Assessment of fire behaviour of polyisocyanurate (PIR) insulation foam enhanced with lamellar inorganic smart fillers

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ABSTRACT

Modern day energy codes are driving the design and multi-layered configuration of exterior wall systems with significant emphasis on achieving high performance insulation towards improving energy performance of building envelopes. Use of highly insulating polyisocyanurate (PIR) based insulation materials enhanced with eco-friendly lamellar inorganic fillers contributes to meeting energy performance requirements, environmental challenges and cost reduction without undue compromise of the overall building fire safety. Towards that end, the aim of the current work is to assess the fire behaviour of PIR foams enhanced with lamellar inorganic smart fillers, namely Layered Double Hydroxides (LDHs) and ZrP. Experimental results indicate that fire reaction properties and thermal stability of foam samples enhanced with three types of lamellar inorganic smart fillers are evaluated using cone calorimeter (CC) and thermogravimetric (TGA) analysis. The initial degradation temperature of PIR-layered filler samples increases compared with neat PIR foam, indicating that incorporation of flame retardants decelerates the degradation of PIR foam and as result increases the thermal stability of PIR foam. Thermal decomposition of the PIR samples occurs in two distinct stages associated with the degradation of the urethane-urea linkages of the hard segment, releasing low calorific capacity products and the degradation of polyol derived products with higher calorific capacity than those derived from isocyanate. Increasing the filler content results in increased char formation and decreased peak Heat Release rates (HRR).

KEYWORDS:

polyisocyanurate insulation; layered doubled hydroxides; zirconium phosphate; fire performance; thermogravimetric analysis; cone calorimeter analysis

INTRODUCTION

Modern day energy codes are driving the design and multi-layered configuration of exterior wall systems with significant emphasis on achieving high performance insulation towards improving energy performance of building envelopes. Insulation in walls may comprise of either noncombustible material such as fiberglass or mineral wool, or frequently encountered a wide range of highly insulating combustible foam plastic materials. Most commonly used insulation materials include polymers such as extruded polystyrene, expanded polystyrene, polyurethane foam (PUF) and polyisocyanurate (PIR) with or without flame retardants [1]. Appropriate use of the above materials requires that they meet both energy performance requirements, environmental challenges and cost reduction without undue compromise of the overall building fire safety. Numerous studies [1-3] have established that thermal decomposition of polymeric foams, in both inert and oxygen atmospheres, is a complex process consisting of numerous decomposition pathways that strongly depend on the reactivity of organic compounds employed in its synthesis. PIR foams are part of the polyurethane (PUR) rigid foam family and their main characteristic is that they contain a high percentage of cyclic isocyanurate chemical linkages and use of polyester polyol instead of the standard polyether polyol used in PUR's. PIR are based on the reaction of polycyclotrimerization of diisocyanates or isocyanate terminated prepolymers to form triazine-trione ring structured isocyanurate rings [4] that, from the thermodynamic point of view, are more thermally stable than urethane bonds found in PUR foams as it dissociates at approximately 200°C as opposed to 350°C for polyisocyanurates [5].

Regarding the flammability of polymer insulation-related flame retardants, the substitution of commonly used halogen-based flame retardants for eco-friendly "greener" ones such as mineral fillers like Layered Double Hydroxides (LDHs) and zirconium phosphate nanocomposites [2, 3], is currently of great interest for avoiding the release of corrosive and toxic volatile compounds from combustion. In contrast to halogenated flame-retardants, layered compounds attract significant attention and are explored as second-generation fire-retardant materials to alternatively be used as efficient and more environmental friendly additives to various polymers with the ability to improve their flame retardancy and thermal stability and smoke suppression [6]. LDHs consist of synthetics layered compounds containing positively charged metal hydroxide layers with change balancing anions located in between. More specifically, LDHs are described by the generic formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2\ A^{n-}_{x/n}]$ x yH_2O, where M^{II} is the divalent cation, M^{III} is the trivalent cation, A is the interlayer anion with n- charge and x and y are fraction constants [7]. LDHs may be formed with all dipositive metal ions from Mg^{2+} to Zn^{2+}, and almost all transition metal trivalent ions and are classified as members of the hydrotalcite ($MgAlCO_3$) supergroup [8]. Their increased fire retardancy is observed in both gas and solid phases as they develop non-flammable gases diluting flammable gases and promoting surface charring. Their mechanism during thermal degradation mainly includes the release of water and carbon dioxide, diluting combustion gases, and reducing endothermic decomposition of metal hydroxides. Specifically, this latter inorganic-reinforced carbonaceous residue thermally protects the underlying polymer as the formation of this residue and slows down the combustion process of PUF [2, 6]. At elevated temperatures, LDHs have been shown to release water and go through endothermic decomposition. Different authors have recently studied several types and contents of LDH in polymeric-based insulation materials [2, 3]. Despite their effectiveness, LDHs have until now limited commercial success as fire retardants because of their difficulty to disperse and distribute in polymers, which limits their effectiveness [2] and most available studies concern their incorporation in PUF. A recent study [9] firstly investigated the potential synergistic effect between organically modified nanoclay LDH and flame retardants on PIR nanocomposites on improving the fire retardancy and fire behaviour.

