JOURNAL OF CIVIL ENGINEERING AND MANAGEMENT
2008
14(1): 45–48

THE INFLUENCE OF FLAME RETARDANT ADDITIVES ON FIRE PROPERTIES OF EPOXY MATERIALS

Marzena Półka
The Main School of Fire Service, The Combustion and Fire Theory Division, Słowackiego str. 52/54,01-629 Warsaw, Poland. E-mail: mpolka@sgsp.edu.pl

Received 4 Jan 2008; accepted 4 Feb 2008

Abstract. Fire properties of modified and unmodified epoxy materials have been studied. The following types of additives were used: MoO_3, Sb_2O_3, melamine. Heat and smoke release rates in different external fluxes (30, 50 kW/m^2) were studied by the Cone calorimeter. The results of investigation have shown that molibdenum oxide (VI) is more smoke supressant than antimony oxide (III) and melamine in the range of heat exposure under consideration.

Keywords: flame retardant, heat release rate, smoke supressant.

1. Introduction

Statistical studies of fire death in the world demonstrated that approx 80 % fire fatalities are due to fire effluents (smoke and toxic gases) (Purser, Gwynne 2007; Nelson, Maclennen 1988; Clarke 1984). Toxicity of decomposition and combustion products reduce visibility in fire and contribute to the inability of victims to escape from a building fire (Babrauskas, Mulholland 1988; Purser, Bensilum 2001; Fillippidis *et al.* 2006; Sychta 1985; Półka 2007; Konecki, Półka 2006). Epoxy resins are one of the popular material to produce plastics in many application areas, eg building construction, transport, recreation, electronic industries etc. One of the biggest disadvantages of epoxy resins is their flammability and production of smoke in fire. Hence, chemical composition has been modified in technological processes for many years in all the world. The main aim of the research is to change simultaneously flammability properties and smoke release rate of plastic materials in order to expand their application areas. The subject literature comprises many experimental data referring to reducing the intensity of smoke of epoxy resin (Grand, Wilkie 2000; Babrauskas, Grayson 1992; Mulholland 1988; Östman 1992; Babrauskas 2003).

Research objectives:

- selection of the proper inorganic fillers for the studied epoxy resin,
- elaboration of the quantity-quality chemical composition of the plastic,
- examination of heat and smoke release rates of modified and unmodified epoxy resin.

2. Experiment

2.1. Description of experimental material

According to our instruction, the composition of the samples of epoxy resin (Epidian 561) with or without fire retardands was elaborated and made by “Organic Sarzyna”, Polish Chemical Corporation. It is coloured, two-component, flooring material:

Component A is a modified epoxy resin containing inorganic pigments and fillers (40 % by weight, dense mass);

Component B is a modified aliphatic polyamide – hardener ET (low-viscous liquid; the quantity of hardener for 100 g of Epidian was 10 g).

The coating thickness of samples of Epidian 561 with hardener ET was 3÷5 mm. The gel time (sample 100 g at 20 °C) was about 35 min. The mixture viscosity at 25 °C was 1000÷2500 mPa·s.

Modified sample of Epidian 561 contain:

Component A (as above) containing inorganic pigments and fillers (32 % by weight) and 8 % molybdenum oxide (VI) or antimonum oxide (III) or 8 % of melamine;

Antimonum oxide (III) and molybdenum oxide (VI), melamine- POCh, Gliwice, Poland);

Component B is a modified aliphatic polyamide – hardener ET (low-viscous liquid, the quantity of hardener for 100 g of modified Epidian was 10 g). The modified epoxy resin with inorganic pigments, fillers and flame retardants showed a high-density mass;

Epidian 561 is an epoxy composition with a good mechanical and chemical resistance recommended for flooring on concrete foundation in objects of industrial buildings.

