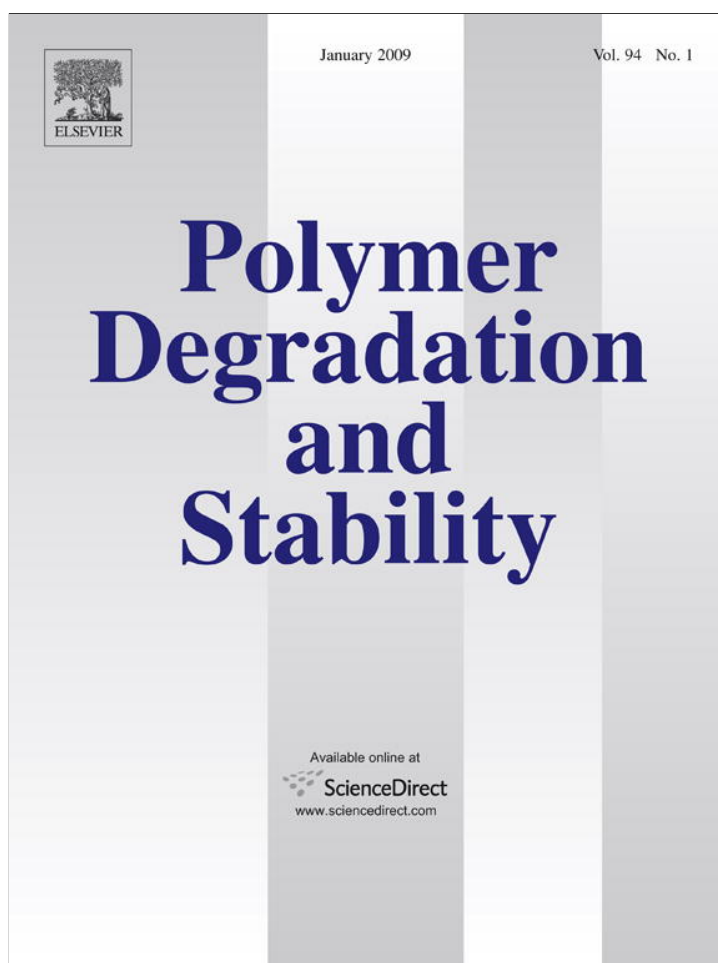


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

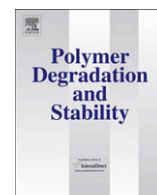
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Cone calorimetry studies of benzoxazine–epoxy systems flame retarded by chemically bonded phosphorus or silicon

M. Spontón, J.C. Ronda, M. Galià*, V. Cádiz

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Campus Sescelades, Marcellí Domingo s/n, 43007 Tarragona, Spain

ARTICLE INFO

Article history:

Received 31 July 2008

Received in revised form

3 September 2008

Accepted 7 October 2008

Available online 17 October 2008

Keywords:

Flame retardance

Cone calorimetry

LOI

Benzoxazine

Epoxy

ABSTRACT

The combustion behaviour of phosphorus- and silicon-containing benzoxazine–epoxy systems has been studied by LOI and cone calorimetry giving clear evidence that incorporation of 3.5% P into the benzoxazine–epoxy systems resulted in flame retardation while the silicon-containing copolymer was found to have no improvement in the LOI and cone calorimeter data, with values similar to the polymers without heteroatom, thus indicating that the 3.9% silicon content has no flame retarding effect. The peak heat release rate is reduced significantly for the phosphorus-containing benzoxazine as a result of a combination of condensed-phase and gas-phase mechanisms. The incorporation of phosphorus or silicon into the modified benzoxazine–epoxy system increases the smoke hazard and the CO emissions compared to the heteroatom-free system.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

During the last decades much work has been concentrated on developing new flame-retardant materials with high performance for applications such as electronic and aerospace industries. These must exhibit high glass transition temperature, low internal stress, good adhesion, low dielectric constant, low toxicity and high flame retardancy. The bromine-containing epoxy is found among the most used polymers in the manufacture of electronic devices. However, the bromine-containing advanced epoxy resin releases hydrogen bromide, dibenzo-*p*-dioxin and dibenzofuran during combustion, which cause corrosion and toxicity. The concept of sustainable development requires fire-retardant technologies to be developed which have minimum impact on health and the environment throughout the life cycle of the material: that is to say, its synthesis, fabrication, use, recycling and disposal. The incorporation of phosphorus or silicon functionality in the polymeric structure is recognized as one of the most efficient ways to obtain an environmentally friendly flame-retardant system [1].

