Environmentally friendly flame retardants for cellulose-based materials - Continuation

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Preface

This report summarizes Brandforsk project 720-005. It is a continuation of a previous Brandforsk project (718001). We are immensely grateful for the interest and financial support from Brandforsk.

We would like to thank the reference group: Mattias Delin from Brandforsk, Thomas Gell from GellCon, Robert Jansson McNamee from RISE, Leif Andersson from Protega, and Anders Lundberg from Swedish Civil Contingencies Agency (MSB). Our meetings have been very valuable with many different points of view and recommendations.

We would also like to thank our collaborators Michael Försth and Alexandra Byström from the Division of Structural and Fire Engineering, LTU, for performing the cone calorimeter measurements and giving advice on fire related matters, and Suchandra Sar for performing the leaching tests.

We appreciate the contribution from our Fire Engineering student Aleksis Nevanperä Ymerstam from LTU.

The NMR measurements were performed at The Swedish NMR Centre at Umeå University, with the kind assistance of Tobias Sparrman.

Abstract

Flame retardants are commonly used as a way to reduce the risk of fire. However, many of the currently used flame retardants are toxic and hazardous for the environment. Therefore, there are incentives to find safer alternatives.

With the aim of finding an environmentally friendly and non-toxic flame retardant made from natural products systematic investigations on cotton samples treated with mixtures of phytic acid (PA), metal ions (M), and amino acids (AA) were performed. PA is the main storage form of phosphorus in plants and can be found in e.g. nuts and cereals. AA are the building blocks of enzymes and proteins. Many common metal ions are important nutrients.

Combustion tests, thermal gravimetrical analyses (TGA), and cone calorimetry tests were combined to find the best combination of ingredients for optimal flame retardant properties.

MAS NMR analyses were used to describe what is happening with the flame retardant at different temperatures and could be correlated to the results from the thermal analyses.

Leaching tests were performed to determine the amount of PA and AA dissolved from the flame retardant coating in contact with water.

All tested combinations of ingredients have flame retarding ability and lead to self-extinguishment. The amount of sodium ions relative to PA affects the charring ability. The addition of AA improves the flame retardant efficiency compared to having only sodium ions. Arginine was the amino acid which showed the best result because it can theoretically produce the largest amount of non-combustible gases per molecule. However, the amount of AA relative to PA is important. The addition of multivalent metal ions reduces the flame retarding ability a little compared to samples with only sodium ions and AA, but the solubility decreases considerably.

Sammanfattning

Att använda flamskyddsmedel är ett vanligt sätt att minska brandrisken. Dessvärre är många av de flamskyddsmedel som används idag giftiga och skadliga för miljön. Därför finns det drivkrafter för att hitta säkrare alternativ.

Med målsättningen att hitta ett miljövänligt och giftfritt flamskyddsmedel framställt av naturprodukter har systematiska undersökningar utförts på bomullsbitar behandlade med olika blandningar av fytinsyra (PA), metalljoner (M) och aminosyror (AA). PA är växters huvudsakliga lagringsform av fosfor och kan hittas i t.ex. nötter och sädesslag. AA är byggstenar för enzymer och proteiner. Många vanliga metalljoner är viktiga näringsämnen.

Förbränningstester, termiska gravimetriska analyser (TGA) och konkalorimetertester kombinerades för att hitta den kombination av ingredienser som ger bäst flamskyddsegenskaper.

Med MAS NMR kunde flamskyddsmedlets termiska nedbrytningsförlopp beskrivas och korreleras till resultaten från de termiska testerna.

Lakningstester utfördes för att bestämma mängderna AP och AA som löser ut sig från flamskyddsbeläggningen vid kontakt med vatten.

Alla testade kombinationer av ingredienser har flamskyddsförmåga och leder till självsläckning. Mängden natriumjoner i förhållande till PA påverkar förkolningsförmågan. Adderande av aminosyror förbättrar flamskyddseffektiviteten jämfört med att ha bara natriumjoner. Arginin var den aminosyra som gav bäst resultat eftersom den kan teoretiskt producera störst mängd icke-brännbara gaser per molekyl. Mängden AA i förhållande till PA påverkar också. När flervärda metalljoner läggs till minskar flamskyddsförmågan en aning jämfört med prover som innehåller bara natrium och AA, men lösligheten minskar betydligt.

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1 Introduction

1.1 Background

Many of the popular textiles used for clothes and interior details are made of natural fibers and are considered to be sustainable and renewable. The most common natural fibers are cellulose-based, e.g. cotton and linen, which are plant-based, and viscose and lyocell which are wood-based. However, they can all easily catch fire [1,2].

Every year many fires kill and injure people in their homes. Fires also cause considerable economic losses, both direct property losses, but also a societal cost for rescue service and clean-up after the fire. Therefore, there are many incentives to have a fire-safe built environment, as well as fire-safe textiles, and many governments and rescue services try to encourage this by suggesting the use of flame retardants on furniture and interior details [3-5].

Any flame retardant works by removing at least one of the four components needed for a fire (fuel, oxygen, heat, and a chain reaction) [6-9]. However, many of the flame retardants used today are harmful to the environment and human health, and some have even been banned [3]. During their production, they may give rise to by-products and waste solvents which can be flammable and toxic. Therefore, there is an increased demand to develop environmentally friendly and non-toxic ways to fire-proof products [1].

In addition, various environmental policy goals and instruments impose demands on a sustainable society. Agenda 2030 [10] has the following goals that will be targeted by the results from the proposed project:
9. Sustainable industry, innovations and infrastructure
9.4 ... make industry sustainable with more efficient use of resources and increased use of clean and environmentally friendly technologies and processes.
9.5 Improve scientific research..., ... encourage innovation
12. Sustainable consumption and production
12.2 ... efficient use of natural resources
12.4 ... achieve environmentally friendly management of chemicals and waste during their full life cycle, decrease their release to air, water and soil to minimize their negative consequences on human health and the environment.
12.5 ... significantly decrease the amount of waste through prevention, reduction, reuse and recycling.

Bio-based substances, which are naturally occurring and non-toxic, can be extracted from biomass, e.g. forest and agricultural waste, with relative ease and low cost. Some of these substances could be used as environmentally friendly and safe alternatives to the currently available flame retardants [3,11]. One such substance is phytic acid. Phytic acid is naturally produced by plants to store phosphorus, which is an important nutrient. Metal ions, which are important for the metabolism, can bind strongly to phytic acid and form insoluble metal phytate complexes, which do not dissolve in water or leach to the environment [12]. In our previous Brandforsk project [13], as well as in a few other studies, see e.g. [14-22], the flame retarding properties of phytic acid combined with other substances, e.g. metal ions, have been investigated.

1.2 Aim

In our previous Brandforsk project [13], we showed the potential of phytic acid and metal phytates to function as environmentally friendly flame retardants on cotton and wood. By combining phytic acid with various metal ions in different molar ratios, pH, and concentrations we could explain the underlying mechanisms of the flame retardant properties in molecular detail.

What we could see was that depending on the mixture of ions, we can get an insoluble coating that decomposes endothermically, hinders the release of pyrolysis gases, dilutes the oxygen in the air, terminates the radical reactions, and forms an intumescent layer, which is believed to alter the thermal properties. Thus, the flame retardant can remove all the necessary requirements for a fire (fuel, heat, oxygen, chain reaction) [6-9]. However, the optimal mixture that can balance all the above-mentioned properties in the most efficient way, was yet to be found.

The main findings from the previous project [13] revealed a few issues that have to be addressed to have a successful phytic acid-based flame retardant: acidity has to be balanced in order to have a flame retardant with good charring ability without damaging the underlying cotton; solubility has to be balanced so that the flame retardant coating will be resistant to water, but without preventing charring and early thermal degradation; gas formation has to be increased in order to dilute the oxygen and pyrolysis gases.

As a continuation, we now want to use the chemical understanding obtained to solve these issues and further optimize the flame retardant, bringing it closer to being useful for improved fire safety in everyday life. A systematic investigation of cotton samples treated with various mixtures of phytic acid, metal ions, and amino acids will be conducted to find which proportions give a surface coating with the best flame retardant properties.

2 Theoretical background

2.1 Fire and flame retardants

For a fire to occur fuel, air (oxygen), and heat are needed. In addition, a fire has to evolve through a rapid chain reaction, and for this to happen, radical species (molecular fragments with unpaired electrons) have to form [8,23].

Combustible solids, e.g. cellulose-based materials like cotton, break down into smaller gaseous fragments when they are heated. It is these volatile pyrolysis gases that act as fuel and can ignite in contact with air. The pyrolytic species are very reactive radical species. When they react with oxygen, new radicals form which rapidly reacts with more oxygen and so on in a complex chain reaction, which propagates at a high rate. The heat emitted during this combustion reaction leads to the production of more volatile gases available for the chain reaction to propagate [6,8-9,24].

Flame retardants prevent or delay a fire by removing at least one of the four components needed for a fire. This can be done through several different mechanisms. As a few examples, the fuel can be removed by a flame retardant that creates a barrier on the surface of the combustible object so that the pyrolysis gases cannot escape out in the air; oxygen can be removed by a flame retardant that decomposes into non-combustible gases which dilute the oxygen to a concentration that cannot sustain a fire, heat can be removed by a flame retardant with heat absorbing properties, and radical species can be removed by a flame retardant that can react with theses species and stop the chain reaction [6-9,11,23,25].

2.2 Phytic acid-based flame retardant

Phytic acid (Figure 1, left), also called inositol hexaphosphoric acid, is a plant nutrient with molecular formula $C_6H_6(H_2PO_4)_6$ and can be found in various food, e.g. nuts and grains. It has been reported to have many potential applications and beneficial health effects [12,26-30]. Phytic acid has a high phosphorus content (28%) and phosphorus-based flame retardants are known to work well on cellulose-based materials, e.g. cotton [6-7]. Several studies have been performed on phytic acid based flame retardants for various combustible materials, including cotton [13-22].

Very insoluble phytate complexes can be formed by replacing H from the phosphate groups in the phytic acid with metal ions. Therefore, phytic acid is naturally found in the form of metal phytate salts [12]. When used as a flame retardant, these insoluble metal phytates can function as a barrier preventing contact between pyrolysis gases and air (removes oxygen).

When phytic acid is heated it will decompose, simply put, into two fragments, phosphoric acid and a hydrocarbon ring (Figure 1, right). This degradation is endothermic (removes heat). The phosphoric acid part will char the surface of the combustible material it is intended to protect. Charring will reduce the amount of pyrolysis gases emitted from the fuel into the air, and it has been shown that the charring of cellulose at a low temperature relative to its ignition temperature will form a less combustible mixture of pyrolytic products (removes fuel) [3,7].

The phosphoric acid as well as some metal ions can form radical species which can combine with the pyrolytic radicals and in that way terminate the chain reaction so that the fire slows or stops (removes the chain reaction) [31-33].

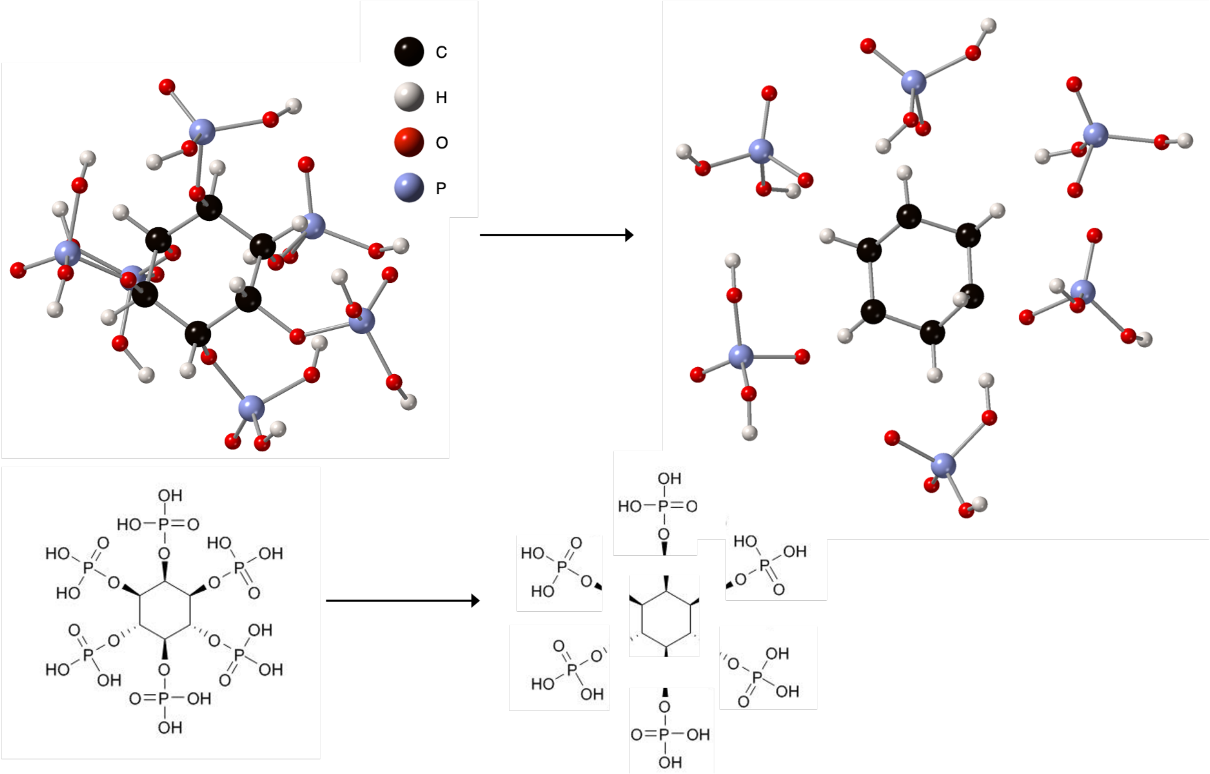


Figure 1. Phytic acid molecule, (top ball and stick model, bottom skeleton model). Left: Before thermal degradation. Right: After thermal degradation.

At higher temperatures (Figure 2) some of the phosphoric acid molecules will polymerize into various polyphosphates, while others will form metal phosphates by binding to metal ions present in the flame retardant coating. The hydrocarbon part of the phytic acid will partly combust and partly fuse into a polyaromatic, carbonaceous structure similar to graphite [13]. The gases produced will intumesce the flame retardant coating, now consisting of graphite, polyphosphates, and metal phosphate [13]. It is known that an intumescent layer will isolate the fuel source (the cellulose-based material) from the oxygen in the air, and improve the thermal properties of the flame retardant so that the fire is impeded (removes fuel and heat) [3,9,34].

