Construction and Building Materials 42 (2013) 266–270

Contents lists available at SciVerse ScienceDirect

Construction and Building Materials

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

Addition of flame retardants in epoxy mortars: Thermal and mechanical characterization

L. Haurie [a,*], A.M. Lacasta [b], A. Ciudad [b], V. Realinho [c], J.I. Velasco [c]

[a] Dpt. Construccions Arquitectòniques II, Universitat Politècnica de Catalunya, Barcelona, Spain
[b] Dpt. Física Aplicada, Universitat Politècnica de Catalunya, Barcelona, Spain
[c] Centre Català del Plàstic, Universitat Politècnica de Catalunya, Terrassa, Barcelona, Spain

HIGHLIGHTS

- We analyze and improve the fire behavior of epoxy mortars.
- A by-product (HyM) has been used as flame retardant and compared with commercial ones.
- HyM mortar shows a higher auto-extinguish ability and a reduction in the smoke release.
- Mechanical properties were only slightly affected by the addition of flame retardants.

ARTICLE INFO

Article history:
Received 10 July 2012
Received in revised form 26 November 2012
Accepted 17 December 2012
Available online 1 March 2013

Keywords:
Fire resistance
Polymer mortar
Flame retardant
Mechanical properties

ABSTRACT

In this work we have studied the effect of different flame retardants on the fire behavior and mechanical properties of epoxy mortars. Flame retardants acting under different mechanisms of action have been compared: phosphate flame retardants as well as magnesium hydroxides and carbonates. Besides the commercial flame retardants we have also used a magnesium basic carbonate obtained from an industrial by-product. The use of an alternative based on an industrial by-product combines an economic and sustainable solution. Different formulations of flame retarded epoxy mortars have been prepared and characterized. The obtained results prove the effectiveness of the tested flame retardants on the improvement of the fire properties of the epoxy mortars without a significant decrease on their mechanical properties.

1. Introduction

Polymer mortars consist of a fine aggregate mixture and a polymeric resin as a binder. Thermosetting polymers like epoxy resins are one of the most used binders due to the combination of good mechanical properties, strong adhesion to concrete and metals, as well as low shrinkage [1]. These qualities along with the easiness of the in situ application of the epoxy mortars have extended their use in the building sector: concrete repairing, metal anchorages or pavement flooring [2]. Nevertheless, one of the major concerns when using polymer mortars is their limited response in front of temperature. Several authors have studied the effect of temperature on the mechanical properties of these mortars. El-Hawary et al. concluded that, despite the thermo-oxidative degradation of the resin with temperature, thermal cycles up to 200 °C increase compressive and flexural strengths due to the hardening of the polymer [3]. Elalaoui et al. confirmed the increase of mechanical properties up to 150 °C, but reported a decrease when the polymer mortars were subjected to higher temperatures [4]. In both cases the samples were cooled before testing; however Ribeiro et al. stated a significant decrease on flexural strength of epoxy and polyester mortars when tested at temperatures above room temperature [5]. In addition to the mechanical properties there should be considered the risks of these polymer mortars in case of fire. In the case of epoxy mortars, despite the elevated amount of aggregates the mortar still shows a strong flammability around 400 °C with dense smoke release. The addition of flame retardants is one of the strategies to improve the fire behavior of the polymeric mortars and increase the safety of building elements in case of fire [6]. The flame retardant used has to be non-halogenated to avoid toxic hazards [7]. The maintenance of the mechanical properties of the resulting mortar is also an important aspect, as well as keeping as low as possible the materials cost. Following these requirements we have selected a synthetic basic magnesium carbonate, hydromagnesite, already used as flame retardant in polyolefin formulations [8,9]. The source of synthetic

* Corresponding author. Address: UPC-EPSEB, Av Dr. Marañon 44-50, 08028 Barcelona, Spain. Tel.: +34 934016493; fax: +34 934017700.
E-mail address: laia.haurie@upc.edu (L. Haurie).

