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Flame retardants based on amino silanes and phenylphosphonic acid

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ABSTRACT

The sol-gel approach offers a new class of flame retardants with a high potential for textile applications. Pure inorganic sol-gel systems do, however, typically not provide an effect sufficient for a self-extinguishing behavior on its own. We therefore employed compounds with nitrogen and phosphorous containing groups. Especially the combination of compounds with both elements, using the synergism, is promising for the aim to find well-applicable, environmental friendly, halogen-free flame retardants. In our approach, the sol-gel network ensured on the one hand the link to the textile as non-flammable binder. On the other hand, the sol-gel-based networks modified with functional groups containing nitrogen groups provided flame retardancy. In this way, a flame retardant finishing for textiles could be obtained by simple finishing techniques as, e.g., padding. Besides a characterization with various flame tests (e.g., according to EN ISO 15025 – protective clothing), we used a combination of cone calorimetry, thermogravimetry coupled with infrared spectroscopy analysis and scanning electron microscopy to analyze the mechanism of flame retardancy. Thus, we could show that the main mechanism is based on the formation of a protection layer. This work provides a model system for sol-gel-based flame retardants and has the potential to show the principle feasibility of the sol-gel approach in flame retardancy of textiles. It therefore lays the groundwork for tailoring sol-gel layers from newly synthesized sol-gel precursors containing nitrogen <u>and</u> phosphorous groups.

1. Introduction

Textiles made of natural and synthetic fibers are ubiquitous in our daily life. Their behavior in case of the exposure to a flame is a very critical issue because of their high flammability and often the start of household fires. Textiles with low flammability can reduce this risk. Nowadays, there are multiple solutions in the market for example applying special non-flammable fibers including m-aramids like Nomex® or Teijinconex®, bulk-modified fibers like Trevira CS®, as well as fibers with flame retardant coatings like Pyrovatex CP® or Proban® [1]. The latter, especially with the application of coatings on standard fibers like cotton and PET (polyethylene terephthalate), represents the most interesting way of production for industry. The basic material is cheap and accessible in high quantities. Furthermore, the production is well established, yielding a broad variety of textile fabrics. Even though there are flame retardant coatings available, the need for production in a cost-effective way in combination with toxicological issues concerning e.g. brominated flame retardants [2–4] make a constant development of new flame retardants necessary. The possibility and the need to replace halogenated flame retardants with nitrogen and phosphorous-based systems motivated the scientific community to look for possible substitutes [1]. For example for cotton, a broad variety of research activities are pursued recently, namely layer-by-layer techniques [5–8], the application of reactive monomeric or polymeric species [9–12], phosphorous-containing biomolecules like DNA [13] or casein [14], UV-curable [15,16] or plasma-curable systems [17] and also coatings based on sol-gel techniques [18–24]. Several of these techniques are actually not restricted to cotton but can also be applied on PET fabrics [14,16,25],

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as well as blended fabrics made of cotton and PET [14,26,27]. Brancatelli et al. [20] or especially Alongi and coworkers [21–24,27,32] carried out a lot of work dealing with the application of inorganic sol-gel-based finishings and combined those with different additives as, e.g., those exhibiting phosphorous. Results are restricted to cotton and show improvements in flame-resistance if silica networks are modified with phosphorous-containing compounds. However, concerning flame retardant coatings based on the sol-gel technique, there is often a lack in performance regarding the very important small-scale flame test (e.g., a test according to EN ISO 15025 with flame application of 10 s on surface/edge) [21]. Foremost, if a reasonably small amount of coating is applied. In contrast, high amounts of sol-gel coating, even of very simple inorganic composition, perform well in such small-scale flame tests with mass add-ons of 50% and more, but at the same time the substrates loose their typical textile properties due to the high amount of inorganic, rigid coating. Another aspect is that while for cone-calorimetry and other tests distinct improvements are often reported, the flame tests will not necessarily confirm an appropriate improvement in case of a fire scenario. Furthermore discussion of char formation is often impeded by the fact that distinguishing between char and residual metal or silicium oxide is difficult. Further research in order to find a sol-gel coating with higher practical value in the textile industry is therefore necessary.

A lot of reports focus on cotton only, therefore the knowledge about the differences in mechanism of flame retardancy is often poor for the different substrates, cotton, PET and blended fabrics. Blended fabrics exhibit in this context special concerns as the behavior in a small-scale flame test evolves differently than a simple combination of the behavior of each single component [28]. Briefly, in PET fabrics, the polymer typically melts and retreats from the flame before the temperature reaches a critical value at which a sustainable burning occurs. The cotton in the blended fabric supplies an initial source of burning material and, equally important, a support structure keeping the PET from retracting from the flame. Blended fabrics exhibit consequently a high flammability and a flame retardant coating would be very beneficial. The sol-gel approach is a promising candidate for this kind of fabric as we will demonstrate in this work.