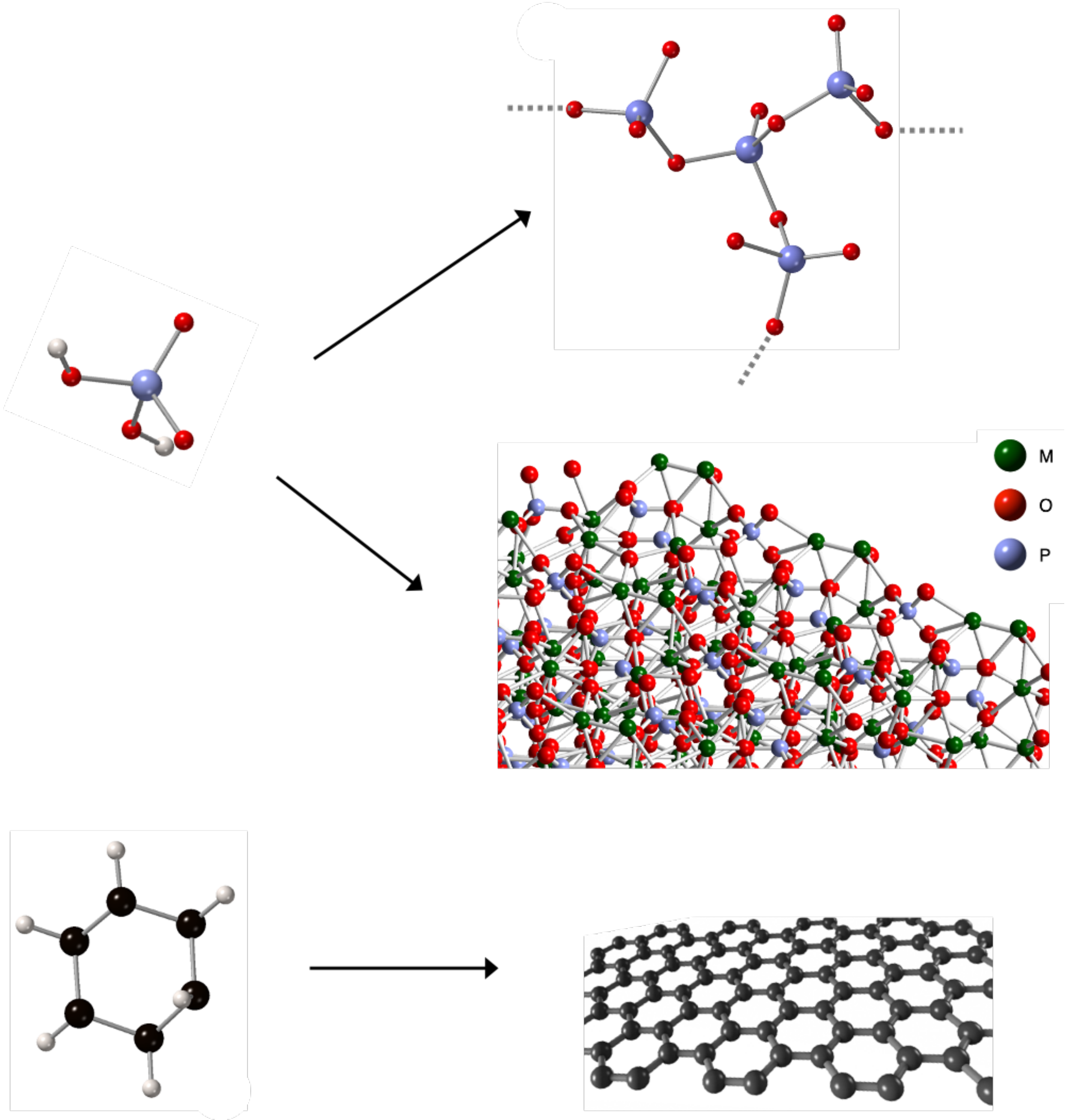


Figure 2. Phytic acid fragments at high temperatures. Top: Phosphoric acid part forms polymeric phosphates and metal phosphates (M=metal). Bottom: Hydrocarbon part forms graphite-like structures.

By adding gas forming species, e.g. ammonia [35], to the flame retardant, the gas formation can be onset at a lower temperature, and the amount of gas that forms will be larger. Gas forming species added to the flame retardant will break down endothermically into non-flammable gases, which will dilute the oxygen in the air so that a fire cannot be sustained (removes heat and oxygen) [3,9].

One naturally occurring and non-toxic group of compounds that has gas-forming properties are amino acids, see Figure 3. They are the building blocks of proteins and enzymes and play important biochemical roles in the body. All amino acids consist of an amino group (-NH_2) and a carboxylic group (-COO), and a hydrocarbon sidechain. There are twenty different amino acids available with their own specific sidechain [36]. The sidechain can be only a hydrogen atom, as is the case for glycine, or much larger as is the case for arginine. The amino acids will release ammonia and carbon dioxide gas during thermal decomposition.

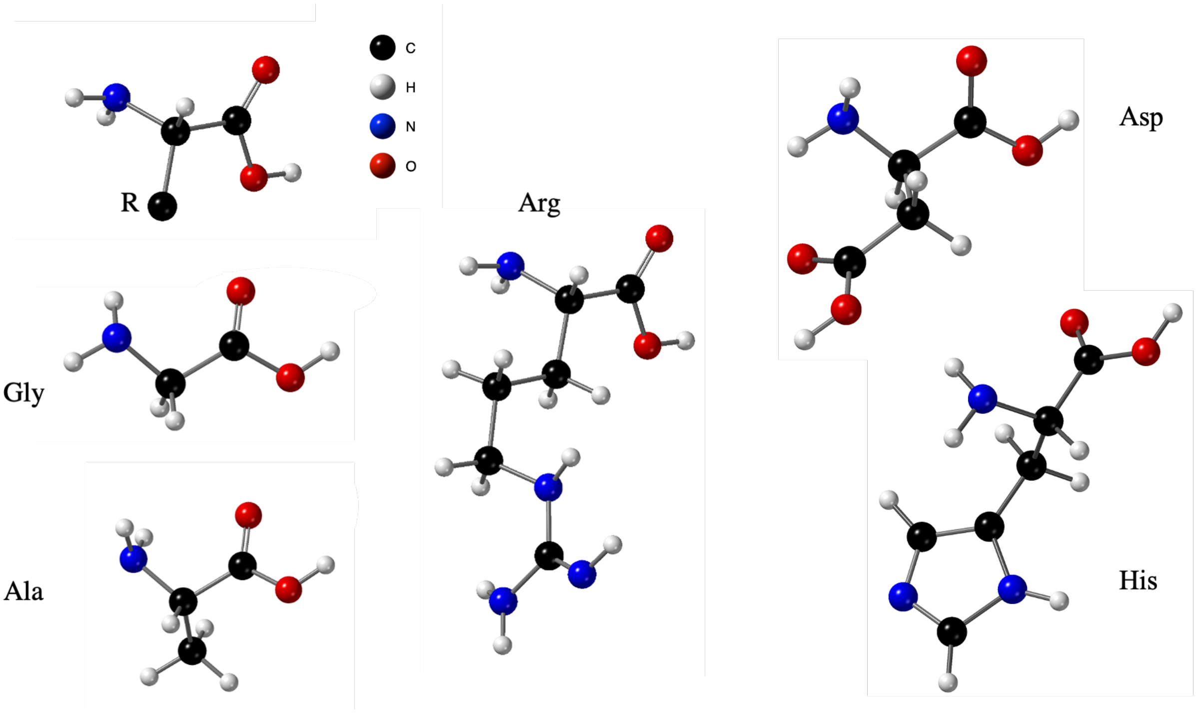


Figure 3. A few examples of amino acids. Top: General structure where R denotes any sidechain. Gly = glycine, Ala = alanine, Arg = arginine, Asp = aspartic acid, His = histidine.

It is known that a combination of phosphorus and nitrogen gives synergistic effects to a flame retardant [6-7] so by combining phosphorus-containing phytic acid with nitrogen-containing amino acids, an increased flame retardancy effect will be achieved.

A common problem with many flame retardants is that they are soluble in water so whenever an object treated with a flame retardant is washed or exposed to humid conditions, the flame retardant will dissolve and the object is no longer protected. Therefore, it is an advantage to have a flame retardant that is insoluble. The addition of multicharged metal ions like Ca^{2+} makes phytic acid insoluble in water, but too insoluble metal phytate complexes decrease the flame retarding ability. One of the reasons is because the amount of acidic H is reduced (they are replaced by the metal ions) so that not enough charring can take place [13]. When the flame retardant is very insoluble it also becomes more thermally stable, because the ionic bonds between the metal ion and phytic acid have built such a strong network. This means that the phosphoric acid cannot form early enough, and therefore cannot char the surface early enough (at a low temperature) to avoid the development of combustible pyrolysis gases. Amino acids can interact with phytic acid and make a bridge between phytic acid and metal ions [12]. The bigger size of the amino acid compared to the metal ion will lead to a weaker network. The coating will still be insoluble, but the sidechain of the amino acid will facilitate the onset of the thermal degradation, see Figure 4.

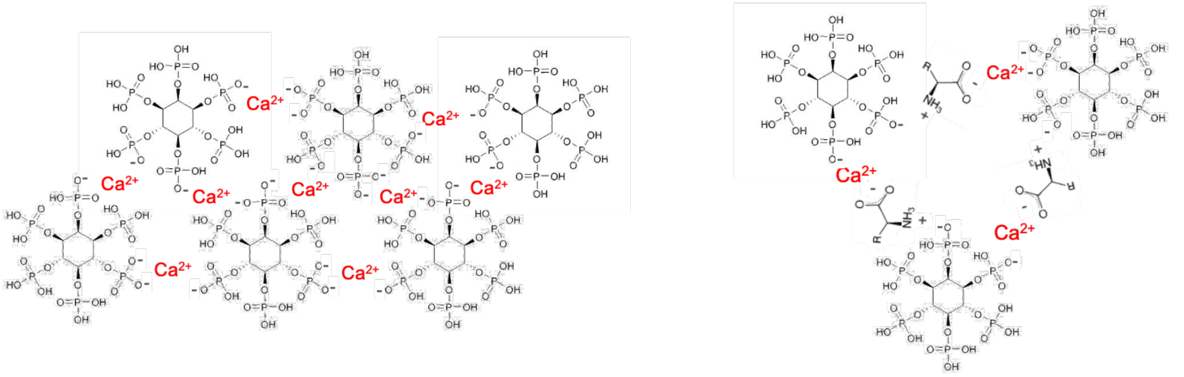


Figure 4. Schematic pictures of phytic acid based surface coatings. Left: Metal phytate complexes are insoluble and thermally stable due to the strong ionic network with short distances between the ions. Right: Incorporation of amino acids to the metal phytate will decrease the strength of the ionic network due to increased distance between the ions.

The phytic acid-based flame retardant will be non-hazardous because all its ingredients are non-hazardous. They will eliminate the use of harmful solvents, because all components are water-soluble on their own, and when they are mixed they combine into insoluble species, and the by-products are ordinary non-toxic salts. The production of phytic acid based flame retardants can use waste material such as brans and manure, possibly even forest residues and metal ions from mining waste, as resources, which will minimize environmental problems surrounding the handling of waste [37].

In case of recycling of a treated product, the flame retardant surface coating can be taken care of by the same method that is used for extracting phytic acid from agricultural waste containing metal phytates [27] (the method does not involve any hazardous chemicals or procedures) and may be reused in a new product. Most of the phytic acid used today, e.g. in skincare products and in some medical applications, is extracted in this way.

3 Experimental methods

3.1 Sample preparation

All experiments were performed on pre-washed white 100% cotton (138 g/m^2). 3×10 cm^2 pieces were cut for combustion tests. Samples 1×1 cm^2 were prepared for analytical tests. For cone calorimeter tests, cotton pieces 11×11 cm^2 were used.

One mole phytic acid (PA) has in total 12 H^+, which can be replaced by different ions (see Figure 4). The number and identity of the ions will have different effect on the flame retarding properties. Cotton samples were treated with aqueous solutions containing different molar ratios of PA, various amino acids (AA) and various metal ions (M) in order to investigate the flame retarding properties. The sample composition will be identified by the general notation $M_x(AA)_yPA$ where x, and y are the molar ratios of metal ions and amino acid.

A number of aqueous solutions were prepared where phytic acid (PA), various amino acids (AA), and sodium hydroxide were mixed in different molar ratios. A general description of the solutions can be found in Appendix 1.

Cotton samples were dipped in the solutions for 20 seconds and then left to dry in the open air for 1.5 days. The amount of flame retardant (FR) absorbed on the cloth pieces was determined by comparing the final weight after drying with the weight before dipping.

As a second step, to prepare insoluble surface coatings, aqueous solutions of multivalent metal ions (M) were sprayed on the dried samples above and dried for at least another 1.5 days and the weight gain was measured.

3.2 Combustion tests

Cotton pieces treated with the different flame retardant solutions were mounted above a propane burner inside a fume hood according to the description in Figure 5.

During our previous projects [13,22,35,38-39], small butane gas burners were used for the combustion tests. Difficulties arose to control the constant flame height using those burners, especially because the fuel gas pressure decreased over time, causing a decrease in flame height. To overcome that difficulty, 10 L propane cylinders were used in the present project. There is a pressure controller in between the cylinder and the burner; controlling the pressure ensures a constant flame height (of 9 cm) during all the experiments. The cotton pieces were placed at a distance of 3 cm above the tip of the flame, in accordance with the previously developed method [35].

To capture video images during the combustion tests, one camera is set outside the fume hood (front camera) and another camera is set at 135° angle, inside the fume hood. During all the experiments, images were recorded with both the cameras simultaneously.