0950-0618/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.conbuildmat.2012.12.012

hydromagnesite is an industrial by-product produced during the calcination of magnesite [10]. We have also used a commercial grade of magnesium hydroxide flame retardant to compare the resulting mortar formulations. Both hydromagnesite and magnesium hydroxide are endothermic flame retardants that decompose in the range of 200–550 °C and 320–360 °C respectively, with an associated endothermic heat of 800 J/g and 1370 J/g in each case [11].

In order to evaluate the performance of flame retardants acting under different mechanisms of action we have also employed two polyphosphate based flame retardants. In this case the main action mechanism is due to the formation of a protective char on the condensed phase by means of an intumescent effect. Examples of this type of flame retardants are the compounds containing nitrogen and phosphate like melamine polyphosphate or ammonium polyphosphate. The nitrogen contained in the molecule acts as a foaming agent, the polyphosphate as a catalyst and the polymer substrate as the char forming agent [12].

We have formulated the flame retarded epoxy mortars by substituting part of the conventional siliceous aggregate for flame retardants. These mortars have been analyzed in order to evaluate their improvement in fire behavior as well as to corroborate that they do not undergo a significant loss on mechanical properties.

2. Experimental

2.1. Materials

The epoxy mortar supplied by Sika S.A.U. consisted of three components: 13.3%$_{wt}$ resin *A*, 6.7%$_{wt}$ resin *B* and 80%$_{wt}$ siliceous aggregate. Mechanical properties provided by the supplier are in the range of 30–40 N/mm^2 for flexural strength and 80–90 N/mm^2 for compression strength. Synthetic hydromagnesite (HyM) was obtained from an industrial by-product in the pilot plant of Magnesitas Navarras S.A. Magnesium hydroxide (MH) was the commercial grade Magnifin H5 from Martinswerk GmbH. Melamine polyphosphate (Mel) grade Budit 3141, and ammonium polyphosphate (APP) grade FRCROS 70 were both supplied by Budenheim Iberica S.A.

2.2. Samples preparation

Epoxy mortars have been manually prepared mixing the two components that constitute the epoxy resin and subsequently adding the inorganic aggregate and the corresponding flame retardant. Once blended and stirred the homogeneous mixtures were casted in suitable molds to cure at room temperature for at least 24 h. Samples were tested between 5 and 7 days after curing. In order to define the percentage of each flame retardant we performed preliminary tests covering a broad range of flame retardant addition [13]. Table 1 shows the composition of the prepared mortars expressed as phr (parts per hundred resin). As it can be observed the amount of endothermic flame retardant in the polymeric mortars is higher than for the polyphosphates. This fact is due to the poor efficiency at lower percentages of endothermic flame retardants [14,15]. However, even at higher levels mortar formulations prepared with hydromagnesite and magnesium hydroxide are less expensive than the ones containing polyphosphates.

2.3. Characterization

2.3.1. Thermal analysis

Differential scanning calorimetry (DSC) was performed on the plain epoxy mortar to determine the glass transition temperature as well as the heat associated with the exothermic combustion. Test was done in air atmosphere at a heating rate of 20 °C/min.

Table 1
Samples composition.

Sample	Composition (phr)		
	Epoxy resin	Aggregates	FR
E	100	400	0
E_{Mel}	100	380	20
E_{APP}	100	380	20
E_{MH}	100	340	60
E_{HyM}	100	340	60

Thermogravimetric analyses have been performed, for all the samples indicated in Table 1, in a muffle furnace coupled to a precision balance. This device allowed us to analyze a considerable amount of sample, and therefore mortar fragments of 4–6 g have been tested in air atmosphere with a heating rate of 3 °C/min within the range of 25–1000 °C.

2.3.2. Flame testing

2.3.2.1. Cone calorimeter. The cone calorimeter is a standardized device widely used to analyze the fire behavior of small samples. This equipment registers the heat release rate (HRR) of a sample exposed to a constant heat flux. The cone calorimeter tests were carried out following the procedures indicated in the ISO 5660 standard [16]. Square specimens (100 × 100 × 4 mm) were irradiated with a heat flux of 50 kW/m^2.

