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Phosphinates and layered silicates in charring polymers: The flame retardancy action in polyurethane foams

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ABSTRACT

Nanocomposites of a charring polymer (like polyurethane foam) filled with aluminum phosphinate (AlPi) with or without melamine cyanurate (MelCy) have been prepared by microwave processing and their thermal stability and fire behavior have been studied. Results on the interaction between flame retardants and layered silicates were provided as well as detailed investigation of the char strength, which has been carried out using a suitably developed method based on dynamic-mechanic analysis.

Generally, the thermo-oxidative stability in presence of layered silicates was higher than the counterparts even if an additive rather than synergic effect took place; however, in some cases the interaction between clays and phosphinate led to a significant decrease of weight residue. In nitrogen the residue amounts were about the same but a higher amount of phosphorus was retained in the solid phase in presence of clays. Cone calorimeter results showed that the use of phosphinates led to a decrease of the PHRR; further addition of clays did not reduce the PHRR owing to the worse quality of char layer as demonstrated by the char strength test. However, it has been shown that the partial substitution of aluminum phosphinate with melamine cyanurate gave improved results: the AlPi–MelCy filled foams showed similar pHRR and THE but lower TSR and higher char strength than AlPi filled foams. It was also confirmed that phosphinate acted by flame inhibition but its action was depressed by the use of nanoclays owing to their interaction.

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1. Introduction

Recently, polymer nanocomposites emerged as one of the most promising developments in the area of flame retardancy, appearing to offer significant advantages over conventional formulations. Much attention was diverted to the use of layered silicates (clay) owing to their great potential for producing materials characterized by improved flame retardancy along with superior physical properties [1,2]. It has been reported that the use of nanoclays generally led to an increase in thermo-oxidative stability since they reduce permeation of oxygen [3]; in some cases also an increase in thermal stability was observed [4]. Often a decrease in the peak of heat release rate (PHRR) and/or a decrease in the total heat evolved during cone calorimeter test were claimed [2,5]. The main mechanism reducing the PHRR in all non-charring polymeric systems was the formation of a residual inorganic–carbonaceous protection

layer as shown by many authors while in charring materials (including intumescent systems) the main mechanism was the mechanical enhancement of char and/or optimization of the morphology of the char [6–9]. Moreover, in melting system, the presence of layered silicates led to a dramatic change of the melt viscosity, which may be helpful in preventing or reducing dripping behavior, therefore limiting flame spread by preventing the transfer of burning material to adjacent surfaces, thus resulting in a reduced HRR [10]. Research results, however, pointed out that clays, while exerting astonishing effects on some fire properties of the polymer, were not sufficient for commercial applications, since they failed to act as stand-alone flame retardants in important regulatory fire tests [10,11]; therefore, to successfully reduce the fire load, polymer nanocomposites should be used in conjunction with conventional flame retardants.

Recently phosphinates have emerged as very effective flame retardants in some polymers. Organic phosphinates (mainly diethyl aluminum phosphinate, AlPi) in conjunction with nanoparticles and in some cases melamine polyphosphate (MPP) have been studied in polyamide 6 (PA6) [12–17], polyethylene-terephthalate

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(PET) [18—20], polybutylene-terephthalate (PBT) [21,22], poly-methylmethacrylate (PMMA) [23], poly(3-hydroxy-butyrate-co-3-hydroxyvalerate)/poly(butylene adipate-co-terephthalate) (PHBV/PBAT) [24] and polylactic acid (PLA) [25] while inorganic aluminum phosphinate in conjunction with nanofillers has been studied in polyurethane foams (PU) [26]. It has been generally recognized that phosphinate showed mainly a gas phase action in cone calorimeter test, even if some condensed action has been reported in some papers. Bourbigot et al. [13] showed that no reaction leading to the formation of new species between the additives (AlPi, MPP, montmorillonite) or the additives and the matrix occurred; the main benefit of combined use of phosphinate and organically modified montmorillonite (o-MMT) was due to the higher mechanical resistance of the char for the formulation containing o-MMT and to the foamed structure of such char layer, leading to a strong reduction of second peak of heat release rate (HRR) which was related to the formation of cracks in the charred layer limiting its efficiency. Dahiya et al. [17] showed also that the addition of layered silicate (Cloisite 30B) to AlPi did not hinder this gas phase action while Gallo et al. [21] showed that the gas-phase action of the phosphorus is moderately decreased when iron oxide nanoparticles were added to AlPi due to the formation of iron-phosphinate terephthalate salts. When this interaction occurred, fewer phosphinate units were released into the gas phase as more phosphorus was kept in the solid phase. While the use of AlPi and melamine cyanurate has been studied in polyester polymers (PET, PBT) [27—29] showing some good results, to our best knowledge the combined use of AlPi, melamine cyanurate and nanofillers has never been studied.