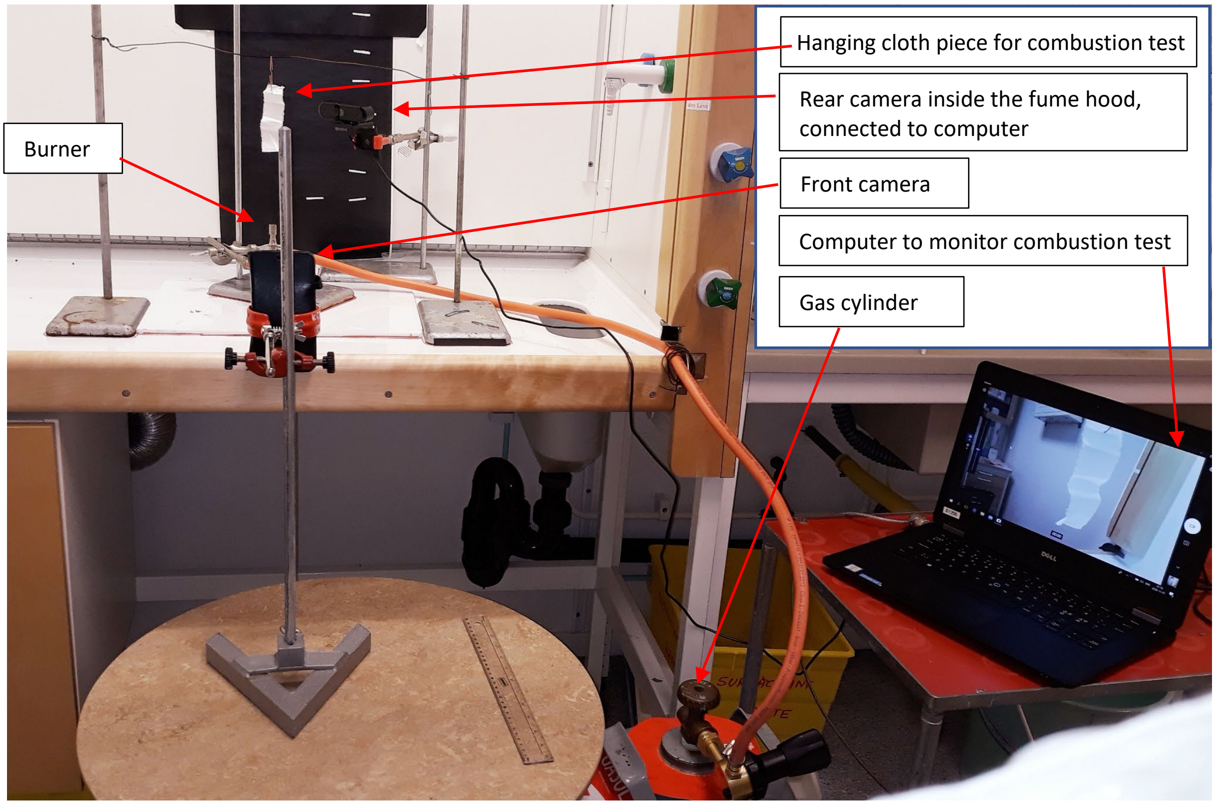


Figure 5. Experimental setup for combustion tests.

First, the cameras were turned on, then the flame was ignited. After the flame height was ensured to be 9 cm, the cloth was placed above the flame. The flame was turned off as soon as the cloth ignited, and it was noticed whether self-extinction was happening or not. If the fabric did not start to burn, it was removed after 1 minute and the damage to the fabric, if any, was noted. The mass loss was determined by weighing the samples before and after. The tests were repeated three times for each sample.

In addition, temperature measurements to estimate the flame temperature at different heights above the flame were performed by measuring the temperature at 0, 1, 3, 5, 7, and 10 cm height, respectively, above the flame tip. The temperature was measured by a thermocouple, 0.25 mm thick, mounted horizontally at the specified height, held with a stand and clamp, to remove the possibility of mechanical shaking. Those measurements were made without any cotton specimens involved.

After the temperature measurements with the thermocouple had been performed, a set of combustion tests were performed where pieces of untreated cotton and cotton treated with a flame retardant mixture were placed at the same heights above the flame tip and their respective mass losses were determined and correlated to the estimated temperature at that height.

3.3 Thermal analyses

To investigate mass loss during heating, Thermal Gravimetric Analysis (TGA) was performed on small pieces of the samples (1-2 mg) in a temperature range from 30°C to 800°C and with a heating rate of 20°C/minute. The atmosphere was either air or nitrogen.

Cone calorimetry tests were performed to analyze the combustion process. The samples had an exposure area of 10×10 cm^2. Based on tests on untreated cotton samples with 9.0, 14.9, 17.0, 20.0, and 25.0 kW/m^2 of irradiation, 14.9 kW/m^2 was chosen as the optimal power to use for PA+Na samples and 20 kW/m^2 for PA+AA+M mixtures. The reason for the choices was to have a visible effect on the samples, but not force a fast and immediate combustion. An untreated piece of cloth (blank) can withstand a 9.0 kW/m^2 heat flux, but turns black. At a higher heat flux, it catches fire. The PA+AA+M mixtures, on the other hand, have very good flame retardant properties so unless the heat flux is at least as high as 20 kW/m^2 or more, no significant change occurs on those cloths. Therefore, 20.0 kW/m^2 was preferred for those samples. However, PA+Na is only a moderate flame retardant so at 20 kW/m^2 heat flux, those cloths catch fire immediately and burn completely, without any control. That is why those samples were analyzed with more moderate 14.9 kW/m^2.

Time to ignition and time to flameout were measured and the burning time was calculated. For the samples that self-extinguished, the mass left of the samples after flameout was determined. By dividing maximum heat release rate (HRR) with elapsed time to reach the maximum HRR the FIre Growth RAte (FIGRA) index was determined [40]. The FIGRA index gives an idea of the danger of a fire by considering both the size of the fire and how fast it grows.

The evolved gases produced during a cone calorimeter experiment were analyzed with an IR spectrophotometer. The device has an inbuilt pump that withdraws evolved gases directly from the cone calorimeter chamber. It can detect presence of gases like CO_2, CO, H_2O, NH_3, etc.

3.4 Nuclear Magnetic Resonance

To investigate what is happening with the flame retardants during the heating process, samples of pure flame retardants were heated in a furnace to various temperatures. The samples were thereafter packed in 4 mm zirconia rotors and placed inside a strong magnetic field (11.7 T) and analyzed by ^{13}C and ^{31}P MAS NMR to study changes in the phosphorus and carbon parts of the flame retardant, respectively. With this method, it is possible to detect very small changes on the molecular level of the sample because nuclei with different surroundings will resonate at slightly different frequencies when exposed to a radiofrequency field. The difference in resonance frequency of a specific nucleus compared to a reference nucleus is reported as a ppm (parts per million) shift. To remove directional dependence relative to the magnetic field, the spinning speeds of the samples were 10 kHz and 12.5 kHz for ^{13}C and ^{31}P experiments, respectively.

3.5 Leaching tests

Leaching tests were performed to investigate how water-resistant various flame retardant compositions are. Only the best performing samples based on the combustion tests were investigated.

1×1 cm^2 samples of cotton treated with flame retardant solutions were placed in 100 ml freshly collected MilliQ water (pH 7) in a beaker. At regular intervals, 0.5 ml and 1.0 ml aliquots were withdrawn for estimation of phytic acid and amino acid, respectively, in the leachate, by standard methods, as described in Appendix 2.

To check the effect of rainwater on the leaching behavior of cloths treated with flame retardant mixtures, water saturated with CO_2 was also tested in parallel. Rainwater can be considered a form of distilled water, but with pH 5.5 due to the dissolution of aerial CO_2. No significant difference in behavior was observed for water at pH 5.5 compared to 7.0, and therefore only one set of results are presented in this report.

4 Results and Discussion

4.1 Sample preparation

4.1.1 Cotton samples

As is described in Chapter 3.1 and Appendix 1, both 3% and 10% aqueous solutions of PA mixed with various amounts of sodium ions and amino acids were used to treat the cotton pieces. It was found that flame retardant solutions with 10% PA concentration gave better results than 3% PA solutions in the fire tests performed. Therefore, all the results showed in this report are from 10% solutions of different flame retardant mixtures.

For cotton pieces treated with Na_xPA, with x = 0-16, the weight of absorbed flame retardant increases with the increasing number of sodium ions present in the PA salt used, see Figure 6. This is natural since the molecular weight of Na_xPA increases with the increasing number of sodium ions. If all the ions get absorbed in the cloth in the same ratios, the weight increase should follow a 10/3 or 3.33 ratio, i.e., the samples with 10% solution should absorb 3.3 times more flame retardant compared to the 3% solution. It is indeed found that when the number of sodium ions is not very high (x<10), the weight increase follows this 3.3 ratio rule. When the number of Na is very high, the ratios become gradually lesser.

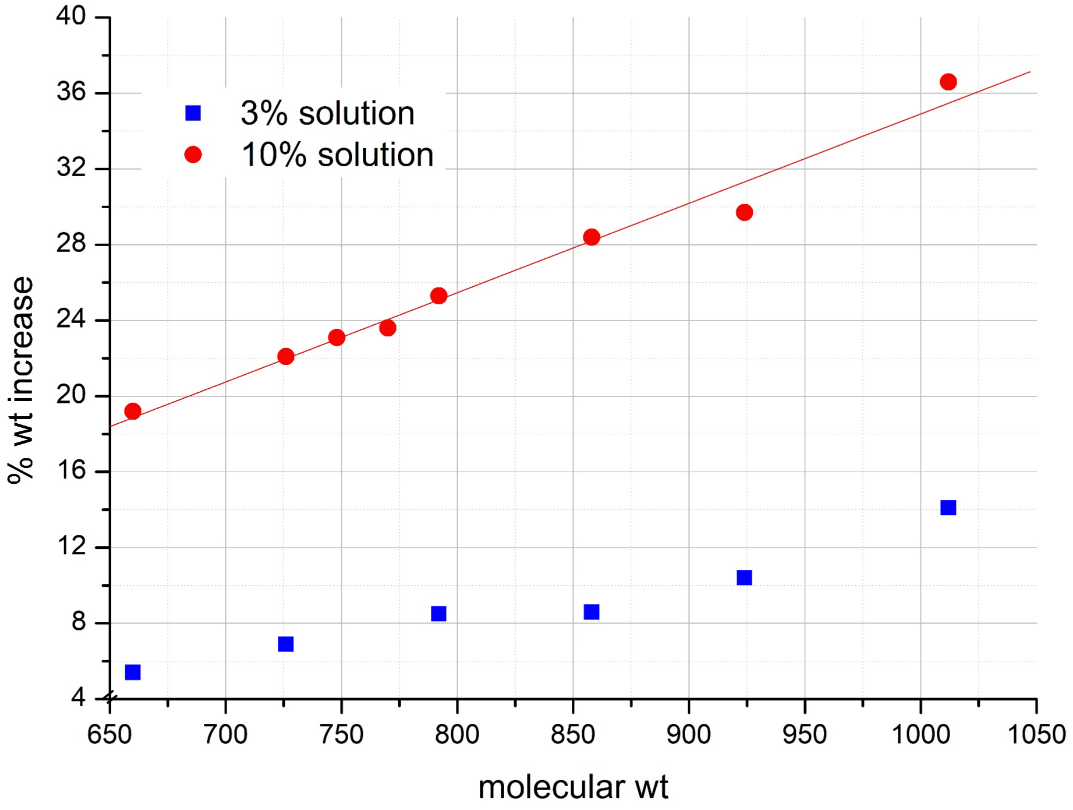


Figure 6. Weight increase of cotton samples after treatment with Na_xPA flame retardant mixtures. Data points for samples with x = 0, 3, 6, 9, 12, 16.

4.1.2 Pure flame retardants

Pure flame retardant samples were prepared according to the description in Appendix 1 and Figure 7 shows what has happened with those samples after being heated in a furnace to 400°C. It is clear that the samples have intumesced, especially the Na_3ArgPA sample (Figure 7a).

Figure 7. Flame retardants heated to 400°C. From left to right: Na_3ArgPA, Ca-Na_3ArgPA, Al-Na_3ArgPA.

4.2 Combustion tests

Screening of cotton samples treated with various flame retardant mixtures (see Appendix 1 for information about the composition of the mixtures) were performed to quickly have an overview of which samples would be of interest to investigate further.

Figure 8 shows a few cotton samples after those combustion tests. Untreated cotton (not shown) burned completely, leaving more or less no residues. In all cases, the samples treated with flame retardant self-extinguished. Samples with only sodium ions (Figure 8a) show the largest amount of charring. Samples with only amino acid (Figure 8b) showed less charring, but the samples were very brittle, possibly due to the high acidity of those samples. Figure 8c shows that when both sodium ions and amino acid are mixed with PA, there is a much-increased flame retarding performance, and if also a multivalent metal ion (Ca^{2+}) is added to the mixture (Figure 8d), the amount of charring is very low before the flames self-extinguish.

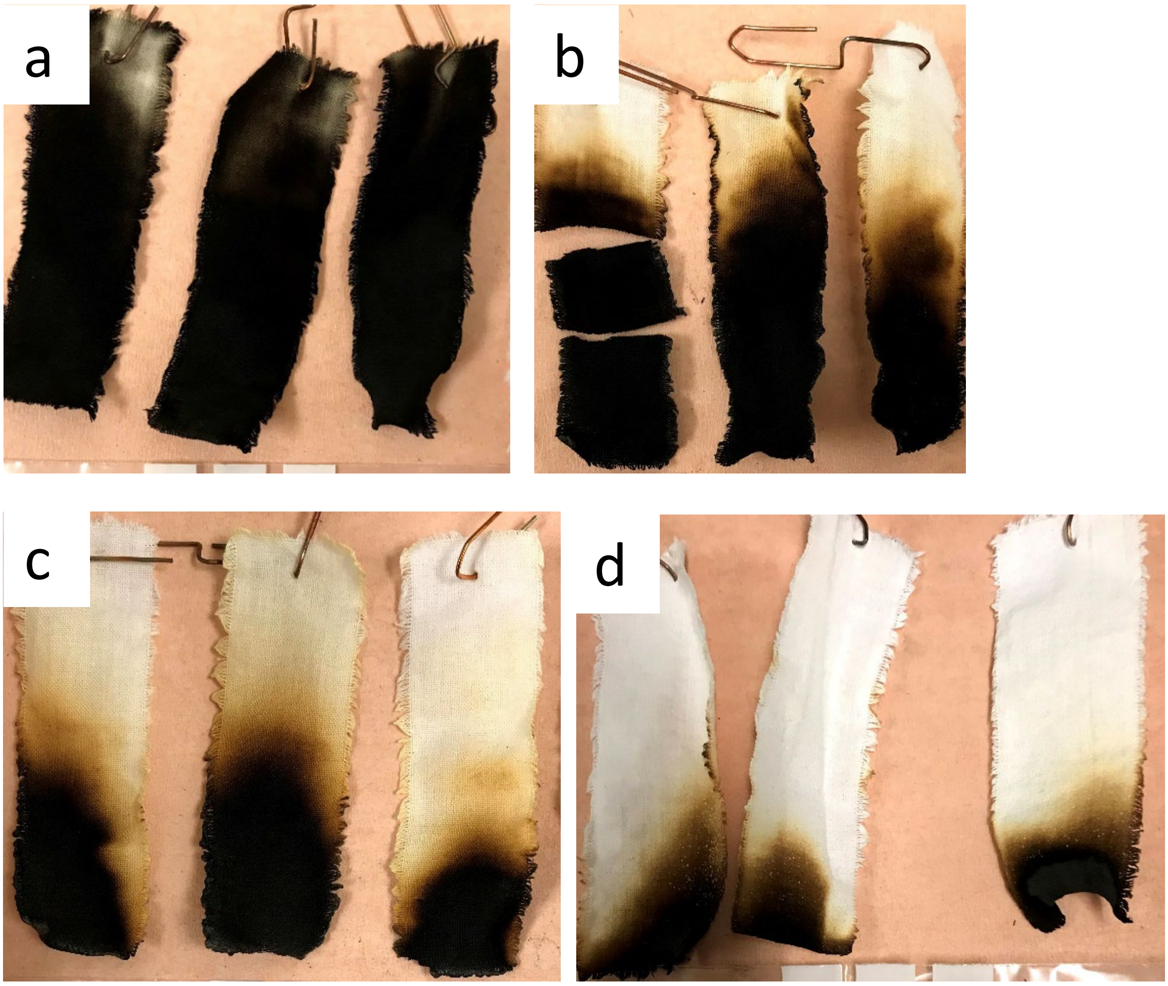


Figure 8. Cotton pieces after exposure to open flame. (a) Na_3PA, (b) ArgPA, (c) Na_3ArgPA, (d) Ca-Na_3ArgPA (1 M Ca^{2+} sprayed on the sample treated with Na_3ArgPA).