We have published a number of papers concerned with the behaviour of flame-retardant phosphorus- [2], silicon- [3], and phosphorus/silicon [4]- containing resins. These resins were obtained by copolymerisation of a variety of monomers containing covalently bonded phosphorus and silicon. The organophosphorus

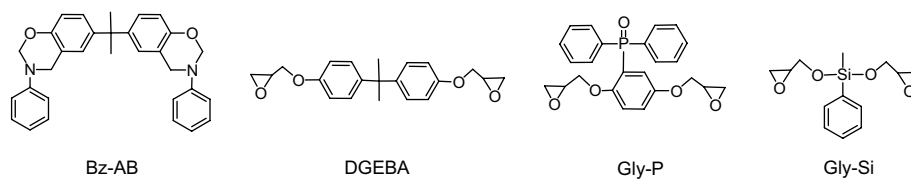
fire retardants mainly act as intumescent flame retardants resulting in a char layer in the condensed phase, which can produce less toxic gas and smoke compared with halogen-containing FRs [5,6]. Besides, phosphorus can also act in the gas phase as a catalytic radical scavenger [7]. Silicon-containing polymers were described to degrade, forming thermally stable silica, which has a tendency to migrate to the char surface serving as a protective layer to prevent further degradation of the char at high temperatures [8].

As a consequence of the complex nature and poor reproducibility of fire, there are many techniques for estimating the flammability of polymeric materials. Each concentrates on certain characteristic of the complex combustion process, for example, the ease of ignition of the material, the flame propagation, and heat release rate. Different tests have been developed and standardised by the International Standards Organisation. The most widely used laboratory test is the limiting oxygen index (LOI) ASTM-D-2683. In recent years, also one of the most important instruments in this field is the cone calorimeter [9], to measure the ignitability, heat release rate, total heat released, effective heat of combustion, specific extinction area, mass loss rate, and evolution of CO₂, CO, and other combustion products with controlled atmosphere.

In this work we investigated the combustion behaviour of thermosetting resins obtained by copolymerizing the benzoxazine of bisphenol A and the previously reported phosphorus- and silicon-containing glycidyl derivatives (Scheme 1) [2,3,10]. The phosphorus-containing systems investigated by us showed very good flame retardance, results even when the phosphorus content was low, and no significant differences with the phosphorous

* Corresponding author.

E-mail address: marina.galia@urv.cat (M. Galià).



Scheme 1.

content were observed. It is worth pointing out the outstanding LOI values obtained. However, the presence of silicon had no significant effect in the flame-retardant behaviour, and the LOI values of silicon-containing resins were similar to those of heteroatom-free resins. This paper reports the results of cone calorimetric studies of these phosphorus- and silicon-containing benzoxazine–epoxy systems.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) Eq. Epoxy (E.E = 192 g/eq) and diaminodiphenylmethane (DDM) were purchased from Aldrich. Benzoxazine derivative of bisphenol A was obtained from Shikoku Chemicals. Diglycidyl ether of (2,5-dihydroxyphenyl)diphenyl phosphine oxide (Gly-P) was obtained from (2,5-dihydroxyphenyl)diphenyl phosphine oxide by reaction with epichlorohydrin and BTMA as catalyst as has been previously described [2].

Diglycidyl oximethylphenylsilane (Gly-Si) was obtained from methylphenyl silane by reaction with glycidol and the Wilkinson catalyst [10]. Solvents were purified by standard procedures.

2.2. Crosslinking reaction

Samples were prepared by the dissolution of benzoxazine and epoxy monomers in equimolar amounts in CH_2Cl_2 . Then the solution was evaporated at room temperature in vacuum. Moulded cured benzoxazine–epoxy resins (Table 1) were prepared with a manual hydraulic press 15-ton sample pressing (SPECAC) equipped with a water cooled heated platens. The mixture was placed in a $50 \times 50 \times 1.9 \text{ mm}^3$ or $70 \times 6 \times 3 \text{ mm}^3$ moulds and compression moulded at 180°C for 3 h under 0.1 mPa. Post-curing was carried out at 220°C for 3 h under the same pressure conditions.