3. Methods

Heat and visible smoke release rates have been studied by Cone calorimetric method described in ISO 5660 standard (ISO 5660 1991). The Cone calorimeter is based on the laws of consumption of oxygen, that the heat evolved on combustion can be determined quantitatively in terms of the oxygen consumed. Smoke evolution was measured by a laser photometer. The parameter – "specific extinction area" (SEA) was determined and the intensity emission of smoke during combustion of materials described. For most flammable materials, eg plastics, organic liquid, wood, the heat released is 13,1 MJ per 1 kilogram of oxygen consumed. Deviations from this average value encountered with various materials do not exceed ±5 %.

3.1. Preparation samples

Three specimens unmodified and modified (Sb_2O_3, MoO_3, 1,3,5-triazine-2,4,6-triamine ($C_3H_6N_6$)) were used in this study, in each at an external flux of heat. The size of the samples: 100 mm×100 mm×5 mm. The sample were conditioned at 23±2 °C. Before examining, the samples were wrapped into an aluminium film and screened at the back with a ceramic blanket and then put in a holder inside the combustion chamber in the Cone calorimeter.

The samples were examined in two external fluxes of heat – 30 and 50 kW/m^2. Research condition of heat and smoke release rates simulated the fire conditions during the 1st fire phase according to the standard curve: fire temperature – time duration of fire (Standard Method… 1983). Initiation of the combustion reaction was started by a piloted ignition. The horizontal orientation of specimens in relation to the cone radiator has been used.

4. Results and discussion of test results

The main findings of unmodified and modified epoxy materials obtained from Cone calorimeter are presented in Table.

The heat release rate (HRR) curves of unmodified and modified epoxy material at external flux of heat 30 kW/m^2 are presented in Fig. 1 and at external flux of heat 50 kW/m^2, are presented in Fig. 2.

The average value of heat release rate of unmodified and modified epoxy material at external flux of heat 30 kW/m^2 and 50 kW/m^2 are shown in Figs 3, 4.

The conducted test of the heat and smoke generation rate and flooring composites made on the basis of Epidian 561 allow to determine the following dependencies:

– the rate of heat and smoke release from the tested epoxy materials are a function of the type of used modifiers and the heat flux falling on the sample,
– introduction of MoO_3, Sb_2O_3, melamine at a concentration of 8 % to flooring composite on the basis of Epidian 561 lowers the release intensity heat by the analysed epoxy material in the heat exposures.

The main findings of unmodified (EP, Epidian 561) and modified epoxy materials obtained from Cone calorimeter (Time – time to ignition of samples, HOC_{av} – average effective heat of combustion, MLR_{av} – average mass loss rate, SEA_{av} – average specific extinction area)

Materials	Time (s)	HRR_{max} (kW/m^2)	HOC_{av} (MJ/kg)	MLR_{av}(g/s)	SEA_{av} (m^2/kg)
External flux of heat (kW/m^2) – 30 kW/m^2					
EP	89	563,67	28,93	0,059	566,150
EP+Sb_2O_3	106	317,82	24,95	0,051	688,730
EP+MoO_3	90	460,81	26,92	0,049	527,020
EP+$C_3H_6N_2$	104	499,48	21,10	0,048	565,270
External flux of heat (kW/m^2) – 50 kW/m^2					
EP	29	671,06	24,58	0068	552,660
EP+Sb_2O_3	28	421,66	22,32	0,065	738,860
EP+MoO_3	27	388,82	24,88	0,069	643,610
EP+$C_3H_6N_2$	44	611,89	19,79	0,048	590,380

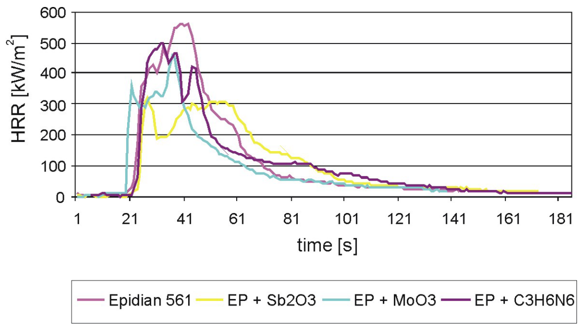

Fig. 1. The heat release rate curves of unmodified (Epidian 561) and modified epoxy material at external flux of heat 30 kW/m^2