In order to estimate the flame temperature at various distances above the flame tip, a set of temperature measurements were performed. Figure 9 shows the temperature variation during measurements at various heights above the flame. The temperature is fairly constant during the measurements for each height (top) and the plot of mean temperature over distance (bottom) follows an exponential decay.

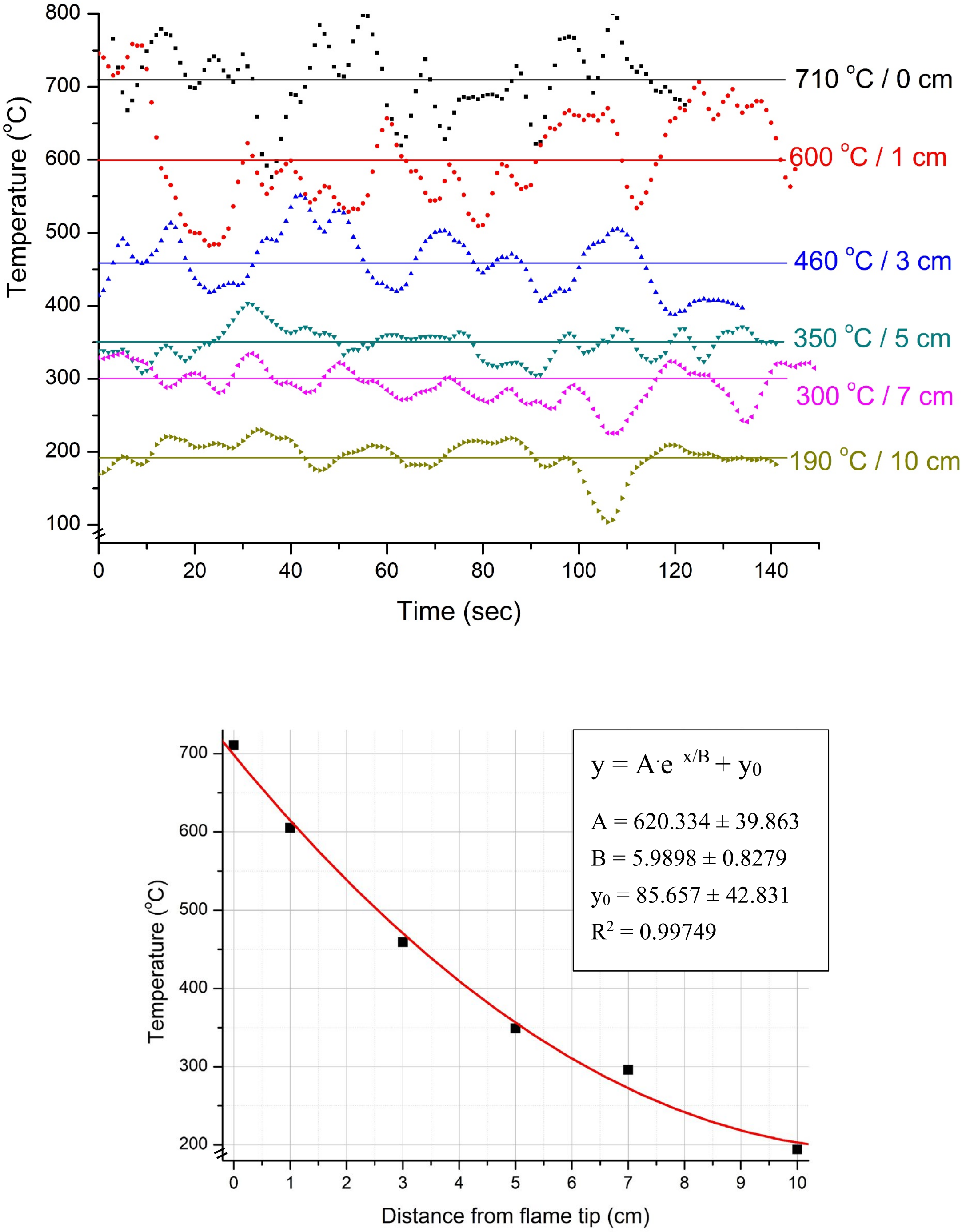


Figure 9. Temperature variation at various distances from the flame tip. Top: fluctuations of temperature over time. Bottom: temperature decrease over distance from the flame tip.

Figure 10 shows to what extent cotton samples (untreated and treated with Na_3Arg_4PA) burn when placed at different heights above the flame tip. For the untreated cotton, a significant difference in mass loss occurs at 5 cm distance (and lower) where the temperature is 350°C or higher. This is the usual ignition temperature of cotton as can be seen from TGA measurements (see Chapter 4.3). At 10 cm and 7 cm distance from the flame tip, the reference pieces of untreated cotton did not burn at all.

The samples treated with flame retardant did not lose any mass when they were placed 10 cm above the flame tip, but as the cloth pieces were placed closer to the flame tip, some mass loss is noticed, indicating that those samples start to lose mass at a lower temperature, compared to an untreated cloth. However, the treated cloths did not catch fire at any distance from the flame tip. Moreover, the maximum mass loss was only 20% even when the samples were in contact with the flame tip.

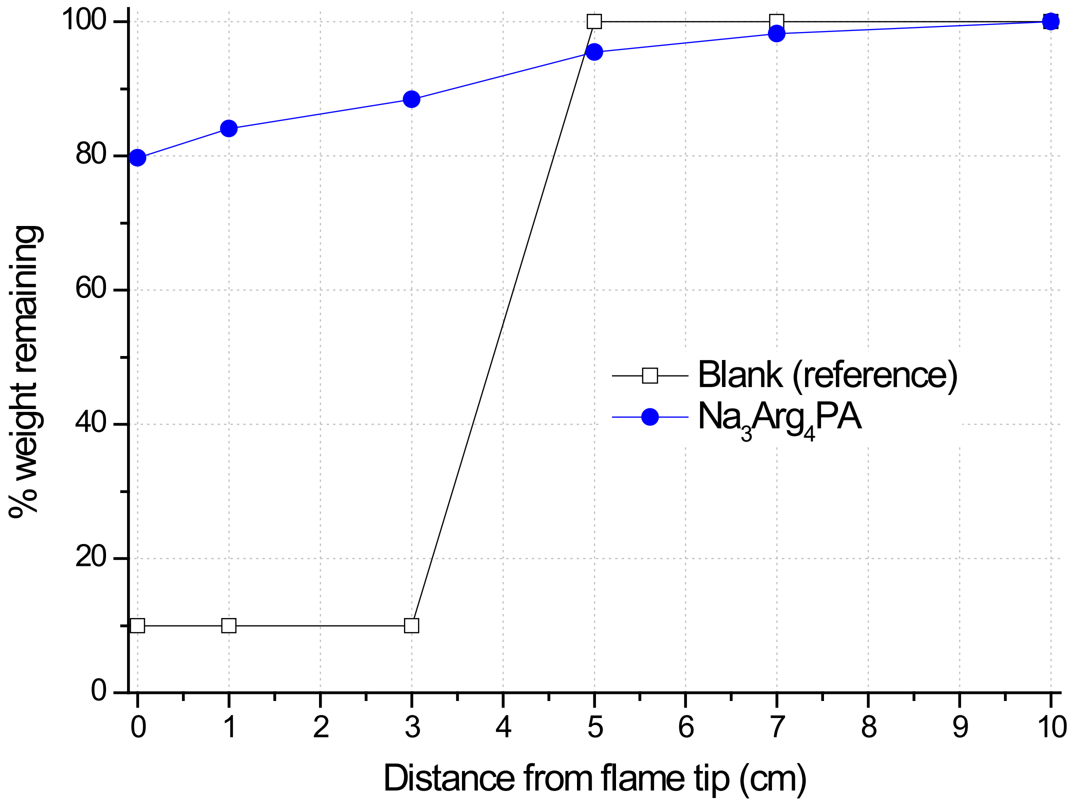


Figure 10. Weight remaining of cotton samples at various distances from the flame tip.

Figure 11 shows what the Na_3Arg_4PA treated cloths looked like after exposure to the flame. The Na_3Arg_4PA treated cotton pieces which were placed at 7 cm and 10 cm distance above the flame remained white after the fire exposure, although the former showed a small decrease in weight. The untreated cotton pieces burnt completely at shorter distances than 7 cm (as illustrated in Figure 10). Almost nothing remained to show as a picture.

The results indicate that, for the respective samples, there is a lower temperature limit for ignition of the cloth pieces below which burning, or mass loss cannot take place. These temperature limits are in accordance with the TGA results described below.

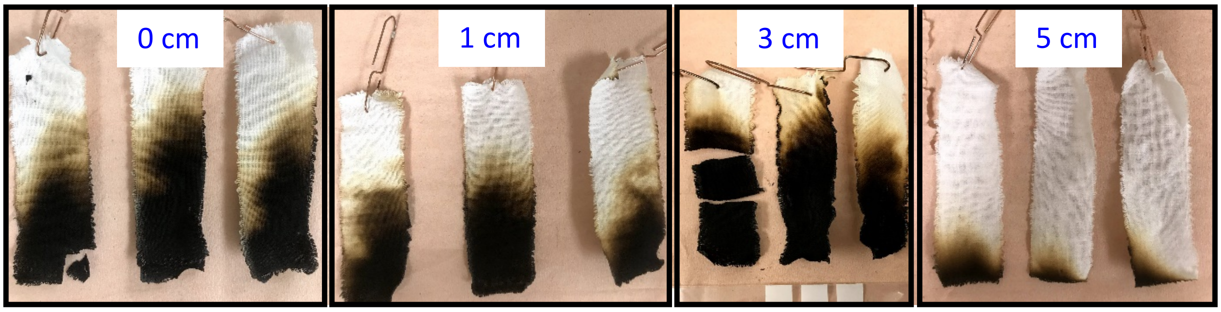


Figure 11. Cotton pieces treated with Na_3Arg_4PA *after 1 min exposure to a flame at different heights. The sample at 3 cm distance was exposed to a flame for five minutes, hence the large amount of charring compared to the samples at shorter distances.*

4.3 Thermal analyses

4.3.1 Sodium ions

Figure 12 shows the results of cone calorimeter tests on cotton samples treated with Na_xPA with various amounts of sodium. All treated samples ignite earlier than the untreated sample, but the HRR and THR are lower, and the samples self-extinguish. A clear trend can be seen that the larger number of Na^+, the more heat is released. Na^+ ions replace H^+ in the PA, and this affects the charring ability because H^+ is needed for the charring. Thus, more Na^+ means less charring and less flame retarding ability.

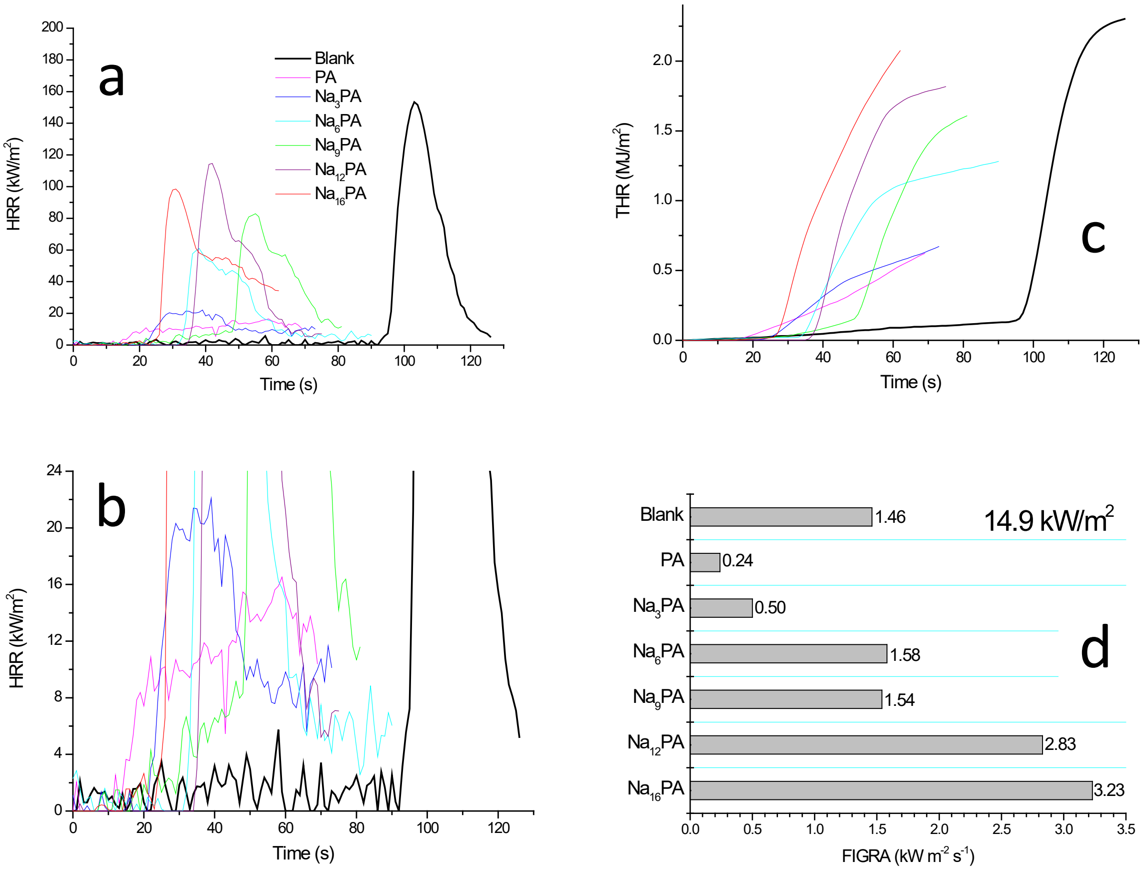


Figure 12. Cone calorimeter tests on cotton samples treated with different flame retardants, based on phytic acid and its sodium salts. (a & b) HRR at 14.9 kW/m^2 heat flux exposure. Both figures show the same results, but with different scale on the y-axes. (c) THR. (d) FIGRA.