2.3. LOI measurements (LOI-ASTM-D-2863)

These were performed on a Stanton Redcroft FTA flammability unit provided with an Oxygen Analyzer. Sample sizes measured $70 \times 6 \times 3 \text{ mm}^3$ and were prepared by moulding.

2.4. Cone calorimetry

The combustion behaviour was investigated using a Fire Testing Technology cone calorimeter (according to ISO 5660) with specimen. Cone calorimeter was used under ventilated conditions including time to ignition (TTI), rate of heat release (HRR), the maximum rate of heat release (PHRR), smoke density, carbon monoxide and carbon dioxide evolution. The heat flux used was 50 kW/m^2 on the specimen, which had an exposed surface area of $50 \text{ mm} \times 50 \text{ mm}$. Edge burning effects were reduced by covering the non-exposed sample surface in heavy duty aluminium foil. The device consisted of a radiant electric heater in a trunk-conic shape, an exhaust gas system with oxygen monitoring and instrument to measure the gas flux, an electric spark for ignition, and a load cell to measure the weight loss. All tests were terminated after 600 s of

exposure. TTI measures the time to achieve sustained flaming combustion for a given cone irradiance. Smoke density was measured by the decrease in transmitted light intensity of a helium–neon laser beam photometer, and expressed in terms of specific extinction area (SEA), with units of m^2/kg . The experiments were repeated three times.

2.5. Thermogravimetric analysis (TGA)

Dynamic thermogravimetric studies were used to investigate the behaviour in an oxidative and non-oxidative environment using a Mettler TGA/SDTA851e/LF/1100 instrument. For both air and nitrogen atmospheres a flow rate of 50 ml/min was used. Samples of 15–20 mg were placed in open alumina pans and heated from 50 to 800°C at a constant heating rate of $10^\circ\text{C}/\text{min}$.

3. Results and discussion

Benzoxazine–epoxy systems have been prepared by curing DGEBA, phosphorus- and silicon-containing glycidyl compounds in equimolar amounts with Bz-BA [10]. Conventional epoxy resin has been prepared by curing DGEBA with stoichiometric amount of DDM with the purpose of comparison (Table 1). The flammability of these new benzoxazine–epoxy systems has been assessed by the LOI test and the results are given in Table 1. As can be seen the pure benzoxazine system Bz-BA exhibits a higher LOI value than epoxy system, as an indicator of its higher flame retardance. When benzoxazine is copolymerised with DGEBA the LOI value results similar without detriment to the polymer flammability and with an improvement of the physical and mechanical properties. The results show that the incorporation of just 3.5% phosphorus significantly increases the LOI value to 48. However, the silicon-containing copolymer was found to have no improvement in the LOI, with a value similar to the polymers without heteroatom, thus indicating that the 3.9% silicon content has no flame-retarding effect.

Whilst the LOI is a useful small-scale test for flame retardance polymer the cone calorimeter provides a wealth of information on the combustion behaviour under ventilation conditions. The cone calorimeter is one of the most effective bench-scale methods for studying the flammability of materials. Typically, the subject material is irradiated with a heat intensity similar to that experienced in a fire situation ($25\text{--}75 \text{ kW/m}^2$). This method enables investigations with respect to heat release rate (HRR), total heat release (THR), mass loss rate (MLR), time to ignition (TTI), specific extinction area (SEA), maximum average rate of heat emission (MARHE), CO and CO_2 emissions and mass loss during combustions [11]. These parameters are reported in Tables 1–3 for different samples at an external heat flux of 50 kW/m^2 .

Time to ignition TTI is used to determine the influence on ignitability, which can be measured from the onset on an HRR curve. The time to ignition shows clear differences in the ignition behaviour of the different samples. Ignition occurs when the mass loss rate produces sufficient volatiles whose effective heat of combustion makes a gas mixture capable of being ignited by a spark. Ignition does not directly correspond to flammability

Table 1
Cone calorimeter data.

Samples	Resins	LOI	TTI (s)	HRR _{peak} (kW/m ²)	THR (MJ/m ²)	THR/TML (MJ/m ²)	MAHRE (kW/m ²)	FIGRA (kW/m ² s)
1	DGEBA/DDM	24.3	33	732	66	6.0	301	6.9
2	Bz-BA	31.8	23	628	56	6.3	258	7.5
3	Bz-BA/DGEBA	32.2	31	556	47	5.5	213	6.4
4	Bz-BA/Gly-P	48.0	23	370	36	4.1	174	4.2
5	Bz-BA/Gly-Si	32.4	21	536	49	6.5	232	6.5

measured by LOI since this is an extinction test and good correlations between both measurements are not expected. DGEBA-containing polymers (samples 1 and 3) have improved times to sustained ignition, as compared to the other benzoxazine systems which ignited at about 23 s. The presence of DGEBA appears to be a significant factor in the ignition time.