Several parameters have been proposed to quantify the fire performance of materials. The heat release rate curve (HRR) is a relevant quantity in the caseof fire, as well as the peak of heat release rate (PHRR), which is the maximum value obtained in the HRR curve [17]. The time to ignition (TTI) is the time required for the irradiated sample to develop a sustainable flame. In this work we have also used the Fire Performance Index (FPI), which has been related with the time available to escape in a real fire situation [18] and the Fire Growth Rate Index (FIGRA), used for regulatory purposes in the Single Burning Item test [19,20].

2.3.2.2. Dripping test. A radiator device described in the Spanish UNE 23.725-90 standard [21] was employed to measure the degree of extinguish ability of combustion.

Samples of 70 × 70 × 4 mm dimensions are placed on a metallic grid 3 cm below a heat source of 500 W, which is taken away and put back after each ignition and extinction. Three samples for each composition were tested and the parameters determined were the number of ignitions and the average time of flame persistence during the first 5 min of combustion.

2.3.2.3. Smoke test. The gases released during combustion were analyzed by burning a sample of 5 g in a chamber provided with a measurement system of the transmitted light comprised of a light source, a set of lenses and a light sensor.

2.3.3. Mechanical properties

Flexural strength and compressive strength tests were performed in a mechanical testing machine MUTC-200 from Incotecnic. Three point bending tests were performed on 4 × 4 × 16 cm specimens at a crosshead movement rate of 5 kg/s. Compression tests were performed on the two fragments obtained in the flexural tests at a crosshead speed of 240 kg/s. Three samples have been tested to determine flexural strength for each mortar formulation, and therefore six samples for compression tests.

In addition, tests above the glass transition temperature (Tg = 60 °C) have been performed for the cases of plain epoxy mortar and epoxy mortar with the hydromagnesite by-product. In these cases the samples have been kept in the furnace at 80 °C for 2 h and immediately tested at the conditioning temperature.

3. Results and discussion

3.1. Thermal stability

The epoxy resin exhibits its glass transition temperature around 60 °C, as can be observed in the DSC displayed in Fig. 1. The exothermic peak corresponding to the combustion of the epoxy resin

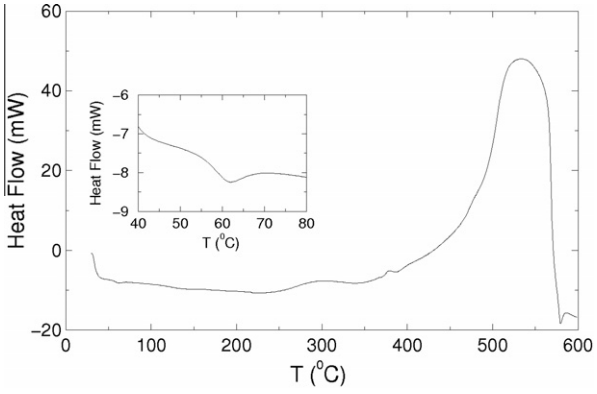

Fig. 1. DSC curve of plain epoxy mortar. Inset shows a detail in the range of the glass transition temperature.

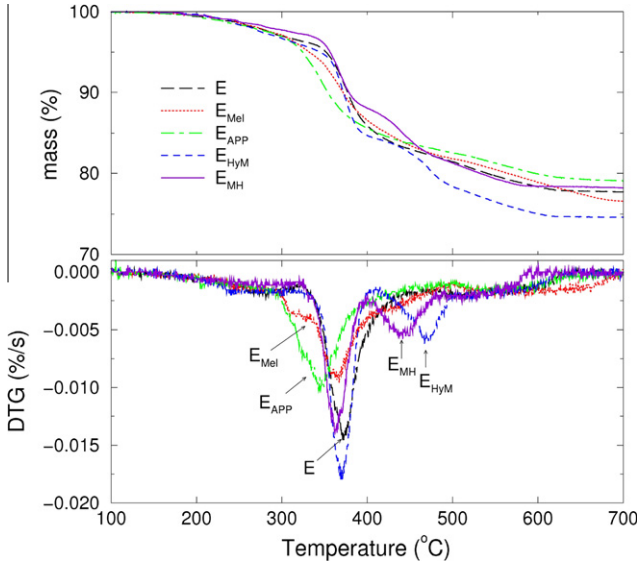

Fig. 2. Thermogravimetric curves. Upper panel: Mass evolution of the epoxy mortars with temperature. Lower panel: derivative curve.

