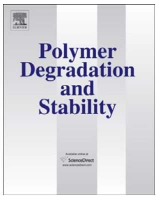
Polymer Degradation and Stability 130 (2016) 155–164

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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



Synergistic effects in the pyrolysis of phosphorus-based flame-retardants: The role of Si- and N-based compounds

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ARTICLE INFO

Article history:
Received 22 March 2016
Received in revised form
6 June 2016
Accepted 13 June 2016
Available online 15 June 2016

Keywords:
Flame retardant
Pyrolysis mechanism
Py-GC/MS
TGA-FTIR/MS
Correlation

ABSTRACT

The modification of cotton fabrics with phosphorus-based flame-retardants (FRs) in the presence of synergistic elements such as nitrogen or silicon is reported. For these purposes, analyses of the combustion behavior and the thermal-oxidative stability of the modified fabrics were performed using pyrolyzis – gas chromatography-mass spectrometry (Py-GC/MS), thermogravimetric analysis coupled to Fourier-transform infrared spectroscopy and attenuated total reflection infrared spectroscopy (ATR-IR). It was found that limiting oxygen index (LOI) values were higher in case a P/N/Si instead of a P/N element combination was used. With the former, increased residual masses were obtained and the amount of phosphorus could be reduced by the presence of silicon. The results obtained path the way for further developments and optimizations of flame-retardants by determining the optimum element combinations and element/element ratios, ultimately leading to high flame retardant effects.

1. Introduction

A huge number of flame-retardants (FRs) have been developed over the last six decades. Many of them, e.g. ammonium phosphates, ammonium bromide, guanidine phosphates or organic N- and P-containing compounds are classified as non-permanent FRs as they are removed upon washing. Additionally, permanent organophosphorus-based FRs like cross-linked tetrakis(hydroxymethyl)phosphonium salts and N-alkyl-substituted phosphonopropionamide derivatives have been established [1,2]. Currently, research focuses on FRs displaying both good flame retardant properties and environmental sustainability. Latest regulations aim on abolishing systems based on halogens and boronic acid [3]. Therefore, the complete substitution of the known and well working systems becomes increasingly an issue. In course of these developments, mainly P- and N-based systems showing a strong synergism when used in combination have moved into the center of interest. However, also Si-, Al- and S-based compounds can contribute to flame retardancy [4,5]. In order to identify new FR-systems, the understanding of the underlying mechanism(s) is reasonable and essential.

Several authors have studied new flame retardant systems in order to find halogen- and formaldehyde-free alternatives [6–8]. Alongi et al. [4,9–11] investigated different sol/gel-based FR systems focusing on phosphorus- or nitrogen-doped silica coatings. Their results show, that the combustion behavior can be strongly affected by phosphorus-rich silica coatings [9]. Furthermore, they suggested that silicon alone enhances the thermal stability of cotton better than phosphorus-doped silica [10]. The same authors also mentioned that combinations of phosphorus and silicon promote carbonization during pyrolysis, resulting in the formation of stable char up to 1100 °C [4]. Brancatelli et al. [12] reported on different hybrid inorganic-organic silica coatings, stating that char formation is enhanced by the addition of phosphorus or nitrogen to the sol. However, since they used a nitrogen-containing sol/gel precursor, no clear interpretation about the influence of the single elements on flame retardancy was possible.

We therefore aimed on a better understanding about the influence of individual elements, i.e., nitrogen, phosphorus and silicon on FR behavior and about any potential synergism. For these purposes, three systems have been compared, (i) standard phosphorus-based FR-modified cellulose (Cell-P), (ii) cellulose containing both P- and N-compounds (Cell-PN) and, (iii) cellulose additionally containing Si (Cell-PNSi).

Three different methods, i.e. thermogravimetric analysis (TGA), infrared spectroscopy (IR) and determination of the limiting oxygen index (LOI), were applied in order to be able to make a statement

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.06.009
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about the combustion behavior of the different FR-systems [13]. Concomitantly, in order to shed more light on the pyrolysis mechanism, it was indispensable to clarify how char formation occurred. The combustion behavior was examined from different perspectives. By using FRs based on different elements, i.e. N, P and Si, differences in the combustion behavior were elucidated. In addition to the above-mentioned analytical tools, scanning electron microscopy (SEM) and pyrolysis-GC/MS (Py-GC/MS) were used. Furthermore, the influence of washing was examined. Together, this comprehensive analytical approach allowed for drawing conclusions about the most effective FR combination.

2. Experimental part

2.1. Materials and methods

Cotton fabrics with a weight of 230 g/cm^3 (bleached and scoured) were used from Kettelhack GmbH & Co. KG. For coating, phosphoric acid (85%), urea, potassium hydroxide (85%), hydrochloric acid (conc.) (Alfa Aesar) and sodium xylenesulfonate (catalyst, Sigma Aldrich) were used. The sol/gel precursor tetraethyl orthosilicate (TEOS, $\geq$99%) was purchased from Merck GmbH. The dispersing agent Tissocyl RLB was received from Zschimmer & Schwarz.

