ACTUAL PROBLEMS OF MODERN SCIENCE

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STUDY OF A BIO-BASED FIRE RETARDANT FOR IMPARTING FIRE RESISTANCE TO COTTON TEXTILES

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1. Introduction

The most common phosphorus-containing formulations for processing cellulosic textiles are [1] tetrakis hydroxymethyl phosphonium chloride (THPC) and N-methylol dimethylphosphonopropionamide (MDPA), marketed under the trade names Pyrovatex CP and Pyrovatex CPN. These compounds interfere with the pyrolysis reaction, which prevents the formation of levoglucosan and flammable volatiles, and increase the formation of char. But the main disadvantage in the use of these compounds is the release of formaldehyde during the curing of the finishing compound and the use of the treated textile materials, since formaldehyde is declared as a carcinogen according to the World Health Organization. Given the shortcomings of the used fire retardants, the strict directives of many countries regarding their chemical composition, the need for the introduction of environmentally friendly durable flame retardant substitutes increases [2].

Recently, researchers have shown interest in phosphorus-containing substances based on bioorganic compounds of phytic acid for the development of flame retardants. Phytic acid is also known as inositol-hexakisphosphate acid or phytate, in the form of a salt, and is regarded as a "green" molecule found in abundance in plant tissues such as beans, grains and oilseeds [3, 4]. As a biocompatible, environmentally friendly, non-toxic and easily obtained organic acid, it is widely used in antioxidant, antitumor, biosensor, cation exchange, nanomaterial and other fields due to its special structure of inositol hexaphosphate [5]. In terms of molecular weight, phytic acid contains 28 wt% phosphorus and is promising as one of the possible and effective materials for the development of flame retardants.

Phytic acid is being studied as a fire retardant to reduce the flammability of materials based on cellulose, silk, wool, mixed fibers. One of the pioneering studies on the use of this biologically based molecule as a fire retardant dates back to 2016 and describes its effects on wool fabrics [9]. The fabrics were immersed in aqueous solutions of phytic acid with a concentration of 10 to 200%, under acidic conditions at pH = 1.2, and then thermally treated at 90°C for 1 hour. As a dopant acid, it was used to significantly improve the characteristics of fire retardant composite paper deposited with polyaniline [6]. The potential fire retardant effect of various metal phytates has been assessed as biosource phosphorus additives for polylactic acid-based composites [8].

Phytic acid is composed of six negatively charged phosphate groups and has a strong tendency to combine or interact with positively charged metal ions or proteins [10, 11]. This means that phytic acid can combine with wool fibers (natural protein fibers) through electrostatic interactions between positively charged amino groups in wool and negative phosphate groups. It also readily chelates with metal ions and provides an acid as well as a carbon source [12]. Phytic acid with chitosan, as well as phytic acid and nitrogen-modified silane hybrids were used by layer-by-layer assembly for the manufacture of thin flame retardant films on cotton fabric [7].

Interesting studies carried out [20] to determine the thermal behavior of phytic acid solutions, which confirm the ongoing processes of carbonization and dehydration of phytic acid as a result of the OH groups decomposition present in the biomolecule between temperatures of 248°C and 447°C. With a further increase in temperatures, the next stage is observed between 447 and 863°C (Dm = 41.5% and DTG T_{peak} = 648°C) and is due to the process of thermal decomposition of phytate groups and the removal of elemental carbon formed in the previous stages. At 870°C, the cumulative weight loss was 97%.

2. Goal of the study

Phosphorus-containing compounds used as fire retardants are thermally decomposed to PO, which blocks the combustion process of textile materials, despite the fact that when matrix combustion is extinguished, H and HO are also formed. However, phosphorus-containing compounds are capable of catalyzing dehydration and carbonization reactions containing OH compounds [13]. Considering this circumstance, studies were aimed at increasing the thermal stability of cotton textile materials using a phosphorus-containing biomolecule.

3. Materials and methods

The change in weight, the rate of change in weight and the magnitude of heat effects under the influence of elevated temperatures on the cellulose-containing textile material were studied by thermogravimetric and differential thermal analysis after examining the samples on a Thermoscan-2 derivatograph. The studies were carried out with treated and untreated fabric samples in a temperature range of up to 700°C using quartz crucibles. During the study, the rate of temperature rise was 10°C. Alumina was used as a reference. The mass of the samples was 0.1 g. The samples were heated in air from 10 to 800°C at a constant heating rate of 10°C/min.

Cotton textile materials were treated with an aqueous solution of phytic acid as the main fire retardant with the addition of tricarboxylic acid, which helps to increase the solubility of phytic acid in water and to increase the carbon residue during the burning of the fabric. To eliminate residual combustion, reduce the length of the charred section, and reduce smoke generation during combustion, inorganic metal compounds are used, therefore, the effectiveness of the addition of aluminum salt was also studied in the work.

4. Results and discussion.

After processing with the finishing composition, the textile materials were dried to constant weight at a temperature of 80°C. The results of the thermal stability of the studied textile materials are compared with untreated textile materials in Table 1.

Table 1. Thermal stability of cotton fabric

Composition	T_{init} (°C)	T_{max1} (°C)	**Residue T_{max1} (%)**	T_{max2} (°C)	**Residue T_{max2} (%)**	Residue at 600°C (%)
Untreated fabric	323	363	**51**	499	**2.82**	< 1
Phytic acid + tricarboxylic acid	230	321	**56**	550	**25.2**	6.8
Phytic acid + tricarboxylic acid + aluminum salt	120	230	**64**	544	**24.5**	6

As follows from the results of heat resistance presented in Table 1, a sample of cotton fabric without treatment demonstrates three stages of decomposition, the initial of which occurs at a temperature of 323°C and two temperatures with peaks T_{max1} at 363°C and T_{max2} at 499°C.