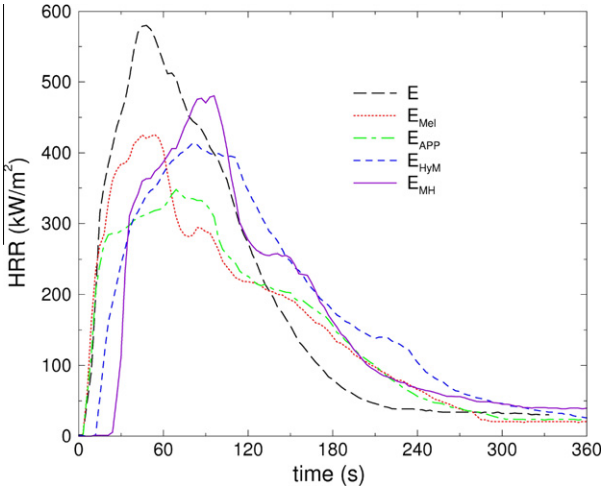

Fig. 3. Heat release rate curves of the epoxy mortars.

has the onset around 400 °C and the maximum value at 520 °C. The heat associated with this process is of 1047 Jg^{-1}.

The upper panel in Fig. 2 shows the evolution of the sample mass, expressed as percentage, with temperature obtained from the thermogravimetric tests. The lower panel is the time derivative of the mass versus temperature. Epoxy resin decomposes between 325 and 425 °C in a single step. Samples E_{APP} and E_{Mel} start to decompose at lower temperatures due to the loss of volatile products like ammonia and water. Polyphosphates decompose in a temperatures range of 250–350 °C depending on the nature and length of the phosphate chains [22]. First, the release of volatile products like ammonia and water occurs, with the formation of polyphosphoric acid that catalyzes the development of a phosphorous rich char [23]. The formation of a thick and hard protective char hinders the access of oxygen to the polymer which can result in a lower fraction of burned polymer. This effective protective char would explain the lower mass loss of sample E_{APP} with respect to *E*. As can be observed, E_{HyM} shows a higher weight loss due to the decomposition of magnesium hydroxide and magnesium carbonate of the hydromagnesite that represents 54% of its original weight. This mass loss is not observed in the sample containing magnesium hydroxide that releases 31% of water during its decomposition. This can be related to the formation of an insulating protective layer of magnesium oxide [24].

3.2. Flame testing

3.2.1. Cone calorimeter

The samples with flame retardants reduce the peak of heat release rate (PHRR) as it can be observed in Fig. 3. Samples E_{Mel} and E_{HyM} containing melamine polyphosphate and synthetic hydromagnesite as flame retardants reduced the PHRR by approximately 30%, while the sample with magnesium hydroxide (E_M) shows only a 20% reduction. The E_{APP} increased this reduction up to 36%. Table 2 summarizes the cone calorimeter results. It can be observed that the endothermic flame retardants, magnesium hydroxide and hydromagnesite increased the time to ignition from 3 s to 21 s and 11 s, respectively. Differences in the flame retardant action mechanisms could explain this improvement compared to APP and Mel. Flame retardants based on ammonium or melamine polyphosphate protect the polymer by forming an insulating char,

Table 2
Cone calorimeter results.

Sample	TTI (*s*)	PHRR (kW/m^2)	FPI*10^{-3}(s m^2/kW)	FIGRA (kW/m^2 s)
E	3	595	5.05	12.61
E_{Mel}	3	417	7.19	8.52
E_{APP}	3	382	7.91	5.19
E_{MH}	21	480	43.71	5.33
E_{HyM}	11	428	25.67	5.05

while inorganic hydroxides and carbonates absorb heat from the system and release inert gases that dilute the combustion gases in the gas phase. The effect of endothermic flame retardants starts right after their decomposition, but development of a protective char takes some time. Once the protective intumescent structure is formed a reduction of the PHRR is observed. This explanation can also be applied to the differences in the values of the FIGRA and FPI index. Both parameters use the PHRR, but while FPI is related to the time to ignition, FIGRA is defined as the quotient between the PHRR and the time at which this peak is produced. Therefore, samples E_{HyM} and E_{MH} exhibit a remarkably higher FPI than E_{APP} and E_{Mel} which do not delay the TTI. However, according to FIGRA values, E_{APP}, E_{HyM} and E_{MH} show the best fire behavior. Comparable trends were obtained by Ribeiro et al. in similar flame retardant epoxy systems [6].