Figure 13 shows the results of TGA analyses in nitrogen atmosphere on cotton samples treated with Na_xPA with various amounts of sodium, and Figure 14 shows the results of TGA analyses in air atmosphere on the same cotton samples. The cotton samples treated with PA and Na_3PA start to degrade at a lower temperature than the samples with a larger amount of sodium. As described above (Chapter 2.2), charring at a low temperature relative to the ignition temperature will form a less combustible mixture of pyrolytic products [3,7]. The mass loss before this expected ignition temperature is less than 50% with very small differences between the samples. PA treated cotton burns completely while cotton treated with Na_3PA retains almost 20% of its mass in the end.

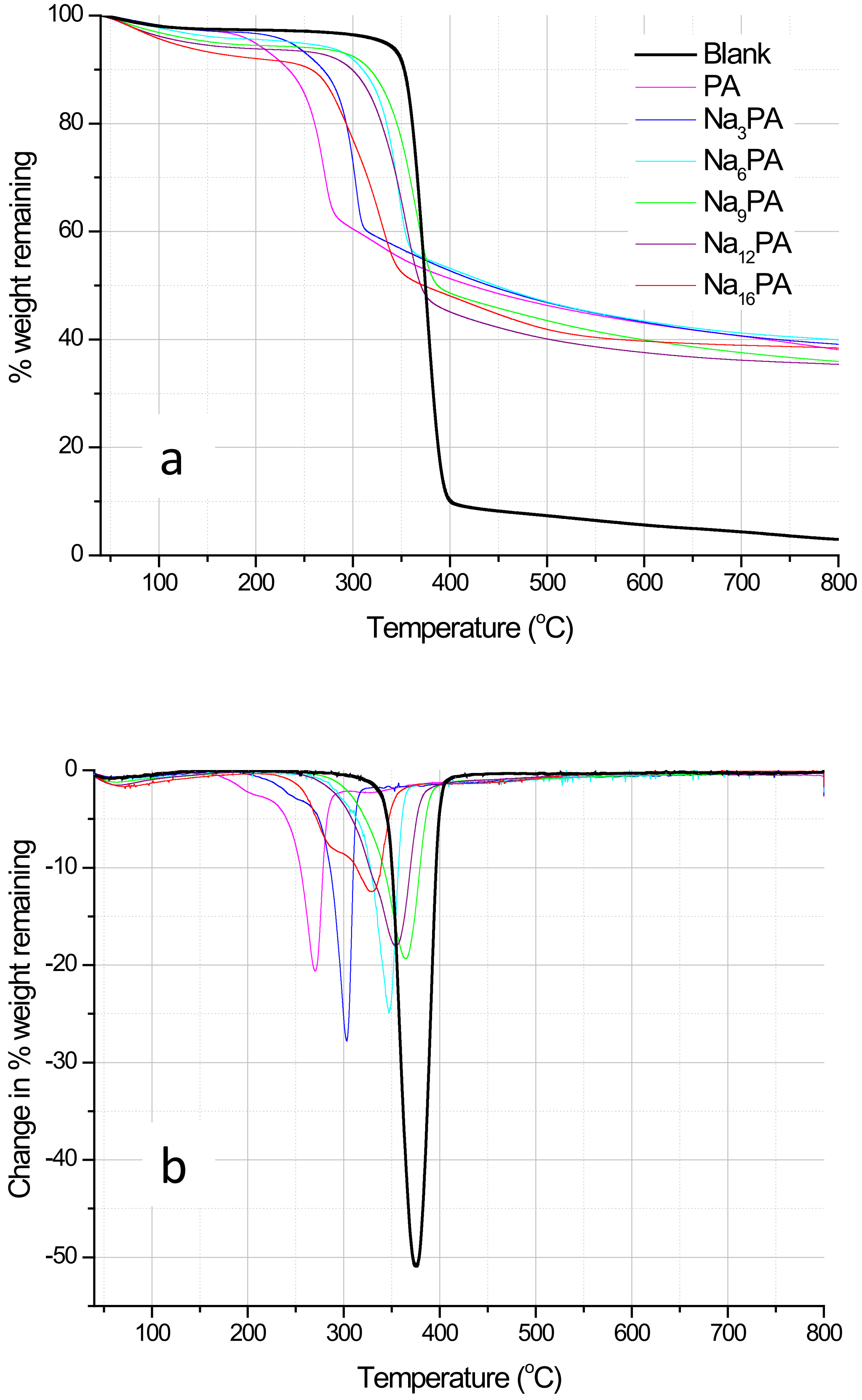


Fig 13. TGA curves (a) and their derivatives (b) of PA and its sodium salts recorded in nitrogen atmosphere.

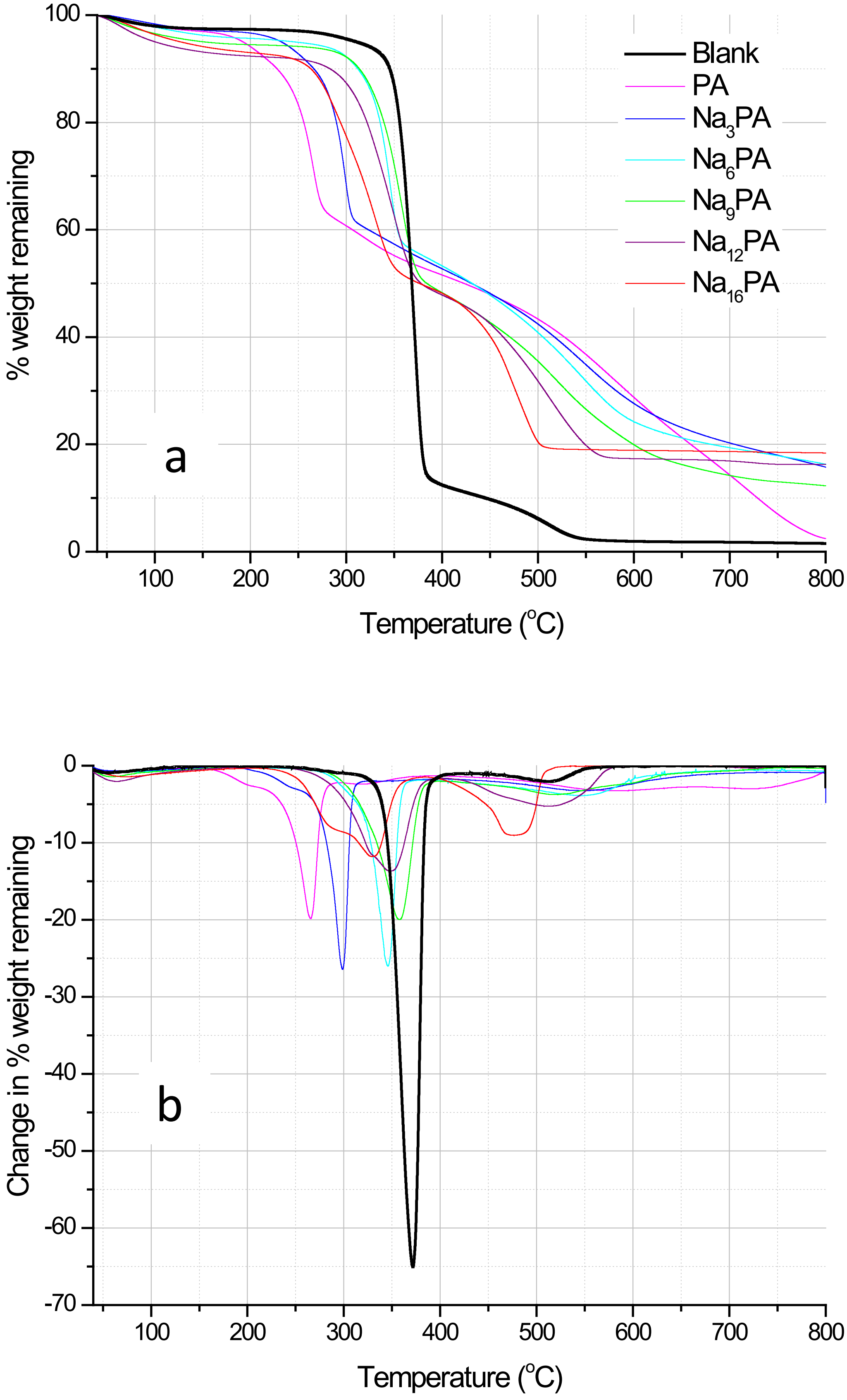


Fig 14. TGA curves (a) and their derivatives (b) of PA and its sodium salts in air atmosphere.

With an FTIR gas analyzer connected to the cone calorimeter, the amount of CO_2 and other volatile gases formed during the experiment can be measured. Figure 15 shows that the amount of CO_2 produced during the cone calorimeter experiments increases monotonously with the increasing number of Na^+ present. A higher amount of CO_2 produced means that more of the material has burnt.

As could be seen in Figure 12, the FIGRA index becomes successively higher when the number of sodium ions increases. PA itself is acidic. If PA is present in cotton cloth as flame retardant, it chars the cotton upon heating, and thereby prevents the cloth to catch fire. When more and more sodium ions are added to PA material, the acidity is reduced due to the replacement of acidic protons with sodium ions. Thereby, the charring possibility also becomes lesser with higher amount of neutralization. This neutralization causes increased burning of cloth, and more and more CO_2 is produced if the cloth is exposed to intense heat flux, as happens during cone calorimeter experiments.

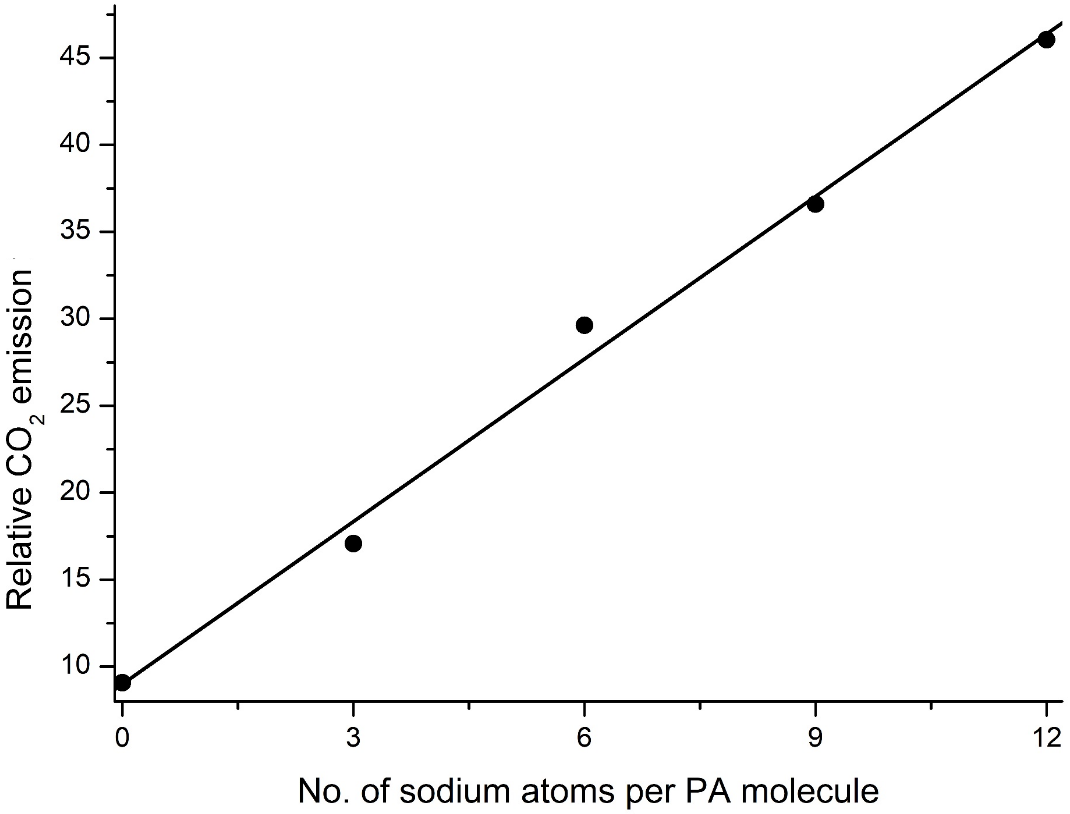


Figure 15. FTIR analysis: the amount of CO_2 evolved during cone calorimeter measurement from cloths treated with PA and its sodium salts.

4.3.2 Amino acids

With the addition of amino acids, a gas-forming component is added, which improves the flame retarding ability by diluting the pyrolysis gases. The gases formed when amino acids degrade are non-flammable (CO_2 and NH_3). Cotton samples treated with only Na and PA (Chapter 4.3.1) burn rapidly and completely at 20 kW/m^2 heat flux, while the samples with AA added can withstand this power.

Figure 16a shows the effect of adding various amino acids to the flame retardant mixture with Na_3PA. The three-letter abbreviations of the amino acids are explained in Appendix 1. Arginine (Arg) shows the best result with the smallest FIGRA index (see Figure 16c). Figure 16b shows that the amount of Arg added is also important with 0.7-1.0 Arg giving the lowest FIGRA index (Figure 16d). Possibly, smaller amounts of Arg will not form enough gaseous products during thermal degradation, while for larger amounts, the heat released from partial combustion of the hydrocarbon part of Arg will itself contribute with relatively much heat and thus counteract the flame retardant process.