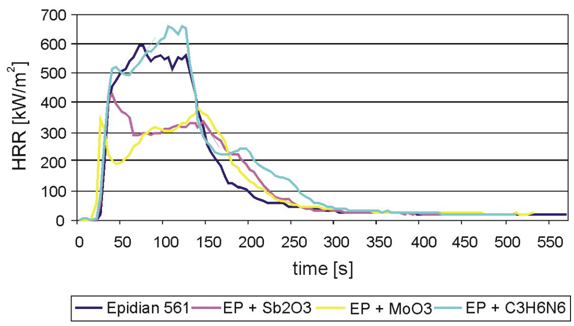

Fig. 2. The heat release rate (HRR) curves of unmodified (EP) and modified epoxy material at external flux of heat 50 kW/m^2

1. Maximum values of heat release rates (HRR_{max}) and medium values (HRR_{av}) of modified epoxy material in exposure of heat flux of 30 kW/m^2 are lower by ca 20–40 %, as compared to HRR_{max} and HRR_{av} respectively

of unmodified Epidian 561. The HRR_{max} values in the heat flux of 50 kW/m^2 for Epidian 561 modified by molybdenum trioxide are lower by ca 45 % as compared to HRR_{max} for unmodified epoxy material. The average value of HRR for Epidian 561 with admixture is lower by ca 20 % at 30 kW/m^2 as compared to unmodified material. At a higher heat exposure – 50 kW/m^2, this relation is similar, yet differences in the HHR_{av} value are lower than in comparison with an unmodified material.

2. Maximum values of heat release rates (HRR_{max}) and medium values (HRR_{av}) of modified epoxy material in exposure of heat flux of 30 kW/m^2 are lower by ca 20–40 % as compared to HRR_{max} and HRR_{av} respectively to unmodified Epidian 561. The HRR_{max} values in the heat flux of 50 kW/m^2 for Epidian 561 modified by molybdenum trioxide are lower by ca 45 % as compared to HRR_{max} for unmodified epoxy material. The average value of HRR for Epidian 561 with an admixture is lower by ca 20 % at 30 kW/m^2 as compared with an unmodified material. At a higher heat exposure – 50 kW/m^2, this relation is similar, yet differences in the HHR_{av} value are lower than in comparison with an unmodified material.

A more effective flame retardant at a lower heat exposure (30 kW/m^2) is Sb_2O_3 , as compared to MoO_3 and melamine. The HRR_{max} value of Epidian 561 with Sb_2O_3 is by ca 45 % lower as compared to HRR_{max} for Epidian 561 with MoO_3 and ca 50 % as compared to melamine. At a higher heat exposure (50 kW/m^2) the HRR_{max} value for Epidian 561 with MoO_3 is slightly lower than the HRR_{max} value for Epidian 561 with Sb_2O_3 , and by about 50 % lower than HRR_{max} EP with melamine.

The average HRR values for modified epoxy samples at exposure of 30 kW/m^2 are almost identical, while at exposure of 50 kW/m^2 the HRR_{av} value for Epidian 561 with melamine are by ca 15 % lower as compared to the HRR_{av} value for Epidian 561 with Sb_2O_3.

HRR curves for modified epoxy materials have two peaks and a characteristic ”saddle”, which indicates that a charred layer is created on the surface of material. The carbonised layer, which is a barrier for the inflow of oxygen and heat, prevents spreading the burning process.

3. Times to ignition of the tested epoxy samples in heat flux of 50 kW/m^2 are shorter on average by 100–200 % as compared to times to ignition of epoxy materials at exposure of 30 kW/m^2.

4. Times to ignition of the samples of flooring on the basis of Epidian 561 modified by flame retardants are insignificantly higher as compared to unmodified Epidian 561. As regards the modification of epoxy material by antimony trioxide, time to ignition is much longer at a heat exposure of 30 kW/m^2 as compared to unmodified Epidian 561. On the other hand, the longest time to ignition by ca 40 % at 50 kW/m^2 was obtained for epoxy material with melamine.