Fig. 4 illustrates the mass loss curves obtained from the cone calorimeter test. Flame retarded mortars slow down the mass loss rate, although E_{HyM} exhibits a higher mass loss rate after 125 s. This fact could be related with the decomposition of magnesium hydroxides and carbonates that take place around 250 °C and 400 °C respectively. Char formation decreases total mass loss in samples containing APP and Mel and E_{MH} reaches the same final mass than *E*. All this is in good agreement with the results obtained from the TGA previously described in Fig. 2.

3.2.2. Dripping test

The epoxy mortar has very limited auto-extinguish ability, as it can be observed in Table 3. Once the flame appears and the heat source is removed, it lasts more than 3 min to extinguish it. When mortars incorporating flame retardants were tested, significant differences with regard to the persistence of the flame and hence with the auto-extinguishing capability were observed (Table 3). The average time of flame persistence is shortest for EHyM and therefore this sample exhibits the highest number of ignitions. Short combustion times and often elevated number of ignitions are

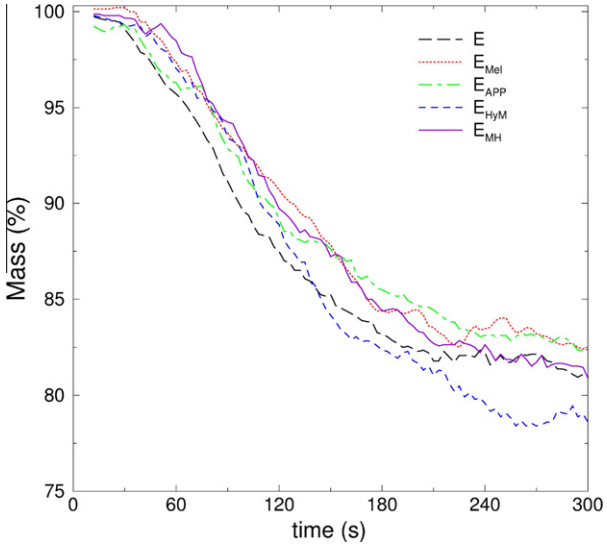

Fig. 4. Mass loss of epoxy mortars samples recorded during the cone calorimeter tests.

Table 3
Dripping test results.

Sample	TTI (s)	Nr of ignitions	Avg. combustion extent (s)	Mass loss (%)
E	125.5	1.0	196.5	5.8
E_{Mel}	116.3	3.3	53.1	3.3
E_{APP}	112.3	3.7	45.2	2.7
E_{MH}	125.8	1.5	183.2	4.3
E_{HyM}	92.0	9.0	24.3	4.6

characteristic of a material that easily auto-extinguish the flame when the heat source is removed. Mortars with both polyphosphates show similar trends, decreasing the flame persistence and increasing the number of ignitions with regard to the plain mortar. The values of the sample containing magnesium hydroxide are similar to those of the epoxy mortar without flame retardant, but the behavior during the test was completely different. In the case of EMH the flames were short and localized in specific parts of the tested sample, while for E high flames covered the whole specimen. The higher weight loss of the mortar without flame retardant is explained due to this pronounced burning.

3.2.3. Smoke test

The addition of flame retardants reduces the smoke production, as it can be seen in the light transmittance evolution curves displayed in Fig. 5. Samples containing hydromagnesite and magnesium hydroxide produce less smoke which is translated to a better visibility in case of fire. These endothermic flame retardants release inert gases, like water vapor or carbon dioxide, during their decomposition, which dilutes the combustion gases and hinders combustion and smoke production [25]. Furthermore, the magnesium oxide formed during the decomposition of both fillers has been described as an effective smoke suppressant due to its high surface areas and its catalytic activity related with the promotion of carbon deposition and oxidation processes [26].