Alpha zirconium phosphate (α-ZrP) structure, with chemical formula $Zr(HPO_4)_2$ x H_2O, is composed by stacking layers made of planes of zirconium atoms bonded, on both sides, to monohydrogen phosphate groups. Each phosphate group is bonded to three Zr atoms of the plane, while each zirconium is octahedrally coordinated by six oxygens of six different monohydrogen phosphate groups. The water molecules are located in the zeolitic cavities of the interlayer region [10]. Zirconium phosphate can be easily functionalized through intercalation reactions and has been widely studied in literature as nanostructurant filler for polymer composites. Thanks to the highly tunable properties and unique cation exchange properties, ZrP exhibits several advantages over conventional natural clays (e.g. montmorillonites), including higher purity and ease of intercalation and/or exfoliation [11-13]. One of the most interesting aspects of this layered material is its capacity to reduce the rate of combustion of the polymers [14] and its flame retardancy properties are proven to reduce the total heat evolved and the cone calorimeter measured heat release rate [15,16]. Even reduced amounts of nanoparticle α-ZrP addition in virgin materials greatly affect their thermal stability and burning behavior, as inhibition of thermal decomposition and higher char yields formation can be observed [16].

The focus of the current work is to study potential synergistic effects between PIR and layered fillers with “smart” flame retardants on improving the flame retardancy and fire behavior of rigid insulation foam samples. Towards this end, fire reaction properties and thermal stability of foam samples enhanced with three types of lamellar inorganic smart fillers has been investigated using thermogravimetric analysis (TGA) and cone calorimeter (CC). The effects of LDH concentration on the thermal degradation and flammability of PIR are also examined.

EXPERIMENTAL

Materials

PIR samples with a constant isocyanate index (NCO/OH) equal to 3.0 were obtained from lab-scale prototyping experiments conducted at SELENA Labs. Laboratory samples were produced by high pressure impingement mixing type of foam machinery, operating at constant processing parameters. Reacting mixtures were poured centrally into horizontal 35cm x 35 cm x 5 cm mold, heated at 50°C, with steel facers attached to the bottom and the lid. Three new types of PIR foams samples with layered fillers, namely PIR-$MgAlCO_3$ filler (PIR-LDH1), PIR-MgAlStearate filler (PIR-LDH2) and PIR-ZrP octadecylamine filler (PIR-ZrP3) are investigated and assessed versus a pure PIR sample. LDH2 and ZrP3 are organically modified layered fillers, in which organic modification acts also as compatibilizer between filler and polymer matrix.

Test methods

Cellular structure of the samples was evaluated using scanning electron microscopy (SEM) and crystal structures of samples were analyzed by X-ray diffraction (XRD). The thermal stability was evaluated in terms thermogravimetric analysis (TGA) under N_2 (inert gas) environment in a Mettler Toledo TGA apparatus. About 10 mg foam sample was placed in an alumina pan with no lid. The heating rate was 20ºC/min with a N_2 flow of 150 ml/min. The following parameters were determined: initial degradation temperature, $T_{5\%}$ (temperature at 5% weight loss), corresponding maximum temperature, T_{max}, and weight loss, W, for each degradation step and char residue at 1000ºC. Cone calorimeter (CC) tests were performed with a Dark Star Research Ltd (UK) apparatus according to the ISO 5660-1 [16] at 50 kW/m^2. The dimensions of the samples are 100mm x 100mm x 24mm and the density of the samples is approximately 50 kg/m^3. Experimental results includes time to ignition (TTI), Combustion Time (CT), total HRR (THR), peak HRR (p-HHR), average HRR (Av-HRR), average mass loss rate (Av-MLR), smoke production rate (SPR), smoke and CO yield. Additionally, the unexposed surface temperature was measured using a type K thermocouple.