There are multiple ways to analyze the flame retardant behavior and to investigate the mechanism. Besides the already mentioned small-scale flame test, a cone calorimeter test allows additional insight into the flame retardant behavior [29–31]. A cone calorimeter test simulates the effect of a radiative heat source in a developing fire scenario [29]. The analysis of the changes in heat release rate with time allows to determine several parameters like the peak heat release rate, the time to ignition, as well as the fire load, i.e. the total amount of energy which is released by the material in the case of a fire. Inorganic silica layers applied as flame retardants can in this test for example shield the underlying textile and in this way increase the time to ignition [21,22,32]. Often however, textiles with flame retardant coatings have a lower thermo-oxidative stability, decomposing at lower temperatures in thermogravimetry measurements [6,7,13,15,20,23]. That means the decomposition of the finished good starts at lower temperatures, either simply since the applied substances decompose at lower temperatures or since a synergistic coaction of the applied substances and the fiber polymer leads to decomposition at reduced temperatures. The lower thermo-oxidative stability leads to a different decomposition pathway favoring char formation. Assuming constant heat absorption, those samples will consequently rather show a lower or unchanged time to ignition in cone calorimetry [6,13,23]. Furthermore, if the sample is deformed during the cone calorimeter test, changing the sample-heater-distance the heat input also changes often leading to non-negligible effects on the heat release rate behavior in time [29]. Besides the time of ignition, thermodynamic effects are monitored in a cone calorimeter test. The reduction of the peak heat release rate is in this context the most important criterion. It determines if the material is accelerating or decelerating a developing fire [33]. For example, the application of endothermic decomposing materials, like aluminum hydroxide or magnesium hydroxide, lead to a reduction in the peak heat release rate which is often effectively applied for bulk polymers [34]. The peak heat release rate can, however, also be reduced by a promotion in char formation and therefore a lower combustion efficiency which is ideally also reflected in the fire load [6,13,23,29]. This is often the case for phosphorous-based flame retardants, closely associated with the formation of a protection layer.

Furthermore, thermogravimetry gives insight in the mechanism of flame retardancy. As already discussed above, a lower thermo-oxidative stability is often linked with a good flame retardant behavior, leading to a different decomposition pathway and promoting char formation. Especially thermogravimetry coupled with an IR analysis of the gaseous decomposition products allows to investigate the reaction pathway of pyrolysis of the materials and allows also to detect a gas phase action of the flame retardants [34–36]. This method is also well known for applications in the field of textiles [13,15]. The combination of these methods together with electron microscopy before and after the flame tests [37,38] lead to a detailed investigation of the mode of action of the flame retardant-coated textiles.

In this paper, we present a new combination of a functional sol-gel layer with a phosphorous compound, exhibiting good flame retardant properties on textiles. In particular, the coated samples show self-extinguishing in a small-scale flame test with surface and edge ignition (according to EN ISO 15025). This is to our opinion one of the most important criterion for the application on textiles, preventing household fires right where they might start. The amount of sol-gel layer on the coating was limited to about 10% in respect to the original textile in order to omit negative side effects like high stiffness or unpleasant feeling. Furthermore, the mechanism was evaluated with cone calorimetry, thermogravimetry coupled with an IR analysis of the gaseous phase and electron microscopy. The results of these methods are combined and discussed comprehensively, giving insight into the mechanism of flame retardancy. This study is especially important for future works, being a model system for newly synthesized sol-gel precursors with nitrogen and phosphorous groups.

2. Materials and matters

The following chemicals and solvents were used without further purification: (3-trimethoxysilylpropyl)diethylenetriamine (abbreviated: TRIAMO; ABCR, 95%), phenylphosphonic acid (Aldrich, 98%), purified water from Millipore system (Merck, specific resistance 18.2 MΩ/cm), ethanol (“Neutralalkohol Primasprit”, min. 96%, Azelis), sodium hydroxide (Roth, 99%).

A cotton fabric (Sanders, 131.9 g/m^2, plain weave, 47/41.5 thread/cm, thickness 0.23 mm), PET (Schüssler, 204.4 g/m^2, atlas weave, 24.5/27 thread/cm, thickness 0.51 mm) and a blue blended fabric (Kettelhack, 246.5 g/m^2, twill weave 2/1, 37/20 thread/cm, thickness 0.42 mm) with blended yarn (ratio cotton to PET of 65:35) were used as substrates.

For the sol-gel coating on the cotton and the blended fabric 12.5 g TRIAMO (0.045 mol) was mixed with 25 ml of ethanol/water (1:1) and 62.5 ml of 2 M hydrochloric acid. For PET slightly different quantities were used, i.e. 7.5 g TRIAMO (0.027 mol) with 55 ml ethanol/water (1:1) and 37.5 ml 2 M hydrochloric acid. The pH was adjusted to 4–5 with a few drops of 2 M hydrochloric acid or 2 M