The heat release rate (HRR) versus time curves for the different systems are presented in Fig. 1. Practically, the heat release rate for low applied heat flux corresponds roughly with LOI results. In our case the LOI values increase as the heat release rates decrease. The HRR curves showed a shape that is normally rather typical for non-charring samples of intermediate thickness. There is an initial increase in HRR, followed by a dominant peak of HRR at the end of burning. The HRR of the DGEBA/DDM system is characterized by an intense peak, whereas the HRR of Bz-BA containing systems was reduced strongly. The HRR results provide a much better indication than do the LOI values that benzoxazine copolymers show flame-retardant behaviour. Their HRR_{peak} values are reduced, more significantly in the phosphorus-containing benzoxazine compared to the other resins. Further confirmation is provided for the total heat evolved (THR) by each polymer as given in Table 1.

The behaviour of the HRR for the phosphorus-containing systems arises from a combination of condensed-phase and gas-phase mechanisms as a result of the increased residue and the reduction in total heat evolved per total mass loss (THR/TML), respectively [12]. This last parameter is a measure for the effective heat of combustion of the volatiles, multiplied by the combustion efficiency during the cone calorimeter test. The THR/TML for our phosphorus-containing sample showed a reduction of around 40% in comparison to epoxy or heteroatom-free benzoxazine system, which indicated a flame inhibition effect as a fire retardancy mechanism.

The Average Rate of Heat Emission (AHRE) curve is reported in Fig. 2. This parameter is defined as the cumulative heat emission divided by time and its peak value (Maximum Average Rate of Heat Emission, MAHRE) has recently been proposed as a good measure of the propensity for fire development under real scale conditions [13]. MAHRE for phosphorus-containing benzoxazine system (sample 4) (Table 1) shows a notable reduction (about 40–50%) with respect to epoxy (sample 1) and heteroatom-free benzoxazine system (sample 2). Similar behaviour can be found for benzoxazine-epoxy systems (samples 3 and 5) showing that the addition of epoxy to the benzoxazine does not exert a great influence in the MAHRE value and that the presence of silicon does not diminish the propensity for fire development.

Table 2
Residue from cone calorimeter and thermogravimetric tests.

Samples	Resins	Cone calorimeter (g/g)	TGA nitrogen		TGA air	
			T _{5%} ^a (°C)	Char ^b (%)	T _{5%} ^a (°C)	Char ^b (%)
1	DGEBA/DDM	0	351	17	330	0
2	Bz-BA	4	313	30	322	0
3	Bz-BA/DGEBA	5	341	26	340	0
4	Bz-BA/Gly-P	11	339	30	338	20
5	Bz-BA/Gly-Si	4	261	36	291	14

^a Temperature of 5% weight loss.

^b Char yield at 900 °C.

The Fire Growth Rate Index (FIGRA) [14] (Table 1) is calculated by dividing the peak heat release rate by time to peak heat release (TTPH), giving a unit of kW/m²s, which can estimate both the predicted fire spread rate and the size of a fire. The higher the FIGRA, the faster the flame spread and flame growth are assumed to be [15,16]. The FIGRA of the materials ranges between 6 and 7 kW/m²s while that of the phosphorus-containing benzoxazine-epoxy system decreases to 4.2 kW/m²s, meaning that this system performs much better than the other studied systems.

Percentage mass loss curves obtained as a function of time from cone calorimeter test and thermogravimetry in air and nitrogen for the resins are presented in Fig. 3. The residual mass remaining after complete combustion in the cone calorimeter of DGEBA/DDM (sample 1) is negligible (Table 2). The benzoxazine-containing samples left a residual mass at the end of their test around 4% except the phosphorus-containing sample with a significant residual mass higher than 10%. This is due to the formation of carbonaceous char indicating a condensed phase mode as a flame-retardant mechanism. This further supports the role of the mechanism being related to the formation of a char layer, as these values correlate well with improvement in the peak heat release rate determined by cone calorimetry [17].