2.2. Phosphorylation of cotton fabrics

Phosphorylation was carried out according to combinations of literature-known procedures [14,15]. Phosphoric acid (0.05, 0.1, 0.35, 0.7, 1.0, 1.4, 2.0 and 2.2 M) was mixed with urea (4.17 mol), KOH (0.1–0.2 mol excess, pH 6–7) and 0.002 mol of sodium xylenesulfonate. Cotton fabrics were impregnated by a two-roll laboratory padder (*Werner Mathis AG*, Zürich) followed by subsequent thermal treatment at 120 °C and 200 °C. The percentage of adsorbed solution (A [wt%]) and the fabric was calculated according to Equation (1) by weighing the fabric prior to (w_b) and after (w_a) impregnation.

$$A = \frac{w_a - w_b}{w_b} \cdot 100 \tag{1}$$

2.3. Sol/gel treatment of cotton fabrics

For 1000 mL of a 4 wt% sol/gel solution, 40 g of tetraethyl orthosilicate were mixed with 957 g of deionized water. Then, 0.5 g of the dispersing agent was added. Upon treatment with an Ultra Turrax (10 000 rpm), an aqueous emulsion was obtained. Starting from this sol, gel formation was catalyzed by hydrochloric acid at a pH value between 3 and 4. Phosphorylated fabrics were dipped and passed through a two-roll laboratory padder. Drying and condensation took place on a tenter dryer at 100 and 150 °C. The amount of coating was calculated as described above.

2.4. Permanence

Permanence of the modified fabrics was investigated by repeated washing cycles at 40 °C for 12 min with 4 g/L ECE-color fastness test washing detergent (phosphorus free). Drying steps were applied after 1, 5 and 10 washings, respectively. The designation “zero washing cycles” means that the samples were simply washed twice with deionized water to remove any unbound compounds from the textile. Each sample underwent this procedure.

2.5. Characterization methods

Flammability of cotton fabrics was quantified by measuring the limiting oxygen index (LOI) in a vertical burning test (Fire Testing Technology). Samples 15 × 5 cm in size were ignited at defined oxygen values. The thermal-oxidative stability of both untreated and modified cotton fabrics was determined on a TA Q 500 from TA instruments between 30 and 1000 °C (heating rate 10 K/min) in synthetic air (gas flow 40 mL/min, protection gas (N_2) 60 mL/min). The combustion behavior of the fabrics was measured by Py-GC/MS (pyrolyzer TDS II, Gerstel; GC/MS coupling: HP 6890/HP 5973, Agilent) and STA-FTIR/MS (Netzsch STA 449F3 Jupiter® coupled with QMS 403 Aëolos® and Bruker Tensor 27). For analyzing changes in morphology during pyrolysis, samples were subjected to ATR-FTIR measurements (Bruker IFS 28, run from 4000 to 400 cm^{-1}), SEM (Zeiss Auriga field emission-scanning electron microscope, samples steamed with carbon) and EDX analysis (XMax 50 detector, Oxford instruments). In addition, the elemental composition was determined by elemental analysis and inductively-coupled plasma-optical emission spectroscopy (ICP-OES). Dissolution of samples for ICP was accomplished in sulfuric acid or in a mixture of H_2O_2/HNO_3 or HNO_3 applying microwave (power: 600 W, heating rate 10 K/min up to 160 °C, isotherm 30 min, cool down). Dissolution of Si was accomplished by CHT R. Beitlich GmbH, Tübingen, Germany in a mixture of 5 mL HNO_3/2 mL H_2O_2/0.5 mL HF applying microwave (power: 1200 W, 15 K/min up to 120 °C for 5 min, 16 K/min up to 220 °C for 20 min, cool down).

Elemental analyses were carried out on an optical emission spectrometer with inductive coupled plasma (Acros, Spectro or Thermo Scientific ICP-OES iCAP 6500). P was measured at $\lambda = 214.914$ nm, the background was measured at $\lambda_1 = 214.784$, $\lambda_2 = 214.813$ nm, $\lambda_3 = 214.985$, $\lambda_4 = 215.022$ nm. S was measured at $\lambda = 180.731$ nm, the background was measured at $\lambda_1 = 180.600$ nm, $\lambda_2 = 180.654$ nm, $\lambda_3 = 180.823$ nm, $\lambda_4 = 180.860$ nm. For calibration, standards containing 0.0, 1.0, 2.5, 3.75, 5, 7.5 mg/L of each element were used. CHN-combustion elemental analyses were performed at the Institute of Inorganic Chemistry, University of Stuttgart, Germany using a Perkin Elmer Analyzer 240. Solid-state NMR measurements were performed at the Institute of Chemical Technology, University of Stuttgart, Germany using a Bruker Avance III 400WB at resonance frequencies of 100.6 (^{13}C) and 162.0 MHz (^{31}P). The specific smoke density was measured at the Bundesanstalt für Materialforschung und -prüfung on a smoke density chamber using an irradiance of 25 kW/m^2 over a period of 10 min (oriented verification ISO 5659-2).

3. Results and discussion

3.1. FR properties of cotton fabrics finished via phosphorylation and sol/gel technique (Cell-P, Cell-PN and Cell-PNSi)

Scheme 1 summarizes the derivatization reactions that have been carried out to obtain the Cell-P, Cell-PN and Cell-PNSi samples.

In order to determine the influence of Si on the FR properties, phosphorylated cotton fabrics were compared to those that had additionally been subjected to sol/gel coating. The nitrogen in Cell-PNSi_0 to Cell-PNSi_10 originated from the urea used during synthesis (Scheme 1). The flammability of the treated cotton fabrics was analyzed by determining their LOI. Although the presence of Si alone rather reduced the LOI (sol/gel (Si) Table 1), a combination of the phosphorylated and a sol/gelsystem (Cell-PNSi) lead to the most persistent FR effect (LOI $\geq$ 25), which also existed after up to 10 washing cycles.

The minor decrease in P-content in both the Cell-PNSi_n and