RESULTS AND DISCUSSION

SEM and XRD

To verify that the LDHs and ZRP are well dispersed in PIR. SEM and XRD analysis were firstly carried out. Figure 1 shows the SEM morphological evaluation of neat PIR (left) and PIR-LDH1 (center) and XRD spectra of neat PIR and PIR-ZrP3 (right). The SEM results depicts the regular and cellular structure of plain PIR and PIR-LDH1 verifying that addition of LDH fillers does not modify the cellular structure. The XRD spectra of PIR-ZrP3, compared to those of neat PIR indicate that ZrP layer has been exfoliated in the matrix as a great amount of polymers has entered into the gallery space separating ZrP layer during in situ intercalation polymerization process.

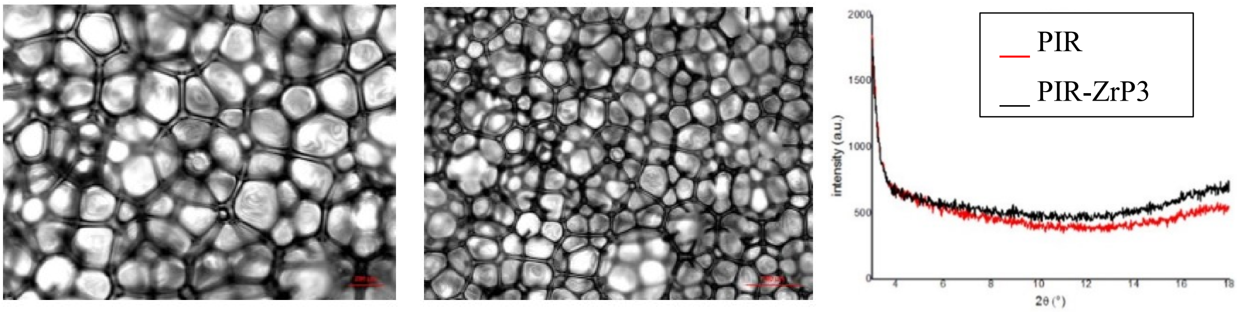

Fig. 1.SEM morphological evaluation of neat PIR (left) and PIR-LDH1 (center) and XRD spectra of neat PIR and PIR-ZrP3 (right)

Thermogravimetric analysis (TGA)

Figure 2 presents the weight loss and weight loss rate of all formulations. It can be observed that the degradation of all PIR foams in inert atmosphere occurs in two steps. The results are summarized in Table 1. The initial degradation temperature, $T_{5\%}$, corresponds to 255°C for pure PIR. It can be seen form Table 1, that $T_{5\%}$ increases compared with net PIR foam, indicating that incorporation of flame retardants decelerates the degradation of PIR foam and as a result increases the thermal stability of PIR foam higher temperature range. The first pyrolysis step takes place from 200 to 400°C and the maximum rate degradation temperature, $T_{max,1}$, is substantially decreased with the layered filler addition and only in PIR-6%ZrP3 remains approximately at the same levels. This first step is related to the degradation of the urethane-urea linkages of the hard segment, releasing low calorific capacity products; residue weight values of this first reaction are denoted as W_1. The second stage of decomposition corresponds to the degradation of polyol derived products with higher calorific capacity than those derived from isocyanate [3] and lower residue weight, W_2. The second degradation step of the pure PIR foam takes place between 400 and 600°C, and the maximum rate degradation temperature, $T_{max,2}$, is 477°C with the final char residue 19.5% of the initial mass. With LDH/ZrP fillers, the temperatures are generally decreased due to degradation of the fillers at lower temperature. Increasing filler content results in increased char formation.

Table 1. TGA data of pure PIR, PIR-LDH1, PIR-LDH2 and PIR-ZrP3.

