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Novel tetrapotassium azo diphosphonate (INAZO) as flame retardant for polyurethane adhesives

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ABSTRACT

An inorganic azo diphosphonate (INAZO), $(KO)_2(O)P\text{-}N{=}N\text{-}P(O)(OK)_2 \cdot 4H_2O$, was synthesized and tested as a novel type of flame retardant additive for castor oil and oligomeric methylene diphenyl diisocyanate (PMDI) based two component polyurethane adhesive with or without using dolomite ($(CaMg(CO_3)_2)$ as filler. Flammability according to UL 94 test and performance under forced-flaming conditions (cone calorimeter) were investigated at the additive loadings of 5, 10 and 20 wt %. It was shown that INAZO improves flame retardancy by significantly reducing heat release rate (HRR), maximum average rate of heat emission (MARHE) and total smoke release (TSR) values in comparison to $CaMg(CO_3)_2$ filled polyurethane adhesives. The macroscopic structure of the sample residues after cone calorimeter measurement was also analysed. The action mechanism of the developed INAZO flame retardant is suggested to be mainly in the condensed phase. UL 94 V-0 rating was achieved in the vertical burning test when 10 wt % loading of INAZO was used, whereas the reference flame retardant ammonium polyphosphate (APP) required a loading of 20 wt % to reach the V-0 classification.

1. Introduction

In addition to high bond strength and flexibility, PUR adhesives have good adhesion to wood, metals, ceramics and a number of plastics. They find, therefore, end-use in an ever-widening array of industrial applications [1].

Polyurethane adhesives can be classified according to their curing mechanism into three main categories. In the first class, so-called two component systems, a polyisocyanate or an isocyanate terminated prepolymer and a low molecular weight polyol are mixed and immediately applied to a base material (adherend) to be cured. The second class consists of moisture curing PUR adhesives and the third class is comprised of the lacquer type of thermoplastic polyurethane adhesives that exhibit high cohesive forces by simple evaporation of the solvent or water. The two component adhesive systems have generally a cross-linked structure and show superior heat resistance and durability in comparison to other classes of polyurethane adhesives. Besides polyol and isocyanate, two-component adhesive formulations may contain inert filler(s) that decrease price and improve dimensional stability, catalysts that regulate their pot-life and water scavengers that eliminate undesirable bubble formation during curing.

Nowadays, many products used for instance in construction, transportation and electronics need to fulfil stringent fire safety standards and preferentially in combination with low emissions of toxic and corrosive gases during combustion. In many applications the amount of polyurethane adhesive can exceed 10 wt % (e.g. in mineral wool, glass fibre reinforced composites, wood particleboards, etc.) and, therefore, also the adhesive must be flame retarded. For instance, haloalkyl phosphate esters are well-established effective flame retardants for various flexible and rigid polyurethane formulations [2]. However, halogen (e.g. bromine or chlorine) based flame retardants have several disadvantages such as tendency for bioaccumulation, potential of corroding metal components and the ability to generate toxic and corrosive hydrogen halides during combustion. Furthermore halogenated flame retardants need often toxicologically critical antimony oxides as synergists.

As a consequence, there is an ever growing interest to develop new environmentally friendly halogen-free flame retardant systems. The majority of halogen-free alternatives belong to phosphorus, inorganic and nitrogen (PIN) flame retardants; representative examples of each category are ammonium polyphosphate (APP), metal hydroxides (e.g. aluminiumtrihydroxide) and

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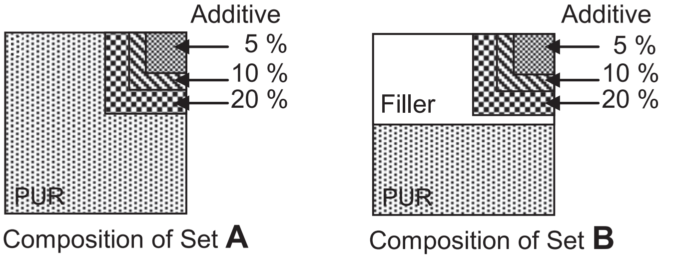


Fig. 1. Composition of samples in set A and set B.

melamine compounds [3,4]. Many of the PIN flame retardants are less lipophilic than brominated FRs, some are even ionic, which lowers the bioaccumulation potential of these substances. In the past, extensive work has been done to find effective, halogen-free flame retardants for PUR foams and elastomers [5], but studies published on flame retardant PUR adhesives based on vegetable oil polyols are very rare [6,7].

We have recently discovered a new interesting family of nitrogen based flame retardants, i.e. azoalkanes of the general formula R′-N=N-R, that exhibit self-extinguishing properties for polypropylene compounds [8,9]. More recently we have also reported the synthesis and use of an innovative multifunctional radical generator, i.e. bis(1-propyloxy-2,2,6,6-tetramethylpiperidyl)-4-diazene (AZONOR), which besides passing the challenging UL 94 VTM-2 standard alone at comparatively low loadings also provides an excellent protection to weathering [10]. As an extension of that work, we intended to broaden the scope of diazene based compounds to inorganic azo phosphonates, i.e. potassium-diazene-1,2-diyldiphosphonate tetrahydrate (INAZO), and to test its fire retarding properties in two component polyurethane adhesives. To the best of our knowledge, no inorganic azo compound has earlier been tested as flame retardant for polymeric materials.