However, all the neat polymers comprising organic phosphinates already reported in literature showed a "non-charring behavior" during cone calorimeter test [30], that is the HRR curve showed a strong initial increase up to a quasi-static HRR value and after that a peak of HRR occurred (thermally thick non-charring materials); the quasi-static HRR value can be reduced to a shoulder for intermediate thick non-charring materials. The PHRR of non-charring materials at the end of burning was not caused by a materials property itself, but by the thermal effect of an increasing thermal feedback from the isolated back surface of the sample. Thus it was proposed that switching off the PHRR at the end of burning reported for nanocomposites of non-charring polymers was most probably a thermal effect within the specimen and not due to a changed chemistry of the pyrolysis [6,31]. In presence of nanofillers a heat shielding effect was observed that led to an increase in the surface temperature resulting in a substantial increase in reradiated heat flux. Less heat flux was transformed in pyrolysis and thus the mass loss rate was reduced. The decreased mass loss rate resulted in the reduction in HRR [6].

In this work we studied nanocomposites of a charring polymer (like as polyurethane foam) filled with organic phosphinates (with or without melamine compounds) to see whether the flame retardancy improvements already reported for non-charring polymers filled with the same flame retardants and layered silicates were still present. Results on the interaction between flame retardants and layered silicates were provided as well as detailed investigation of the char strength has been carried out using a suitably developed method based on dynamic-mechanic analysis.

2. Experimental

2.1. Materials

The raw materials employed in polyurethane foam synthesis were polymeric MDI (methane diphenyl diisocyanate), Voranate M600 (Dow Chemicals) characterized by NCO% = 30.5; average

functionality = 2.8, viscosity to 25 °C = 600 mPa s; polyester polyols: Isoexter 4530, hydroxyl value = 510 mgKOH/g, viscosity to 25 °C = 11,000 mPa s; Isoexter 4537, hydroxyl value = 350 mgKOH/g, viscosity to 25 °C = 4900 mPa s; polyether polyol: Isoter 842G, hydroxyl value = 160 mgKOH/g, viscosity to 25 °C = 250 mPa s. Polyols were kindly supplied by Coim, Italy. Catalysts employed were: Niax C-8, i.e. N,N-dimethyl cyclohexylamine (DMCHA) and Niax A-33, i.e. pentamethyl-diethylene triamine (PMDETA), both kindly supplied by Momentive Performance Materials; surface-active agent: poly-siloxane—polyether copolymer: Niax Silicones L-6900 supplied by Momentive Performance Materials; blowing agent: blend of 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane (Solkane 365/227, Solvay Fluor) and water. The amount of blowing agent used was calculated in order to obtain foams with a density of $35 \pm 3 \text{ kg/m}^3$. The organically modified layered silicate used was Cloisite 30B (referred in the following as C30B), that is bis(2-hydroxyethyl)methyl tallow ammonium modified montmorillonite, supplied by Southern Clay Products.

The flame retardants used were aluminum tris-diethylphosphinate (AlPi) and a mixture comprised aluminum tris-diethylphosphinate and melamine cyanurate (MelCy), both kindly supplied by Clariant (Germany). The phosphorus content of the ranged between 23.3 and 24 wt% for the first one and 15.4 and 16.4 wt% for the second one. Also an unfilled PU foam has been prepared as a reference material; it will be named REF.

Polyurethane foams were prepared using a two steps procedure. A fixed amount of clays (3 or 5 wt% on total foam mass), which was previously dehydrated overnight in an oven at 110 °C, was dispersed in polyols mixture; clay dispersion was promoted by a microwave treatment [32]. After that, the catalysts, surface active agent, flame retardant (fixed amount, 10 wt% on total foam mass) and blowing agent were added to the polyols mixture and stirred for 1 min with a high speed mechanical stirrer. The isocyanate was added to this mixture; the components were mixed for 15 s with a high speed stirrer and then poured into an open mold for free rise polymerization. The foams were then put in an oven at 70 °C for 24 h, to complete the polymerization reaction, before cutting the samples for characterization.

The samples will be named firstly indicating the flame retardant amount and kind (i.e. 10_AlPi—MelCy or 10_AlPi) and after the clay content (0, 3 or 5%): for example sample 10_AlPi—MelCy_3% represents a PU foam filled with 10 wt% of aluminum phosphinate and melamine cyanurate and 3 wt% of C30B.

2.2. Characterization

Morphological characterization was performed by X-ray diffraction, using a Philips powder diffractometer X'Pert equipped with a CuKα ($\lambda = 1.54$ Å) radiation source with a scan step size of 0.03, and by transmission electron microscopy (TEM) using a FEI Tecnai G12. Samples for TEM analyzes were embedded in acrylic resin and cut at about 80—100 nm using a Leica Ultracut UCT microtome; the analyses have been carried on at 100 kV.

The thermal stability was studied by thermogravimetric analyzer SDT Q600 (TA Instruments), under nitrogen and air atmosphere with a heating rate of 20 °C/min from 25 to 800 °C using alumina pans. Solid residues collected at 700 °C after TGA analysis have been analyzed by FTIR on a Nicolet spectrophotometer Nexus 670 as KBr disks. For each sample 64 scans were recorder in the spectral range 4000—400 cm^{-1} in the transmittance mode with a resolution of 4 cm^{-1}. Moreover, solid residues collected at 700 °C after TGA analysis in nitrogen have been analyzed by Energy Dispersive X-ray spectroscopy analysis (EDX) performed on E.S.E.M. (environmental scanning electron microscope, Philips XL 30); quantification was based on ZAF standardless method.