Sample	**Density**		**Stage 1**		**Stage 2**		
		$T_{5\%}$	**$T_{max,1}$**	**W_1**	**$T_{max,2}$**	**W_2**	**Char res.**
	kg/m3	**°C**	**°C**	**wt.%**	**°C**	**wt.%**	**wt.%**
PIR	50.4	255	373	64.5	477	36.2	19.5
PIR-2%LDH1	50.0	258	329	81.1	422	58.1	29.9
PIR-2%LDH2	50.5	273	363	74.2	426	56.1	30.5
PIR-2%ZrP3	54.0	271	355	77.5	426	59.0	30.7
PIR-4%LDH1	48.0	266	329	82.2	411	60.0	33.3
PIR-4%LDH2	49.5	272	339	75.5	416	59.9	33.1
PIR-4%ZrP3	45.0	266	366	74.7	409	61.6	30.3
PIR-6%LDH1	54.0	257	333	80.8	407	60.0	33.1
PIR-6%LDH2	48.0	274	337	81.3	424	57.4	32.6
PIR-6%ZrP3	55.0	278	376	76.9	482	50.8	31.9

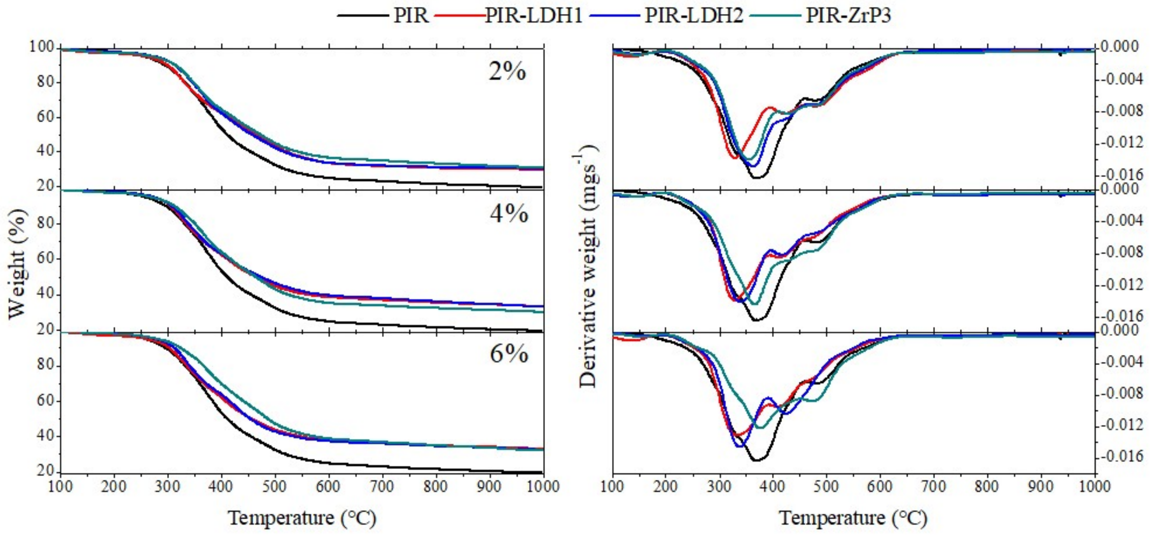

Fig. 2. TG (left) and DTG (right) of pure PIR, PIR-LDH1, PIR-LDH2 and PIR-ZrP3 in N_2 atmosphere.

Cone Calorimeter analysis

Almost all samples instantly ignited as shown in Table 2 summarising all the cone calorimeter data. Figure 3 shows the heat release rate and smoke production rate histories of all formulations. The presence of layered filler contributes to a decrease of p-HRR and HRR data correlate well with addition of fire retardants, demonstrating the beneficial effect of layered filler addition for fire performance. The decrease in the HRR of this second stage, is more pronounced, achieving a reduction of up to 40% for PIR-2%LDH3. PIR-4%ZrP3 results in higher char residue, as the surface char layer reduced both the oxygen and heat fluxes towards the polymer surface thus limiting the volatile compounds and therefore the Av-MLR [9]. The ultimate fire retardancy mechanism is turning polymer into protection barrier chars that absorb energy and shield the rest of the PIR from radiation. The carbonation layer protects the polymer by not giving access to oxygen to sustain combustion. The smoke yield and CO yield of all fillers-containing formulations are similar to and in some cases less than those of neat PIR indicating that they don't promote production of toxic gases.