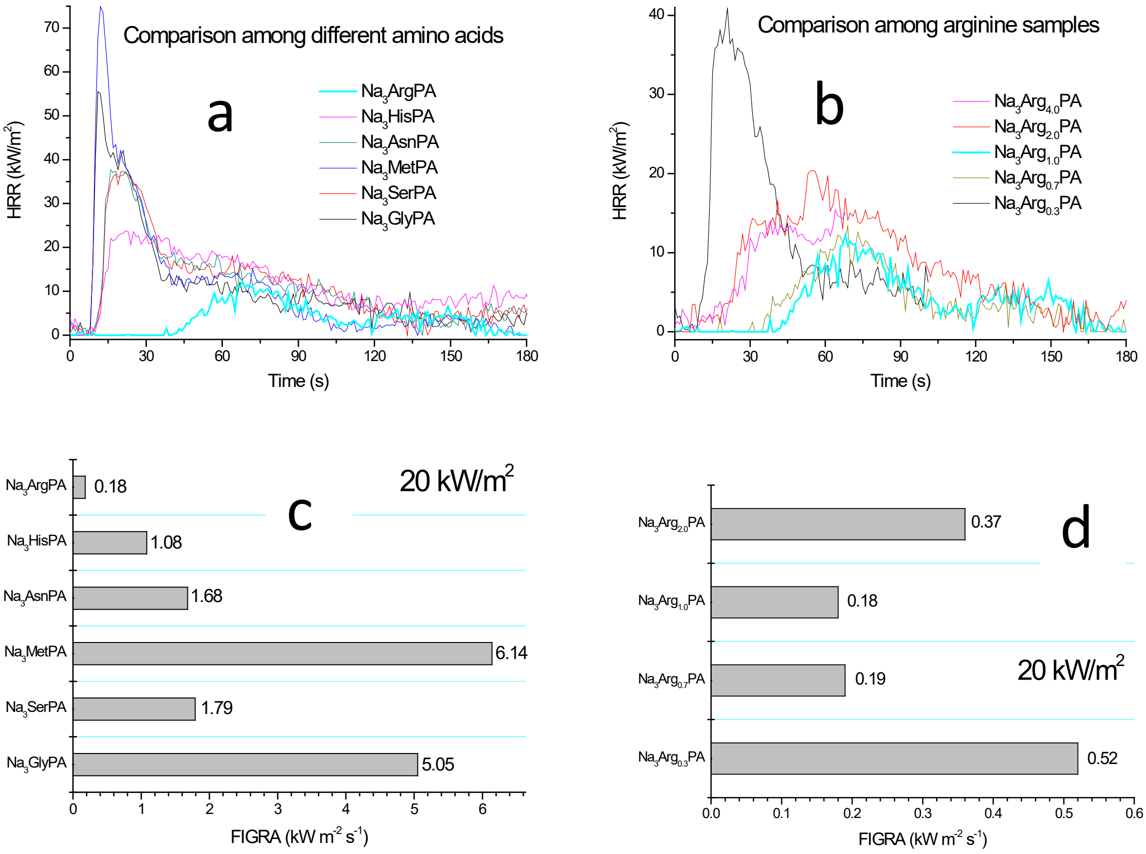


Figure 16. Cone calorimeter tests on cotton samples treated with flame retardants based on Na_3PA salt. 20 kW/m^2 heat flux exposure (a) HRR for different amino acids, (b) HRR for various amounts of arginine, (c) FIGRA for Na_3PA and different amino acids as flame retardant. (d) FIGRA for Na_3PA and various amounts of Arg as flame retardant.

It is clear from the cone calorimeter data that arginine (Arg) is the amino acid which gives the best FIGRA index with histidine (His) in second place. From the molecular structures of a few amino acids in Figure 3 it can be seen that Arg can theoretically decompose into one CO_2 group and four NH groups leading to a total of five non-combustible gas molecules while His can theoretically degrade into a maximum of four non-combustible gas molecules. Asparagine and serine (not shown in Figure 3), which also have quite good FIGRA index can decompose into three non-combustible gas molecules, while glycine and methionine, which have high FIGRA index, can only decompose into two gas molecules. The molecular structure of Glycine (Gly) can be seen in Figure 3. Although the cotton samples were very thin and the relative amount of AA added was small, some intumescent behavior could be seen on the samples after self-extinguishment, compared to samples without AA. This indicates that increased gas formation has occurred.

Since Arg gave the best result in the cone calorimeter, TGA tests focus on this amino acid. In Figure 17 (nitrogen atmosphere) and Figure 18 (air) varying amounts of Arg has been added to the flame retardant mixture with either PA or Na_3PA (which was the sodium phytate salt that gave the lowest FIGRA index according to data in Figure 12). The addition of aspartic acid (Asp) to one sample with Arg causes degradation at a slightly lower temperature than the samples with only Arg, but in the air atmosphere it gives a larger mass loss at very high temperatures.

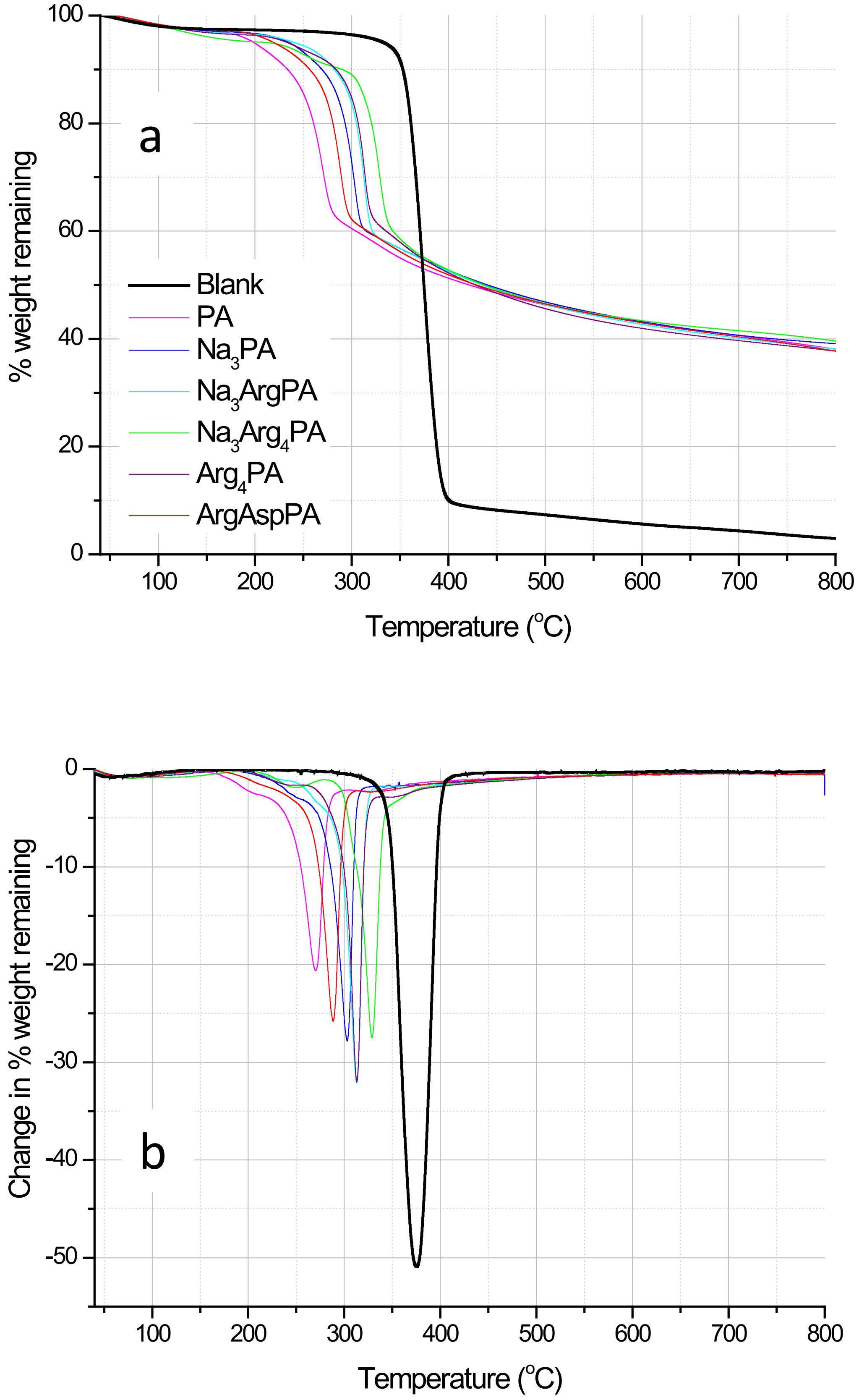
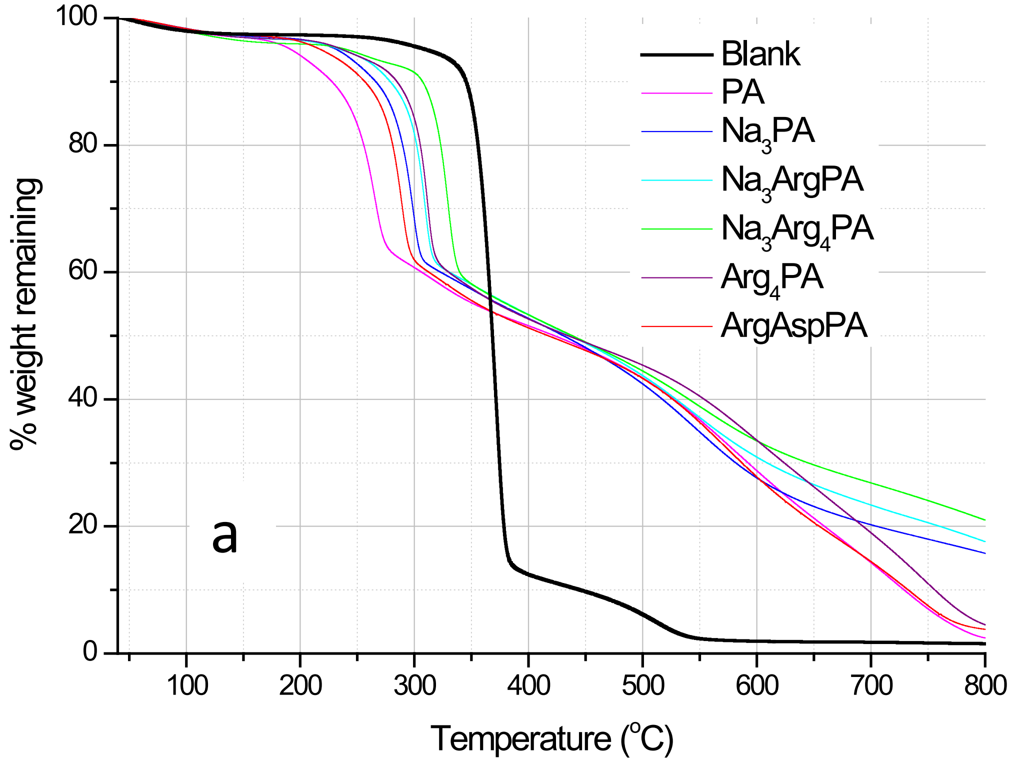


Figure 17. TGA curves (a) and their derivatives (b) on cotton samples treated with flame retardants based on PA, arginine, aspartic acid, and sodium salts in nitrogen atmosphere.



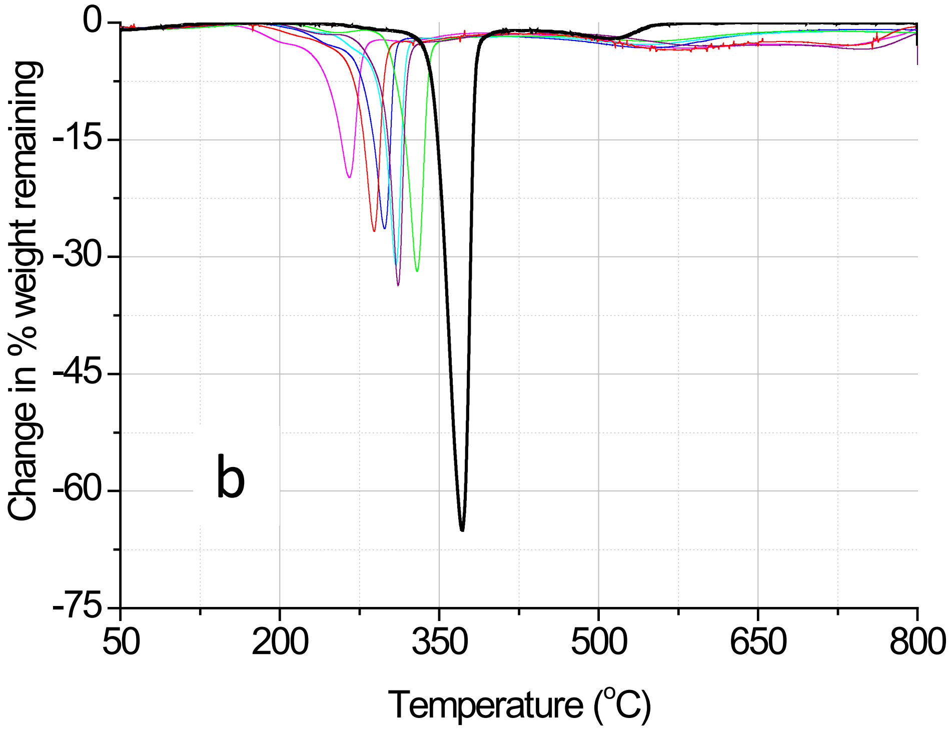


Figure 18. TGA curves (a) and their derivatives (b) on cotton samples treated with flame retardants based on PA, arginine, aspartic acid, and sodium salts in air atmosphere.

4.3.3 Multivalent metal ions

The addition of multivalent ions, such as Ca^{2+} or Al^{3+}, to the flame retardant coating is needed to make it more insoluble. Figure 19 shows the results of TGA analyses in air on cotton samples where Ca^{2+} or Al^{3+} ions are added to the Na_3ArgPA flame retardant. As can be seen from the derivative curves, this induces the onset of thermal degradation at a slightly lower temperature than Na_3PA alone, with Al^{3+} already at 200°C, and in the case of Al^{3+}, also more mass is retained in the end.