Ammonium polyphosphate and melamine polyphosphate are phosphoric salts, which act as flame retardants by the formation of a thermal insulating char on the polymer. This char helps to trap the gases and, therefore it is observed a reduction of the smoke released. However, these compounds do not exhibit high activity as smoke suppressants.

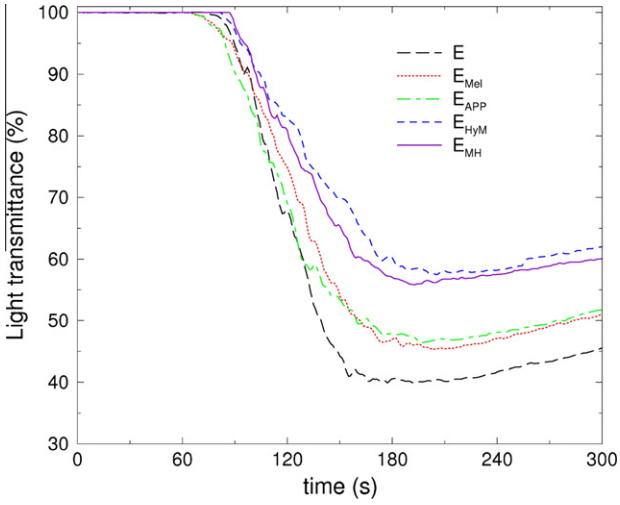

Fig. 5. Evolution of light transmittance with time.

3.3. Mechanical properties

Mechanical tests were performed in order to verify that the flame retardants do not significantly decrease these properties. Results for compressive and flexural maximum strength at room temperature are summarized in Fig. 6. The values of plain epoxy mortar are in good agreement with those supplied by the producer and already indicated in Section 2.1. We observe that the flame retarded epoxy mortars exhibit a good mechanical flexural behavior, obtaining in the case of E_{APP} even higher values of flexural strength than for plain epoxy. A similar behavior is found for compressive strength with the only exception of the mortar containing magnesium hydroxide, E_{MH}, where a significant decrease is observed. This fact could be due to the small particle size of magnesium hydroxide in comparison with the aggregate used in the epoxy mortar formulation. This flame retardant has been added in higher percentage than APP and Mel. Despite that the same amount of hydromagnesite has been added in E_{HyM} (see Table 1), its broader particle size distribution [27] seems to be more suitable to maintain the mechanical properties.

Synthetic hydromagnesite is a satisfactory alternative to commercial flame retardants for epoxy mortars. In order to further

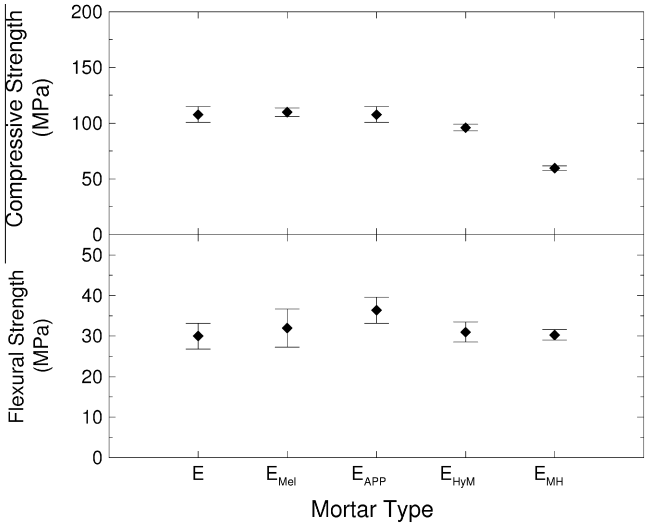

Fig. 6. Compressive and flexural strength of epoxy mortars.