5. Times to achievement of the maximum value of heat release rate (HRR_{max}) by modified epoxy material at heat exposure of 30 kW/m^2 are shorter as compared to times for HRR_{max} for unmodified Epidian 561. At a higher heat exposure the above relation is reverse.

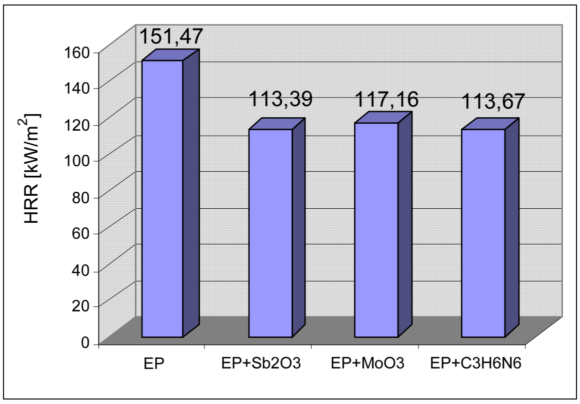

Fig. 3. The average value of heat release rate of unmodified (EP) and modified epoxy material at external flux of heat 30 kW/m^2

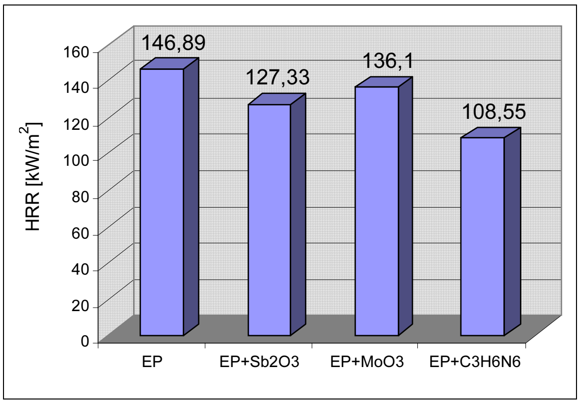

Fig 4. The average value of heat release rate of unmodified and modified epoxy material at external flux of heat 50 kW/m^2

6. The value of total heat release (THR) by modified samples of Epidian 561 are by ca 10–20 % lower, as compared to THR values for unmodified epoxy material.

7. An admixture of Sb_2O_3 to Epidian 561 significantly increases (by approx 25 % of the intensity of smoke release as compared to unmodified Epidian 561. At a heat exposure of 30 kW/m^2 the SEA_{av} (value of epoxy material with MoO_3 and melamine are insignificantly lower than SEA_{av} for an unmodified epoxy material.

5. Conclusions

The obtained complex results of the heat and smoke release rate have shown the following.

1. The admixture of inorganic fire protection agents and, namely, antimony trioxide and molybdenum trioxide and melamine to epoxy flooring composites reduces HRR_{max} and HRR_{av} values, as compared to the unmodified epoxy material. The intensity of heat release by epoxy materials in the tested heat exposures is reduced, and consequently the tested materials become safer with respect to fire threat.

Epoxy materials modified by the applied flame retardants manifest a higher smoke release intensity (exception – Epidian 561 with MoO_3 and melamine at 30 kW/m^2), as compared to unmodified Epidian 561 which affects adversely the visibility conditions on evacuation routes in conditions of a real fire.

2. Modification of epoxy material by antimony trioxide is more effective than modification using molybdenum trioxide, because it affects a much larger extent reducing the heat release rate of epoxy flooring composite; yet, unfortunately, it increases the smoke release intensity by the tested material in analysed heat exposures. On the other hand, the admixture of melamine affect times to ignition at a higher heat exposure.

3. Even the best modified studied epoxy materials with flame retardants, ie modified Sb_2O_3 (if we take into consideration the maximum 421,66 kW/m^2 in external heat flux – 50 kW/m^2) value of HRR as well as other analysed polymer materials with used additives, unfortunately, continue spreading fire quite rapidly and continue the burning process once ignited in fire heat exposure.