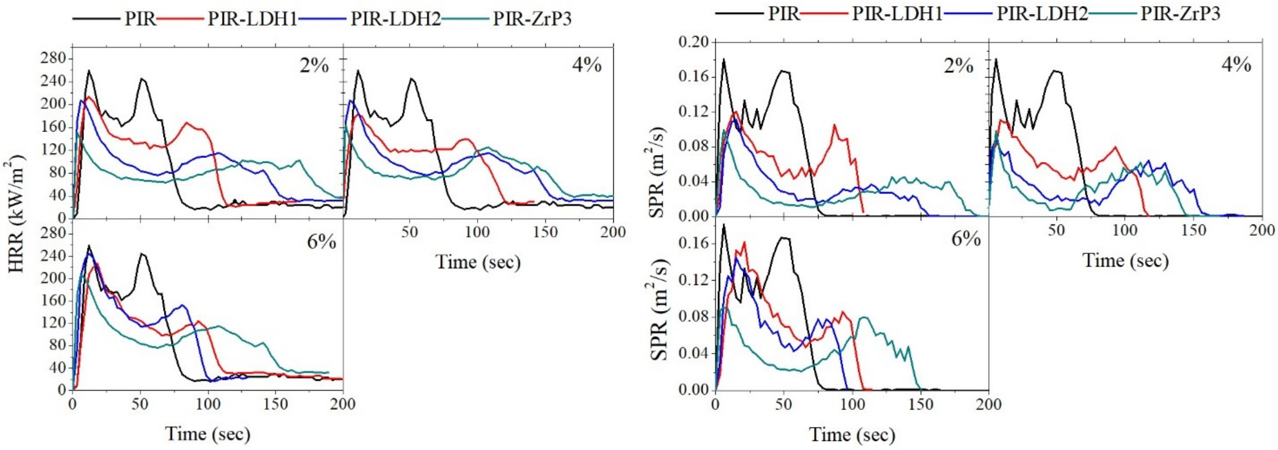

Fig. 3. HRR (left) and smoke production (right) rates of pure PIR, PIR-LDH1, PIR-LDH2 and PU-ZrP3.

Table 2. Flammability and smoke emission behavior of pure PIR and PIR-layered filler samples.

Sample	HF	TTI	CT	THR	p-HRR	Av-HRR	Av-MLR	Smoke yield	CO yield
	kW/m^2	s	s	MJ/m^2	kW/m^2	kW/m^2	g/s	-	-
PIR	50	1	102	17.85	259.1	135.2	0.1247	0.098	0.0329
PIR-2%LDH1	50	1	100	17.15	213.4	164.9	0.1039	0.069	0.0273
PIR-2%LDH2	50	1	150	17.68	206.7	119.8	0.0697	0.054	0.0382
PIR-2%ZrP3	50	5	192	16.67	152.0	86.8	0.0588	0.049	0.0334
PIR-4%LDH1	50	1	116	15.20	182.4	131.1	0.0722	0.086	0.0186
PIR-4%LDH2	50	1	150	17.96	206.7	149.5	0.1208	0.056	0.0349
PIR-4% ZrP3	50	1	202	18.50	176.0	92.0	0.0437	0.062	0.0646
PIR-6%LDH1	50	7	104	16.98	226.6	163.3	0.1037	0.079	0.0317
PIR-6%LDH2	50	1	95	14.73	244.4	155.0	0.0869	0.081	0.0230
PIR-6% ZrP3	50	1	150	18.22	196.7	132.4	0.0753	0.059	0.0301

CONCLUSIONS

Fire reaction properties and thermal stability of PIR form with MgAlCO3, MgAlStearate and ZrP octadecylamine fillers have been evaluated using TGA and cone calorimeter (CC). It was found that layered fillers promote the formation of reinforced char layer, providing an effective barrier against heat and oxygen, release noncombustible gases, and simultaneously effectively suppress smoke and gases during the combustion process. PIR-4%ZrP3 resulted in higher char residue and decreased p-HRR values. The use of different layered fillers does not lead to increase smoke generation or CO production. Increasing filler content resulted in increased char formation for all samples and decreased peak Heat Release rates (HRR) for LDH1 and LDH2. Further analysis at other heating rates under both oxygen and inert atmospheres will be further analyzed to derive a kinetic model to simulate the pyrolysis degradation mechanism PIR-layered filler foams. Additional combination of different layered fillers will be investigated in the future to further tune the fire resistance properties of PIR nanocomposites.

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