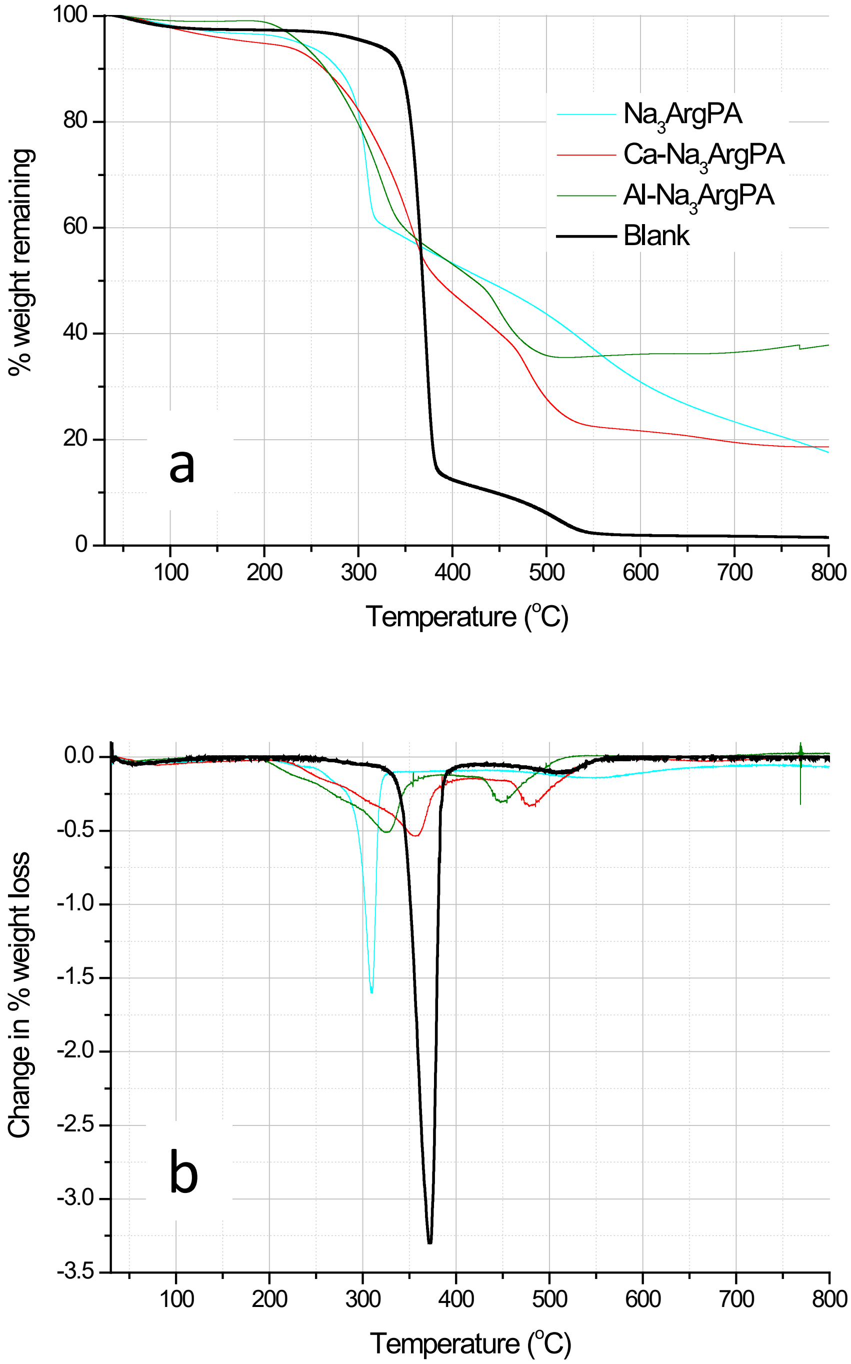


Figure 19. TGA curves (a) and their derivatives (b) on cotton samples treated with flame retardants based on phytic acid, arginine, and their metal salts in air atmosphere.

Figure 20 shows that the addition of Ca^{2+} or Al^{3+} leads to a slightly increased HRR and THR, This induces the onset of thermal degradation at a slightly lower temperature than Na_3PA alone, with Al^{3+} already at 200°C, and in the case of Al^{3+}, also more mass is retained in the end.

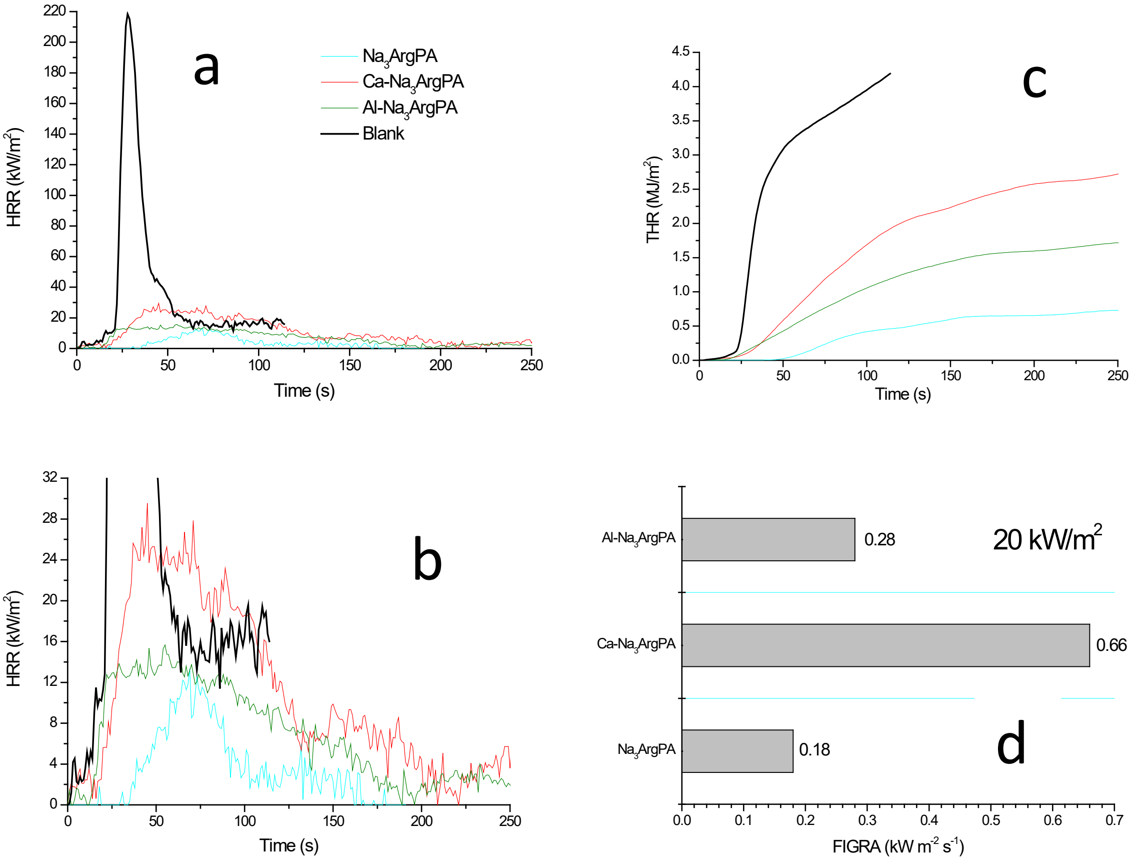


Figure 20. Cone calorimeter tests on cotton samples treated with different flame retardants, based on phytic acid and arginine, plus multivalent metal ions to make the film insoluble. (a & b) HRR at 20 kW/m² heat flux exposure. Both figures show the same results, but with different scale on the y-axes. (c) The corresponding THR. (d) FIGRA index.

4.4 Nuclear Magnetic Resonance

4.4.1 Carbon

Figure 21 shows what is happening with the carbon part of the phytic acid flame retardant when it is heated. Due to the viscous nature of some of the samples at low temperatures, these could not be analyzed. At room temperature (RT) the flame retardant with Al^{3+} ions sprayed on Na_3ArgPA (Figure 21c) shows one large signal from the carbons in phytic acid and five very small peaks from different carbon atoms in arginine. Because the y-axis is not to scale for the different temperatures, the spectrum at 200°C should be interpreted as a relative degrading of the phytic acid part while the arginine is still intact. Thermal decomposition of arginine occurs at slightly higher temperatures (between 220-250°C) [41]. At 400°C the degrading is complete and the phytic acid has been completely converted into a polyaromatic char.

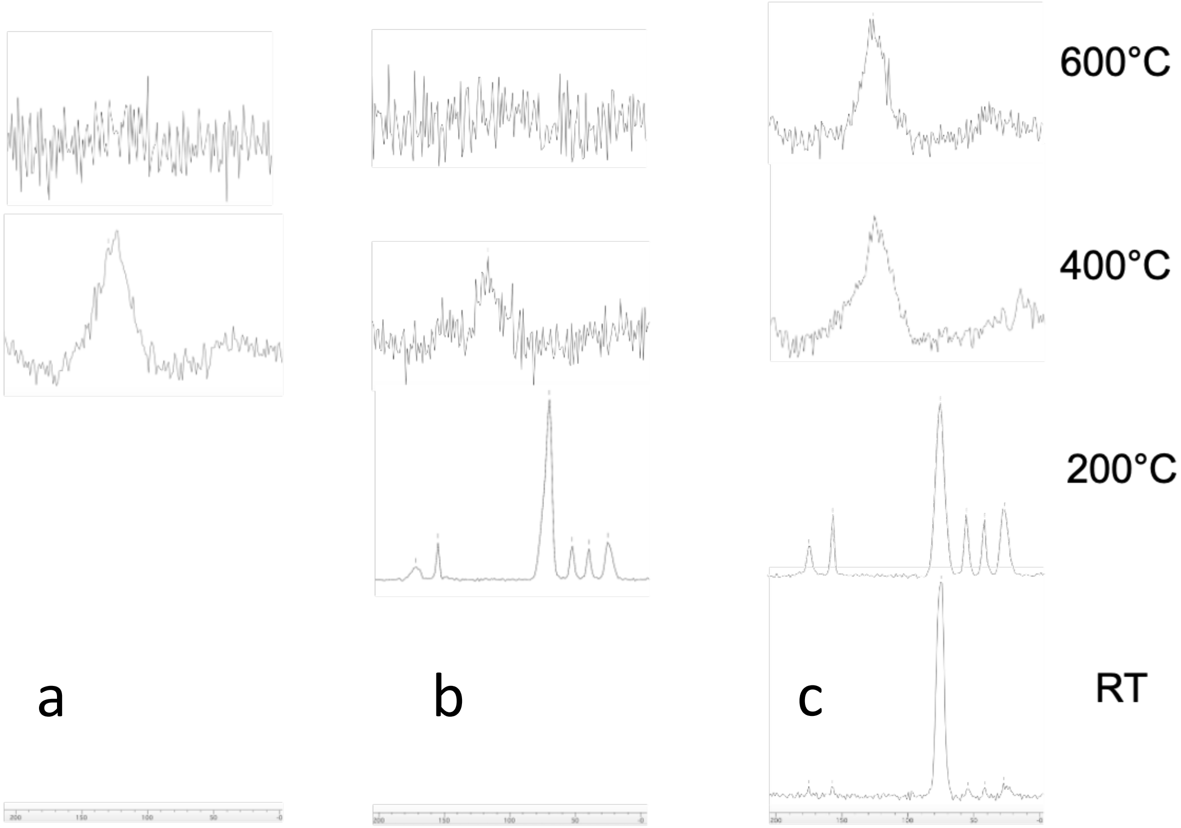


Figure 21. ^{13}C MAS NMR of (a) Na_3ArgPA, (b) Ca-Na_3ArgPA, and (c) Al-Na_3ArgPA heated to different temperatures.

For the flame retardant with Ca^{2+} ions sprayed on Na_3ArgPA instead of Al^{3+} ions (Figure 21b), the same process can be seen. At 400°C the phytic acid has decomposed completely into a char and arginine has decomposed completely into gaseous fragments. It is interesting to note that the char formed in this system is less stable than when Al^{3+} ions are present so at 600°C there is no char left (no signal visible in the spectrum).

Since the y-axis is not to scale it is difficult to estimate the relative amounts of char at 400°C for Na_3ArgPA with and without Ca^{2+} and Al^{3+}, respectively, but assuming that the noise level is similar in all experiments, it seems that Al-Na_3ArgPA should give the most stable char, and Ca-Na_3ArgPA has the least amount of char at 400°C. From the TGA curves (Figure 19) it can be seen that on cotton the flame retardant with Ca^{2+} has decomposed to a larger extent at 400°C compared to the other two samples and it also has the largest HRR and THR (Figure 20) of the three samples.

In addition to charring and gas formation mechanisms of the flame retardant, termination of radical fragments in the gas phase can take place if e.g. sodium ions are present. This mechanism can explain the better flame retardant effect of Na_3ArgPA relative to the versions with Ca^{2+} or Al^{3+} ions present.

4.4.2 Phosphorus

Figure 22 shows what is happening with the phosphate part of the phytic acid when it is heated. At room temperature (RT) the flame retardant with Al^{3+} ions sprayed on Na_3ArgPA (Figure 22c) shows three distinct signals. The TGA data of this flame retardant on cotton (Figure 19) shows that the thermal degradation starts at 200°C and this degrading leads to an increased disorder in the structure of the flame retardant, which can be seen as broader lines in the NMR spectra at elevated temperatures. It is not clear whether the phosphate part of the phytic acid forms aluminum phosphate or polymeric phosphate species because their signals are in the same region, but it is reasonable to believe that a mixture of both is formed because of the limited availability of Al^{3+} compared to the number of phosphate groups.

The spectra of flame retardant samples with Ca^{2+} ions sprayed on Na_3ArgPA (Figure 22b) show large changes with increasing temperature. The narrow peak visible at 400°C is most likely from a calcium phopshate species while the other two peaks are from polymerized phosphates with different degree of polymerization (linear/cyclic or branched network). At 800°C the sample has become very crystalline with many narrow peaks. Na_3ArgPA (Figure 22a) also shows three peaks from sodium phosphate and polymerized phosphates, but with less crystallinity at 600°C.