References

Babrauskas, V.; Mulholland, G. W. 1988. Smoke and soot data determinations in the cone calorimeter, in *Mathematical Modelling of Fires*, ASTM Special Technical Publication, STP 983, 83–104.

Babrauskas, S. V.; Grayson, S. J. 1992. *Heat release in fire*. Elsevier Applied Science, London.

Babrauskas, S. V. 2003. *Ignition handbook*. Fire Science and Technology Inc.

Clarke, B. F. 1984. Fire deaths, causes and strategies for control, in *Technomic*, Lancaster, 36–38.

Filippidis, L.; Galea, E. R.; Gwynne, S.; Lawrance, P. 2006. Representing the influence of signage on evacuation behavior within an evacuation model, *Journal of Fire Protection Engineering* 16 (1): 37–73.

Grand, A. F.; Wilkie, C. A. 2000. *Fire Retardancy of Polimeric Materials,* Marcel Dekker, INC, 286–302.

ISO 5660. 1991. Standard test method for heat and visible smoke release notes for materials and products using oxygen consumption calorimeter (equiv. ASTME 1354-90, 1990).

Konecki, M.; Półka, M. 2006. Analiza zasięgu widzialności w dymie powstałym w czasie spalania materiałów poliestrowych, *Polimery* 4: 293–300.

Mulholland, G. W. 1988. Section 1/chapter 25. Smoke production and properties, in *SFPE Handbook of Fire Protection Engineering*, NFPA, USA, 368–377.

Nelson, H. E.; Maclennen, H. 1988. Section 2/chapter 6, Emergency Movement, in *SFPE Handbook of Fire Protection Engineering, Society of Fire Protection Engineers,* Boston, MA, 106–115.

Östman, B. A.-L. 1992. Smoke and soot, in *Heat Release in Fires*, Elsevier Science Publ. Ltd. New York, 233–250.

Półka, M. 2007. The calculations of visibility range reduction in model scheme compartment – corridor, VŠB-Technicka Univerzita – Ostrava, *Požarni ochrana* 12–13.09.2007, 491–501.

Purser, D. A.; Gwynne, S. M. V. 2007. Identifying critical evacuation factors and the application of egress models, *Interflam 2007*, Conference Proceedings 1: 203.

Purser, D. A.; Bensilum, M. 2001. Quantification of behaviour for engineering design standards and escape time calculation, *Safety Science* 38: 157–182

Sychta, Z. 1985. *Badanie materiałów i kryteria oceny z punktu widzenia stwarzanego zagrożenia pożarowego*, Politechnika Szczecińska, Prace Naukowe.

Standard Method of Fire Test of Building Construction and Materials. 1983. ASTM E 119-83.

DEGUMO GRUPĘ AUKŠTINANČIŲ PRIEDŲ ĮTAKA EPOKSIDINIŲ MEDŽIAGŲ GAISRINIAM PAVOJINGUMUI

M. Półka

Santrauka

Atlikta modifikuotų ir nemodifikuotų epoksidinių medžiagų gaisrinio pavojingumo analizė. Panaudotos šios degumo grupę aukštinančios medžiagos: MoO_3, Sb_2O_3, melaminas. Kūginiu kalorimetru nustatytas šilumos ir dūmų išsiskyrimo intensyvumas, esant skirtingam išoriniam šilumos srautui (30, 50 kW/m^2). Remiantis tyrimo rezultatais nustatyta, kad molibdeno oksidas (VI) efektyviau mažina dūmų išsiskyrimą nei stibio oksidas (III) ir apsvarstyta melamino poveikis šilumai išsiskirti.

Reikšminiai žodžiai: degumo grupę didinantys priedai, šilumos išsiskyrimo intensyvumas, dūmų išsiskyrimą mažinančios medžiagos.

Marzena PÓŁKA. Assistant Professor of Combustion and Fire Theory Division of The Main School of Fire Service in Warsaw (Poland). Her research interests include flame retardants modification and studies of combustion process, analysis of toxicity and smoke visibility of fire products, thermal decomposition of solids. She is charter member of Polish Science Society – “The man in extreme conditions” and member of Society of Engineers and Techniques of Fire.