Table 2 compares the char yields in nitrogen and air atmospheres obtained by thermogravimetric analysis with the residual masses after combustion in cone calorimetry for all the samples. The char yields at 800 °C both in nitrogen and air follow a different trend than cone calorimeter residues. While in nitrogen benzoxazine-containing systems showed an enhanced char formation, in air this is true only for those heteroatom-containing systems. These results do not correlate with a previous described work which demonstrated a close relationship between cone calorimeter and TGA char yields in nitrogen atmosphere highlighting the anaerobic environment during combustion and the role of char formation in improving fire performance [18].

The weight loss curves obtained from cone calorimeter test are similar to those obtained from thermogravimetry in nitrogen but show differences with those obtained from thermogravimetry in air. On heating in a thermobalance at 10 °C/min in air, the resins present a two-step weight loss corresponding to two different degradation mechanisms whereas a single step is observed during the combustion test. This can be due to the different heating conditions during cone calorimeter test where a high heating rate and a high temperature are reached.

Apart from the heat release characteristics the smoke and CO and CO₂ releases are important fire hazards. Smoke emission is caused by the evolution of the products of incomplete oxidation.

Table 3
Smoke, CO and CO₂ releases.

Samples	Resins	Total smoke release (m ² /m ²)	SEA (m ² /Kg)	CO (kg/kg)	CO ₂ (kg/kg)
1	DGEBA/DDM	3003	1051	0.14	2.41
2	Bz-BA	2307	1021	0.22	3.82
3	Bz-BA/DGEBA	1929	858	0.17	3.04
4	Bz-BA/Gly-P	2790	1276	0.29	2.12
5	Bz-BA-Gly-Si	1844	920	0.19	3.64

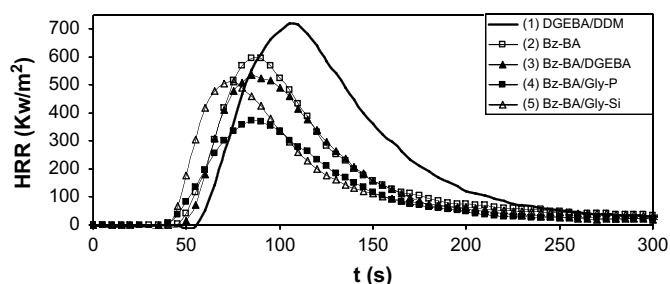


Fig. 1. Heat Release Rate (HRR) versus time curves for the benzoxazine-epoxy systems.

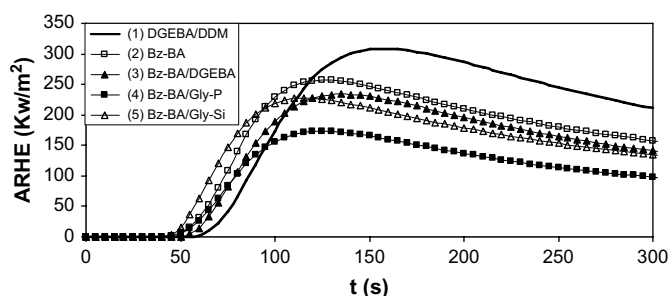


Fig. 2. Average Rate of Heat Emission (AHRE) versus time curves for the benzoxazine-epoxy systems.

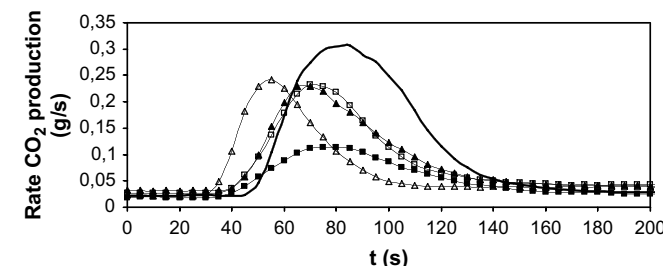
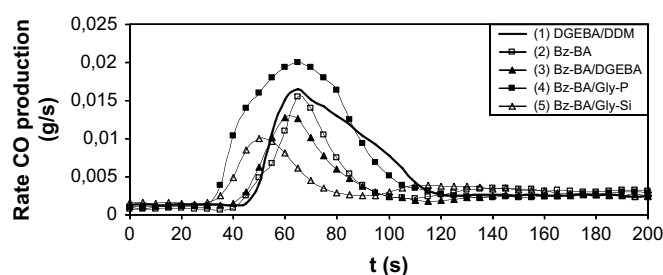


Fig. 4. CO and CO₂ evolution versus time for the benzoxazine-epoxy systems.