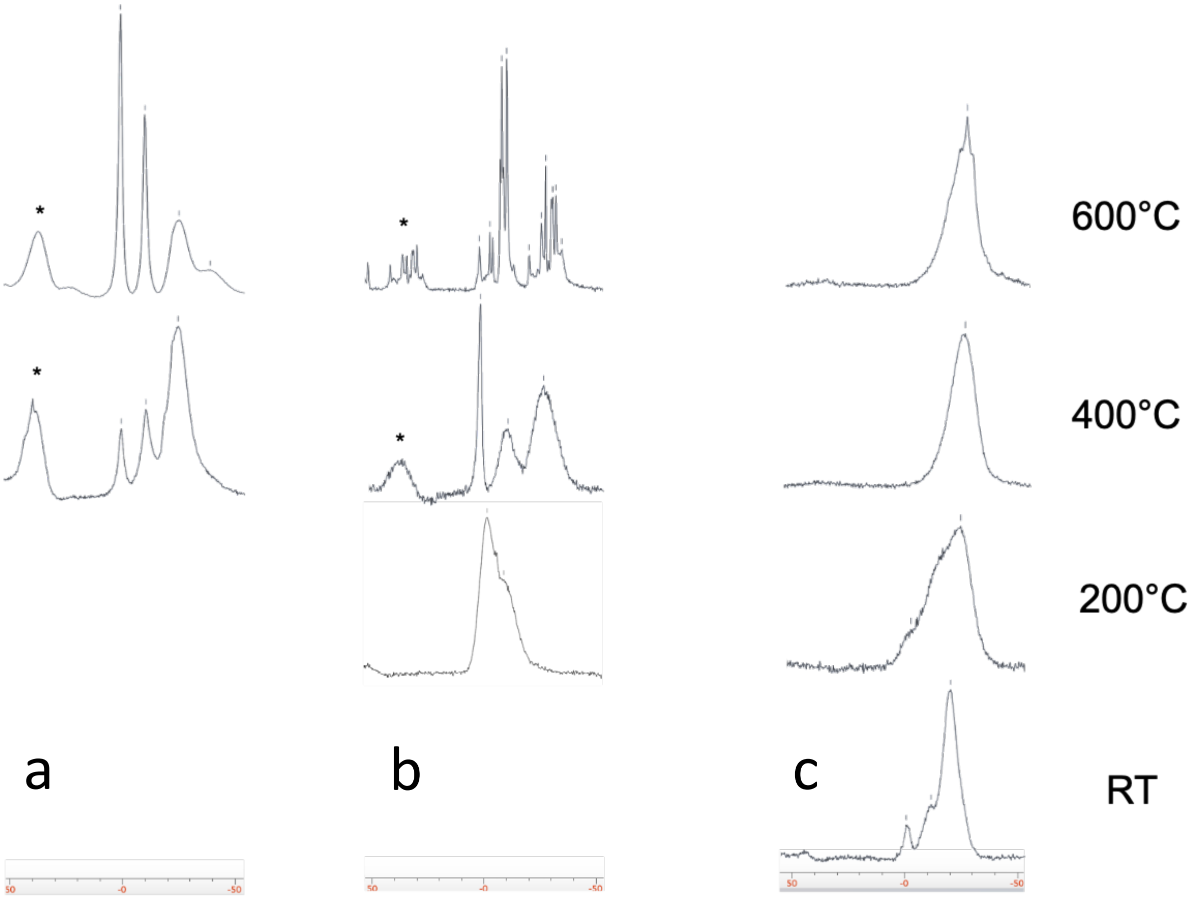
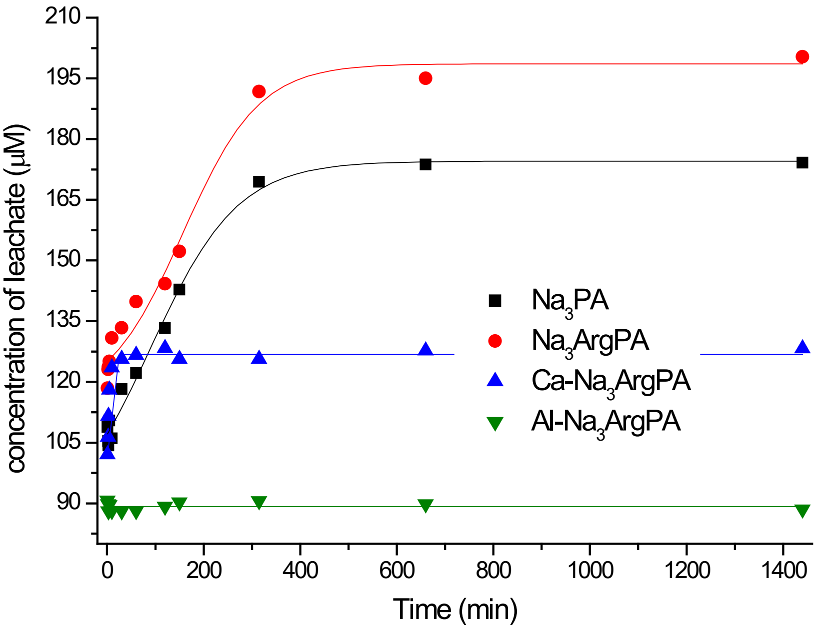


*Figure 22. ^{31}P MAS NMR of (a) Na_3ArgPA, (b) Ca-Na_3ArgPA, and (c) Al-Na_3ArgPA heated to different temperatures. * denotes spinning sidebands which are experimental artefacts due to anisotropy.*

4.5 Leaching tests

Figure 23 shows the results of the leaching tests. The solubility decreases when the ion charge increases (from Na^+, to Ca^{2+}, to Al^{3+}) as an effect of stronger bonds forming between phosphate groups and metal ions. For Al-Na_3ArgPA, 90 µM PA is dissolved, while for Ca-Na_3ArgPA, 125 µM is dissolved. In both cases, the equilibrium is reached very early, when nothing more leaches. For Na^+, the kinetics is slower, so it takes up to 8-10 hours to reach equilibrium. The amount of amino acid that leaches is much lower, only 0.5 µM when multivalent ions are present.



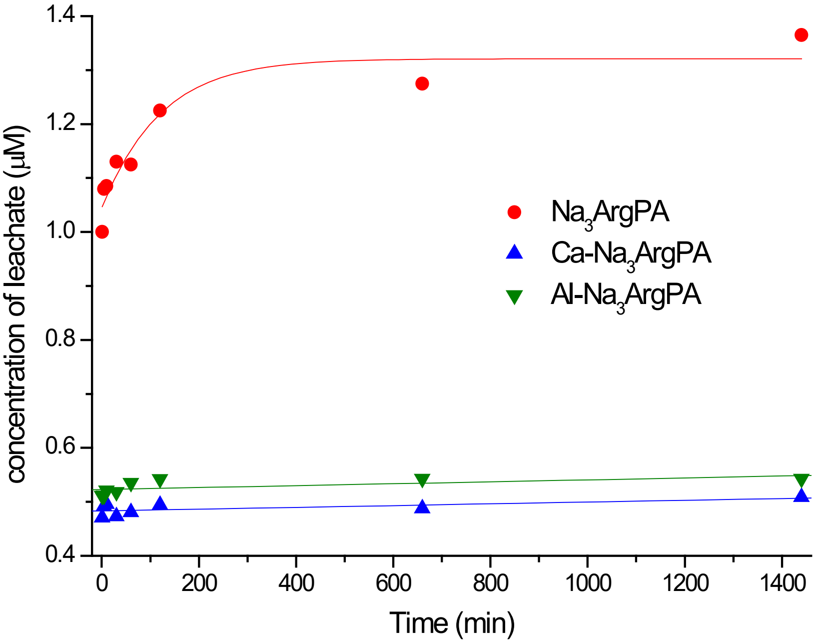


Figure 23. Leaching trend of PA (Top) and AA (Bottom) in aqueous solution.

5 Conclusions

A number of aqueous solutions containing phytic acid (PA), amino acid (AA), and metal ions in different proportions were prepared. Each of the ingredients in the mixtures has their own contribution to the flame retardant efficiency so a series of tests were done on cotton samples treated with the different solutions.

Initial combustion tests revealed that all mixtures have a flame retarding effect. Cotton samples exposed to a flame self-extinguish leaving only a more or less charred surface. The distance between the cotton sample and the tip of the flame was 3 cm. Temperature measurements showed that the temperature at this distance is 460°C, which is above the ignition temperature of cotton. Untreated cotton burns quickly and more or less completely at this distance above the flame. Not even when the cotton pieces treated with a flame retardant mixture is placed in direct contact with the flame tip will they catch fire and burn, although the amount of charring increases. Some smoldering combustion can be seen leading to about 20% mass loss.

TGA measurements show that cotton samples treated with flame retardants start to degrade and char at a lower temperature than untreated cotton, which gives a smaller amount of pyrolysis gases, which also have a less combustible composition. A larger part of the mass is remaining both at the onset of the combustion, but also at the end of the experiment.

Cone calorimeter measurements show that when the amount of sodium ions is increased, as a result of avoiding damage to the cotton from too acidic PA, the FIGRA index increases, which is an effect of reduced charring ability of PA. Three sodium ions give the best FIGRA index without damaged cotton.

When AAs are added to Na_3PA, combustion tests show that much less charring of the cotton samples take place before the fire self-extinguish. The samples can tolerate a higher power in the cone calorimeter without burning. Arginine (Arg) showed the best result. Theoretically, it forms the largest amount of non-combustible gases of all AAs, and thus the largest dilution of the pyrolysis gases. However, Arg also has quite a large hydrocarbon part compared to the other AAs tested, which possibly causes some additional combustion and heat release to the fire, and in this way counteracts the flame retarding effect, when the amount of Arg is increased. Therefore, it may be that other AAs will give a better result if higher concentrations are used.

Spraying multivalent metal ions onto a cotton sample treated with Na_3ArgPA leads to an earlier onset of thermal degradation. According to the TGA measurements, thermal degradation of Al-Na_3ArgPA coating is onset at a lower temperature than the Ca-Na_3ArgPA coating, which in turn starts to degrade at a lower temperature than the Na_3ArgPA coating. The cone calorimeter tests reveal that Na_3ArgPA has a slightly lower FIGRA index than the the flame retardant with multivalent ions, although the flame retardant effect is still good in all three cases. An intumescent effect can be seen in the flame retardant when it has been heated to 400°C. The effect was larger for Na_3ArgPA than for Ca-Na_3ArgPA and Al-Na_3ArgPA.

NMR data correlate well with data from thermal analyses. The phytic acid part of the flame retardant starts to break down at 200°C while the amino acid needs a slightly higher temperature. The char which has formed during the thermal breakdown of phytic acid, is most stable for Al-Na_3ArgPA. The phosphate groups on the phytic acid will form a mixture of polymeric phosphate species and metal phosphates.

The flame retardant stops the fire from developing by using several different mechanisms, which together remove fuel, oxygen, heat, and chain reaction.

The solubility of the flame retardant coatings containing aluminum or calcium ions are lower compared to the solubility of Na_3ArgPA coating.

6 Future research

The flame retardant composition can still be improved to give even better protection of cotton, and also to increase the insolubility.

The tests have so far mainly been performed on the lab-scale, so upscaling tests are needed to evaluate the performance against the different standards used.

The flame retardant composition should also work on wood and other cellulose-based materials, e.g. wood-based fabrics like lyocell and viscose, but the optimal mixture may be a different one, and the method of application may differ, so this needs to be investigated as well.

Considering that the flame retardant prevents fire through many different mechanisms it also has the potential to work on other materials than cellulose-based, e.g. different plastics, for which the main fire retarding mechanism is on the vapor phase rather than charring.

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Appendix

Appendix 1 Preparation of samples

Preparation of solutions

The following list of chemicals were purchased and used:

Phytic acid, aqueous solution (50% *w/w*): $C_6H_6(H_2PO_4)_6$ or $H_{12}PA$

Metal salts:
Sodium hydroxide pellets: NaOH
Calcium chloride hexahydrate: $CaCl_2 \cdot 6H_2O$
Aluminum chloride hexahydrate: $AlCl_3 \cdot 6H_2O$

Amino acids:
Asparagine (Asn)
Aspartic acid (Asp)
Alanine (Ala)
Arginine (Arg)
Glutamine (Gln)
Glutamic acid (Glu)
Glycine (Gly)
Histidine (His)
Lysine (Lys)
Methionine (Met)
Proline (Pro)
Serine (Ser)
Tyrosine (Tyr)

The chemicals were used to prepare a range of solutions where the amounts of PA, metal salt (M) and amino acid (AA) were varied.

3 wt% aqueous phytic acid solution was prepared by weighing 6 g of 50% PA solution into a plastic bottle. It was diluted with deionized water up to 100 g of total weight. Similarly, 10% aqueous phytic acid solution was prepared with 20 g of 50% PA solution.

After that, aqueous solutions were prepared where different amounts of NaOH were added to the PA solutions under stirring. The molar ratios between NaOH and PA were 3:1, 4:1, 5:1, 6:1, 9:1 and 12:1. The theoretical maximum molar ratio is 12:1, but an excess of NaOH representing a 16:1 molar ratio was also prepared.

Another set of aqueous solutions were prepared where different amounts of AA were added to the PA solutions. The molar ratios between AA and PA were 1:1 and 4:1.

A third set of aqueous solutions were prepared where different amounts of both NaOH and AA were added to the solutions of PA. The molar ratios between NaOH and PA were 3:1, 4:1, 5:1, 6:1, 9:1 and 12:1. The molar ratios between AA and PA were 0.3:1, 0.7:1, 1:1, 2:1, and 4:1.

In addition, aqueous solutions of multivalent metal salts (Ca^{2+}, Al^{3+}) were prepared by dissolving the appropriate amounts of metal salts in deionized water to reach 0.1 M and 1.0 M concentrations. The solutions were stored in spray bottles.

Preparation of cotton samples

The cotton pieces were dipped for 1 minute in the PA solutions described above and then left to dry in open air for 1.5 days. Thereafter, for insoluble samples, aqueous solutions of Ca^{2+} or Al^{3+} were sprayed on the cloth and dried for another 1.5 days.

Preparation of furnace treated samples

An aqueous solution of Na_3ArgPA was prepared by putting 66.0 g 50 wt% aqueous PA solution in a round bottom flask and dilute with deionized water to 100 g total weight of the solution. To this solution 6.0 g solid NaOH was added to give a molar ratio of 3:1 between Na^+ and PA. The solution was stirred with a magnetic stirrer until the NaOH had dissolved. Thereafter, 8.7 g Arg was added to the solution to give a molar ratio of 1:1 between Arg and PA. After complete dissolution of the Arg, the solution was freeze-dried to obtain a gel-type material.

Ca-Na_3ArgPA complex was prepared by stirring an aqueous solution of Na_3ArgPA in a beaker for 24 hours until all water had evaporated. A thin transparent film formed at the bottom of the beaker. A 1 M aqueous solution of $CaCl_2$ was sprayed onto this film and the stirred for another 24 hours until the water had evaporated, and a thin transparent film had formed at the bottom of the beaker.

Al-Na_3ArgPA complex was prepared similarly, but with 1 M aqueous solution of $AlCl_3$.

The samples were thereafter placed in a furnace and heated to 400°C.

Appendix 2 Leachate determination

The amount of flame retardants that leach from a material can be determined by UV-Vis spectroscopy on the leachate. The absorbance of light is proportional to the amount of substance that absorbs the radiation so first calibration curves with known concentrations of AA and PA have to be made. The procedure for determining PA has been described previously [0]. The procedure for determining AA is as follows:

Reagents:
A ninhydrin solution was prepared by taking 400 mg ninhydrin, 60 mg hydrindantin, 15 ml DMSO and 5 ml 4 M lithium acetate buffer in a colored 100-mL volumetric flask. The suspension was stirred until all solid particles were dissolved. A stock solution of arginine at 50 µM concentration in 0.05% glacial acetic acid was prepared.

Five test/tubes were prepared as follows (volumes in ml):

Tube	**1**	**2**	**3**	**4**	**5**
Standard	0.0	0.5	1.0	1.5	2.0
Water	2.0	1.5	1.0	0.5	0.0
Ninhydrin reagent	1.0	1.0	1.0	1.0	1.0
Total volume	3.0	3.0	3.0	3.0	3.0

Standards:
The test-tubes were placed in a circular wire rack inside a boiling water bath, covered with aluminum foil, and boiled for 10 min. They were then removed and placed in an ice water bath for 5 min. To each tube, 5 ml ethanol was added. The tubes were vortexed and covered with Parafilm for 5 min. The absorbance at 570 nm were measured, using the solution in tube 1 as a reference. That will give the standard curve.

Determination of AA concentration:
1 mL of the leaching solution were withdrawn and used in place of standard; 1 mL water and 1 mL ninhydrin solution were added (like tube 3). Amino acid concentration is determined, following a similar method as used for standard solution, and then comparison of the absorbance at 570 nm readings to the standard curve.

Project team

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