In the current article, cone calorimeter and UL 94 vertical burn tests were utilized to assess the FR performance of INAZO at the loadings of 5–20 wt %. Ammonium polyphosphate (APP) was selected as a reference flame retardant. In addition, INAZO was tested together with dolomite filler by keeping the inorganic content (additive + $CaMg(CO_3)_2$) fixed at 50 wt % of the total adhesive amount. The effect of the additives on flammability, heat release rate, smoke generation and release of carbon monoxide is reported. Additionally, the macroscopic structure of the formed residues is visually examined from images taken after the cone calorimeter tests.

2. Experimental

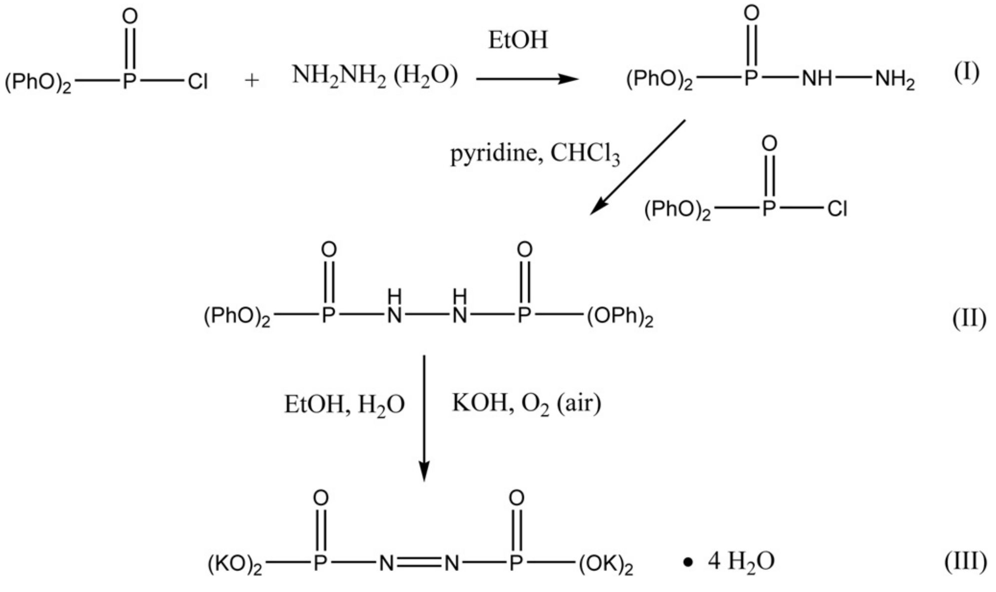
2.1. Materials

Oligomeric methylene diphenyl diisocyanate (PMDI, average NCO-functionality 2.7 and Mw 366 g/mol, Huntsman), Castor oil (OH-functionality 3, Mw 933 g/mol, Alberding Boley), $CaMg(CO_3)_2$ (dolomite, average particle size 13.9 μm, Imerys), zeolite powder moisture scavenger (Sigma–Aldrich) and dibutyltin dilaurate catalyst (Sigma–Aldrich) were received from non-commercial sources (additional details not available). Tetrapotassium azophosphonate and $CaMg(CO_3)_2$ were dried in vacuum over P_2O_5 before use. Exolit AP 422 ($n = 700$ repeating units, Clariant GmbH) was used as received. Other chemicals were purchased from Sigma-Aldrich and used as received. Dolomite was analysed by ICP-OES and contains 23 wt % of Ca^{2+} and 14 wt % of Mg^{2+} corresponding to equimolar amounts of calcium to magnesium in the dolomite crystal structure.

2.1.1. *Synthesis of potassium diazene-1,2-diyldiphosphonate tetrahydrate* ($H_8K_4N_2O_{10}P_2$)*, (INAZO)*

Synthesis procedure has been earlier described in literature [11–14]. However, we used a slightly modified method. Also a more precise characterization of the compound is given below.

2.1.1.1. Synthesis of diphenyl phosphorohydrazidate (I). A solution of hydrazine monohydrate (0.2 mol) in EtOH (48 ml, 96%) was treated dropwise with diphenyl phosphorochloridate (0.1 mol) keeping the reaction temperature below RT [11,14]. Reaction was let to continue for 30 min at RT after the addition. Distilled water was added and the product was let to crystallize out in an ice-bath. After separation by filtration, the white powder was washed with water and recrystallized from dilute ethanol. Solvent was distilled by rotary evaporator at 30 °C. The product was dried in vacuum over P_2O_5. The title compound was collected in 90% yield. NMR ^{31}P ($CDCl_3$) δ − 1.61(DMSO) δ − 0.57.



Scheme 1. Synthesis pathway to potassium-diazene-1,2-diyldiphosphonate tetrahydrate (INAZO).