Due to their aromatic structure, benzoxazine-epoxy systems evolve large amounts of smoke. The rate of smoke emission, indicated by the specific extinction area (SEA) is similar for epoxy and benzoxazine systems and decrease for the benzoxazine-epoxy system (Table 3). The incorporation of phosphorus or silicon into the modified benzoxazine-epoxy system increases the smoke hazard compared to the heteroatom-free system resulting the presence of phosphorus in a very significant increase in smoke production during combustion.

Both CO and CO₂ production often indicate the fire retardancy mechanism. Flame inhibition results in an increase in combustion products typical for incomplete combustion, in particular CO, whereas increased charring bears the potential decrease of the absolute CO production due to an unchanged yield and a reduced mass loss. The temporal behaviour of the CO evolution rate during the cone calorimetric experiments is shown in Fig. 4. Heteroatom-free samples evolved similar CO amounts at a similar rates and the phosphorus-containing sample evolved more CO amount at a faster rate. This could indicate that the chemical incorporation of phosphine oxide into the resins has a more effective flame-retardant effect in the vapour phase. The silicon-containing sample evolved less CO amount at a lower rate, according to a condensed phase action. The charring induced in this silicon-containing sample seems not to influence HRR and THR.

4. Conclusions

In this work we presented a detailed study on the fire behaviour of the phosphorus- and silicon-containing benzoxazine-epoxy systems. Cone calorimetric experiments gave much clearer evidence than did the LOI measurements that incorporation of 3.5% P into the benzoxazine-epoxy systems resulted in flame retardation. DGEBA-containing polymers have improved times to sustained ignition as compared to the benzoxazine systems. The peak heat release rate is reduced significantly for the phosphorus-containing benzoxazine. This behaviour arises from a combination of condensed-phase and gas-phase mechanisms as a result on the increased residue and the reduction of around 40% in total heat evolved per total mass loss (THR/TML), respectively. According to these results, MAHRE and FIGRA show a notable reduction meaning that this phosphorus-containing system performs much better than the other studied systems. The formation of carbonaceous

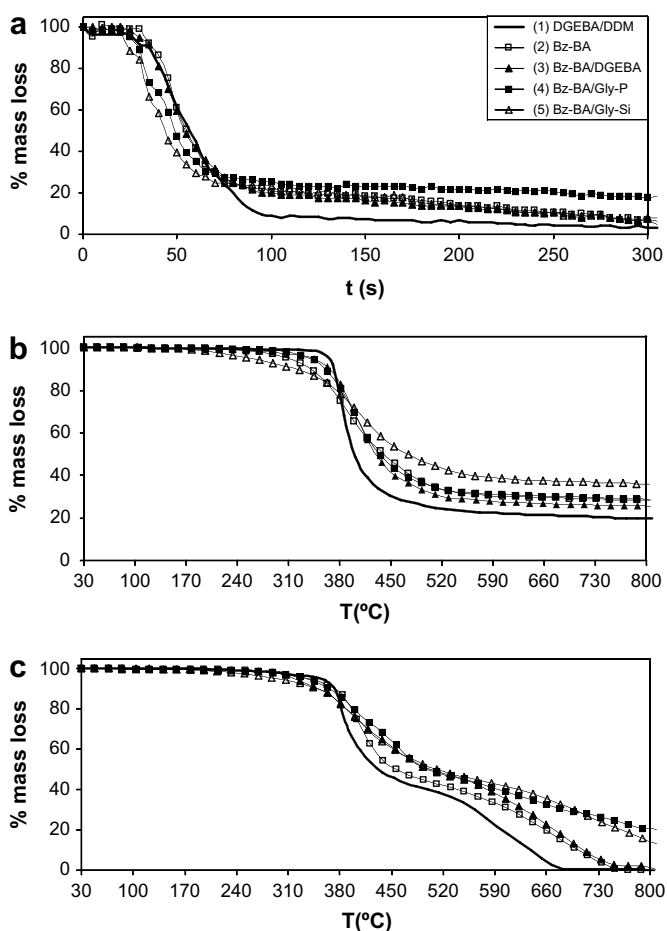


Fig. 3. Percentage of mass loss curves for the benzoxazine-epoxy systems. (a) Cone calorimeter data, (b) TGA data in nitrogen, (c) TGA data in air.

char in cone calorimeter tests and thermogravimetry indicates a condensed phase mode as a flame-retardant mechanism, according to the formation of a char layer.