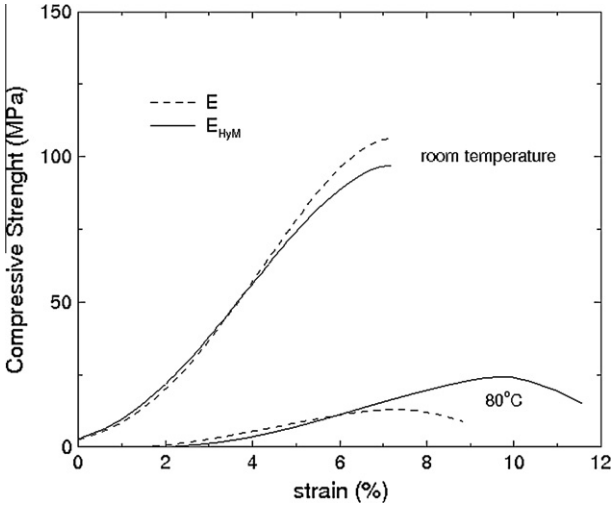

Fig. 7. Compressive stress–strain curves of plain epoxy mortar and epoxy mortar containing hydromagnesite at room temperature and 80 °C.

characterize its performance, mechanical tests at 80 °C were carried out and compared with plain epoxy mortars. Fig. 7 shows an example of the compression strain–stress curves for the formulations E and E_{HyM}, at room temperature and at 80 °C. We observe that in both cases compressive strength falls drastically when the samples are tested at high temperature. However, this decrease is less prominent for E_{HyM} (24 ± 1 MPa), in front of that of plain epoxy mortar, E (13 ± 1 MPa). Again this fact could be explained due to the particle size distribution of the hydromagnesite that combines the presence of fine and coarse particles and, therefore modifies the properties of the epoxy mortar.

4. Conclusions

Both intumescent (E_{APP} and E_{Mel}) and endothermic (E_{HyM} and E_{HM}) flame retardants showed efficient fire retardant activity in epoxy mortars (E). A decrease in the PHRR values was found for all the studied samples. For the endothermic ones, an increase in the TTI value was also registered. This enhancement could be justified by an earlier fire-retardant action related to the heat absorption and dilution gases above 330 °C.

Smoke production of FR composites decreased, compared to the reference epoxy mortar, specially for E_{HyM} and E_{HM}. Moreover, E_{HyM} exhibited an improved auto-extinguishing capacity when the heat source was removed.

Mechanical properties of epoxy mortars were not significantly affected by the addition of flame retardants. In the case of the mortar containing hydromagnesite not only the mechanical properties at room temperatures presented adequate values, but also when the mortar was tested at 80 °C there was observed an improvement in compressive strength.

The satisfactory flame retardant and mechanical properties obtained for E_{HyM} together with the fact that hydromagnesite is obtained from an industrial by-product makes it an interesting alternative to commercial flame retardants.

Acknowledgements

The authors would like to thank Ministerio de Ciencia e Innovación and Generalitat de Catalunya for their support under the projects FIS2009-13360-C03-03, MAT2010- 15565 and 2009SGR-878.

