Fig. 5 shows that compounds founded in the coating A, for example, 1-butene, 2-methyl-2-propenal, benzene, ethylacrolein and phenol are also identified in the polyester resin. In addition, the presence of the oxanamide ($C_8H_{15}NO_2$) in the coating A, RT (min), 13.329 is interpreted as originated of TGIC compound, by the peak at RT 13.775.

Fig. 6 shows the peaks related to the volatile products of the thermal decomposition of coating B. The presence of compounds such as toluene and 2-ethyl-6-methyl-*O*-cresol evidences the occurrence of the bisphenol A (from DGEBA) used in the formulation. These results suggest the use of the methodology, of separation and identification of the volatile products recorded in the TG/DTA–GC/MS coupled system, as a screening of coatings composition.

4. Conclusion

In this work was observed, under thermal heating conditions, that cured coatings of polyester resin formulation containing TGIC, and coating of epoxy resin formulation without TGIC decompose and liberate toxic products as benzene, phenol, among others, as the result of thermal degradation process.

The separation and identification analysis developed by the TG/DTA–GC/MS coupled system had identified toxic products evolved in the decomposition of the polyester and epoxy resins. The identification of similar products in the resin and the polyester coating confirms the origin of the formulation. The thermal oxidation stability of the coatings after curing is greater than those of the individual resins, as expected by the reticulation of the resins chains occurred during the cure process.

The kinetic data demonstrated that the epoxy coating and the polyester coating formulations presented the E_a values of 159 ± 11 and 162 ± 5 kJ mol^{-1}, respectively, calculated to the main step of decomposition (400–480 °C) when the coatings were submitted at the same conditions of degradation.

This study suggests the application of the technique of the TG/DTA–GC/MS coupled system as a potential methodology in the investigation of the powder coatings. The system provides analysis and identification of the toxic decomposition products of powder coatings arising from their degradation.

Acknowledgements

The authors are grateful to the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support via a postdoctoral fellowship and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) of the Secretary for Science and Technology of Brazil for financial support and Akzo Nobel coatings that contributed with the manufacture of the formulations.

References

[1] C.A. May, Epoxy Resins, Chemistry and Technology, 2nd Edition, Marcel Dekker, New York, 1988, pp. 20–105.
[2] P. Piirila, T. Estlander, H. Keskinen, R. Jolanki, A. Laakkonen, P. Pfaffi, O. Tupasela, M. Tuppurainen, H. Nordman, Clin. Exp. Allergy 27 (5) (1997) 510.
[3] L. Meuleman, A. Goossens, C. Linders, F. Rochette, B. Nemery, Eur. J. Allergy Clinical Immunol. 54 (7) (1999) 752.
[4] P. Gottis, J. Cotting, in: Proceedings of the FATIPEC Congress, Brussels, Vol. 23 (B), 1996, pp. 216–231.
[5] E.D. Dumain, T. Agawa, S. Goel, A. Toman, A.S. Tse, J. Coatings Technol. 71 (893) (1999) 55–69.
[6] R. Jolanki, L. Kanerva, T. Estlander, J. Eur. Acad. Dermatol. Venereol. 5 (1995) 598.
[7] A. Cartier, O. Vandenplas, L.C. Grammer, M.A. Shaughnessy, L. Malo, Eur. Resp. J. 7 (3) (1994) 608–611.
[8] L. Gherloni, T. Rossini, V. Stula, Prog. Organic Coatings 34 (1998) 57–63.
[9] A.R. Mc Ghie, Thermochim. Acta 234 (1994) 21.
[10] L.F. Whiting, P.W. Langvardt, Anal. Chem. 56 (1984) 1755.
[11] H.L. Chung, J.C. Aldridg, Anal. Chem. 20 (1992) 123.
[12] T. Arii, Y. Sawada, K. Iizumi, K. Kudaka, S. Seki, Thermochim. Acta 352 (2000) 53.
[13] A.M.L. Silva, R.W.C. Li, J.R. Matos, J. Gruber, J. Thermal Anal. Calorimetry 59 (2000) 675.
[14] T. Ozawa, J. Thermal Anal. 2 (1970) 301.