The incorporation of phosphorus or silicon into the modified benzoxazine–epoxy system increases the smoke hazard and the CO emissions compared to the heteroatom-free system, resulting the presence of phosphorus in a very significant increase in smoke production during combustion. This could indicate that the chemical incorporation of phosphine oxide into the resins has a more effective flame retardant effect in the vapour phase. The silicon-containing sample evolved less CO amount at a lower rate, according to a condensed phase action. The charring induced in this silicon-containing sample seems not to influence HRR and THR.

References

- [1] Lu SY, Hamerton Y. Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog Polym Sci* 2002;27:1661–712.
- [2] Spontón M, Ronda JC, Galià M, Cádiz V. Flame retardant epoxy resins based on diglycidyl ether of (2,5-dihydroxyphenyl) diphenyl phosphine oxide. *J Polym Sci Part A Polym Chem* 2007;45:2142–51.
- [3] Mercado LA, Reina JA, Galià M. Flame retardant epoxy resins based on diglycidylmethyl phenylsilane. *J Polym Sci Part A Polym Chem* 2006;44:5580–7.
- [4] Spontón M, Mercado LA, Ronda JC, Galià M, Cádiz V. Preparation, thermal properties and flame retardancy of phosphorus- and silicon-containing epoxy resins. *Polym Degrad Stab* 2008;93:2025–31.
- [5] Levchik SV, Weil ED. Thermal decomposition, combustion and flame-retardancy of epoxy resins – a review of the recent literature. *Polym Int* 2004;53:1901–29.
- [6] Levchik SV, Piotrowski A, Weil ED, Yao Q. New developments in flame retardancy of epoxy resins. *Polym Degrad Stab* 2005;88:57–62.
- [7] Braun U, Balabanovich AI, Scharrel B, Knoll U, Artner J, Ciesielski M, et al. Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites. *Polymer* 2006;47:8495–508.
- [8] Kashiwagi T, Gilman JW. In: Grand AF, Wilkie CA, editors. Fire retardancy of polymeric materials. New York: Marcel Dekker Inc.; 2000. p. 353–89.
- [9] Scharrel B, Hull TR. Development of fire-retarded materials – interpretation of cone calorimeter data. *Fire Mater* 2007;31:327–54.
- [10] Spontón M, Ronda JC, Galià M, Cádiz V. Development of flame retardant phosphorus- and silicon-containing polybenzoxazine–epoxy systems. *Polym Degrad Stab*, submitted for publication.
- [11] Price D, Bullett KJ, Cunliffe LK, Hull TR, Milnes GJ, Ebdon JR, et al. Cone calorimetry studies of polymer systems flame retarded by chemically bonded phosphorus. *Polym Degrad Stab* 2005;88:74–9.
- [12] Scharrel B, Braun U, Balabanovich AI, Artner J, Ciesielski M, Döring M, et al. Pyrolysis and fire behaviour of epoxy systems containing a novel 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-(DOPO)-based diamino hardener. *Eur Polym J* 2008;44:704–15.
- [13] Duggan GJ, Grayson SJ, Kumar S. New fire classifications and fire test methods for the European railway industry: flame retardants 2004. London: Inter-science Communications; 2004.
- [14] Gao L-P, Wang D-Y, Wang Y-Z, Wang JS, Yang B. A flame-retardant epoxy resin based on a reactive phosphorus-containing monomer of DODPP and its thermal and flame-retardant properties. *Polym Degrad Stab* 2008;93:1308–15.
- [15] Messerschmidt B, Hees PV. Influence of delay times and response times on heat release measurements. *Fire Mater* 2000;24:121–30.
- [16] Nazaré S, Kandola B, Horrocks RA. Use of cone calorimetry to quantify the burning hazard of apparel fabrics. *Fire Mater* 2002;26:191–9.
- [17] Liu W, Varley RJ, Simon GP. Understanding the decomposition and fire performance processes in phosphorus and nanomodified high performance epoxy resins and composites. *Polymer* 2007;48:2345–54.
- [18] Lyon RE. Heat release kinetics. *Fire Mater* 2000;24:179–86.