References

[1] Biron M. Thermosets and composites: Technical information for plastics users. Elsevier Ltd. 2003.
[2] ACI committee 503R. Use of epoxy compounds with concrete. Am Concr Inst, Detroit; 1993.
[3] El-Hawarya MM, Abdel-Fattah H. Temperature effect on the mechanical behavior of resin concrete. Constr Build Mater 2000;14:317–23.
[4] Elalaoui O, Ghorbel E, Mignot V, Ben Ouezdou M. Mechanical and physical properties of epoxy polymer concrete after exposure to temperatures up to 250 °C. Constr Build Mater 2012;27:415–24.
[5] Ribeiro MCS, Nóvoa PR, Ferreira AJM, Marques AT. Flexural performance of polyester and epoxy polymer mortars under severe thermal conditions. Cement Concr Compos 2004;26:803–9.
[6] Ribeiro MCS, Rodrigues JA, Ferreira AJM, Marques AT. Fire behaviour enhancement of epoxy polymer mortars modified with flame retardant systems. Mater Sci Forum 2008;587–588:903–7.
[7] Alaee M, Wenning RJ. The significance of brominated flame retardants in the environment: current understanding, issues and challenges. Chemosphere 2002;46:579–82.
[8] Haurie L, Fernández AI, Velasco JI, Chimenos JM, Ticó-Grau JR, Espiell F. Synthetic hydromagnesite as flame retardant. A study of the stearic coating process. Macromol Symp 2005;221:165–74.
[9] Haurie L, Fernández AI, Velasco JI, Chimenos JM, Lopez Cuesta VM, Espiell F. Thermal stability and flame retardancy of LDPE/EVA blends filled with synthetic hydromagnesite/aluminium hydroxide/montmorillonite and magnesium hydroxide/aluminium hydroxide/montmorillonite mixtures. Polym Deg Stab 2007;92(6):1082–7.
[10] Fernández A I, Chimenos JM, Segarra M, Fernández M A, Espiell F. Procedure to obtain hydromagnesite from a MgO-containing residue. Kinetic study. Ind Eng Chem Res 2000;39:3653–8.
[11] Haurie L, Fernández A. I, Velasco J. I, Chimenos J.M, Lopez Cuesta J.M, Espiell F. Synthetic hydromagnesite as flame retardant. Evaluation of the flame behaviour in a polyethylene matrix. Polym. Deg. Stab 2006;91(5):989–94.
[12] Lu S, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. Prog Polym Sci 2002;27(8):1661–712.
[13] Haurie L., Lacasta A.M., Molina J., Chimenos J.M., Rosell J.R., Mejora del Comportamiento al Fuego de Morteros Poliméricos mediante la incorporación de retardantes de llama. Proceedings of the X congreso nacional de materiales. San Sebastian, Spain; 2008. p .911–914.
[14] Rothon RN, Hornsby PR. Flame retardant effects of magnesium hydroxide. Polym Degrad Stab 1996;54:383–5.
[15] Hörold S. Phosphorus flameretardants in thermoset resins. Polym Degrad Stab 1999;64(3):427–31.
[16] ISO. Reaction to fire tests: heat release, smoke production and mass loss rate. Part 1: Heat release rate (cone calorimeter method). ISO 5660-1: 2002. Geneva: ISO; 2002.
[17] Babrauskas V, Peacock RD. Heat release rate: the single most important variable in fire hazard. Fire Safety J 1992;18:255–72.
[18] Fu M, Qu B. Synergistic flame retardant mechanism of fumed silica in ethylene-vinyl acetate/magnesium hydroxide blends. Polym Degrad Stab 2004;85:633–9.
[19] Schartel B, Hull TR. Development of fire-retarded materials-interpretation of cone calorimeter data. Fire Mater 2007;31:327–54.
[20] EN 13823:2002. Reaction to fire tests for building products—building products excluding floorings exposed to the thermal attack by a single burning Item. European Committee for Standardization (CEN). Brussels, Belgium; 2002.
[21] Aenor. Reaction to fire tests of building materials. Dripping test with electrical radiator used for melting materials (Complementary Test). UNE 23. Madrid: Aenor; 1990. p. 725–90.
[22] Balabanovich AI. The effect of ammonium polyphosphate on the combustion and thermal decomposition behavior of poly(butyleneterephthalate). J Fire Sci 2003;21:285–98.
[23] Cichy B, Łuczkowska D, Nowak M, Władyka-Przybylak M. Polyphosphate flame retardants with increased heat resistance. Ind Eng Chem Res 2003;42:2897–905.
[24] Sain M, Park SH, Suhara F, Law S. Flame retardant and mechanical properties of natural fibre–PP composites containing magnesium hydroxide. Polym Degrad Stab 2004;83:363–7.
[25] Kim M. Flame retardancy and smoke suppression of magnesium hydroxide filled polyethylene. J Polym Sci Part B Polym Phys 2003;41:936–44.
[26] Hornsby PR. The application of fire-retardant fillers for use in textile barrier materials. In: Duquesne S, Magniez C, Camino G, editors. Multifunct Barriers Flexible Struct. Springer; 2007. p. 3–19.
[27] Haurie L, Fernández AI, Velasco JI, Chimenos JM, Lopez Cuesta JM, Espiell F. Effects of milling on the thermal stability of synthetic hydromagnesite. Mater Res Bulletin 2007;42:1010–8.