The combined treatment of textile material with phytic and tricarboxylic acids reduces the onset of destruction of the cellulose substrate to a temperature of 230°C. The studies carried out correlate with the data published in [14, 15], which showed that cotton decomposes in air in three stages: the first stage of decomposition occurs between 300 and 400°C and includes two competitive pathways that trigger the formation of both aliphatic semi-coke and gaseous particles. The second stage occurs at temperatures from 400 to 800°C, during which the aliphatic semi-coke is partially converted into an aromatic, more stable analogue or is oxidized, forming CO and CO_2. When the temperature rises to 800°C, the charcoal formed in the previous stages continues to oxidize.

Metal ions can also effectively catalyze the formation of a stable crosslinked layer of charcoal, preventing smoke and further pyrolysis of polymers. It was shown in [16] that, in fact, gC_3N_4 and PAZn containing nitrogen, phosphorus and zinc can be an ideal combination to improve the fire resistance of the matrix.

The presence of phytic acid on the fabric, as well as phytic acid and aluminum sulfate, shift the temperature towards lower values, for example, 230, 321°C, and 120 and 230°C, respectively. These shifts, as was estimated and in works [17, 18], are obvious in the presence of phytic acid in the compositions. This behavior is observed for cotton fabrics treated with biomacromolecules, when the flame retardant coating is activated to form a stable char that can act as a thermal barrier, in contrast to the formation of flammable gaseous products that can further stimulate the decomposition of the cellulose substrate [19].

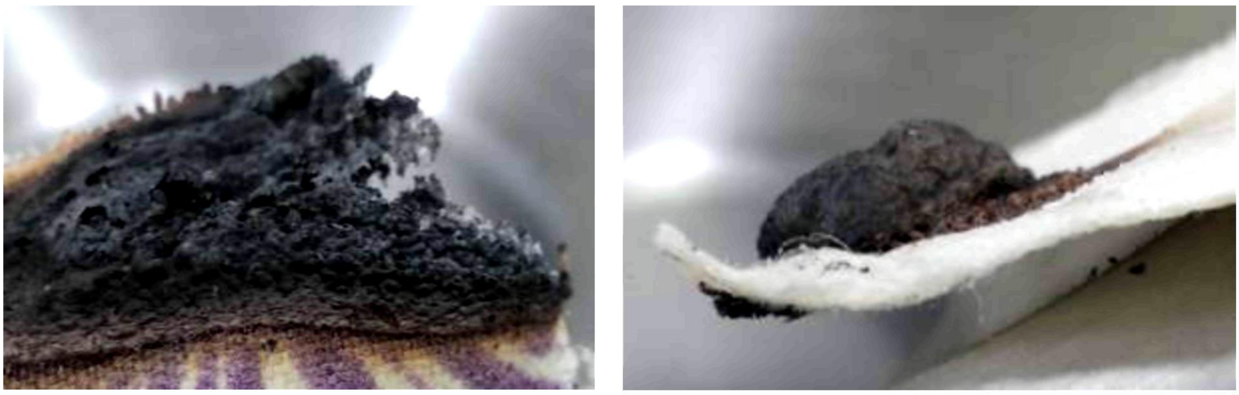
The composition containing $Al_2(SO_4)_3 \cdot 18H_2O$ as a smoke suppressor lowers the decomposition temperature to 230°C, which is explained by the loss of water when the temperature rises in the range from 230°C to 420°C, and at a temperature of 420°C a completely anhydrous form is formed aluminum sulfate. With a further increase in temperature, aluminum sulfate also decomposes above a temperature of 580°C into the γ-modification of aluminum oxide and sulfuric anhydride. The beginning of the thermal decomposition of aluminum sulfate with the release of sulfur oxide helps to limit the residual combustion of the fabric under study.

The maximum temperature at which the final degradation of cellulose occurs, on the contrary, shifts to a higher temperature range, from 499°C for untreated fabric, to 550°C and 544°C for fabrics containing phytic acid. The weight loss in this case varies from 51 to 56% of the residue, and the presence of final residue increases by 6%. The shift in temperature to a higher region confirms the increase in fire resistance of cellulosic textiles treated with compositions containing phytic acid.

For the development of fire-resistant compositions, the creation of intumescent systems has recently been widely studied. When heated, these systems form a bulk foamed carbonized layer that acts as a physical barrier that slows down heat and mass transfer between the gas and condensed phases. Intumescent systems consist of an acid source, a carbon-containing component and a blowing agent. In combination with phosphorus synergists, intumescent agents (nitrogen-containing compounds) increase the stability of coke by forming nitrogen-phosphorus bonds.

Phosphorus-nitrogen synergism is explained by the formation of phosphorus-nitrogen bonds during thermal decomposition. At elevated temperatures, polyphosphoric acid is released, melts, covering the textile fibers with a protective film, protecting it from smoldering. The decomposition of the nitrogen-containing agent is accompanied by the formation of gaseous ammonia, which hinders the access of oxygen and inhibits the oxidation of carbon in the gas phase.

The intumescent effect of the finishing composition after exposure to an open flame from the introduction of thiourea into the composition is shown on the photo in Fig. 1.



a b

Fig. 1. Formation of a carbonized coke layer on the surface of a cotton fabric (a) and a cotton/polyester blend (b)

The formation of a bulk charred area is observed on the surface of cellulose textile materials, as well as a mixture of cotton with polyester. The advantages of processing can also be attributed to the absence of splashing and droplets, which in a real fire can cause additional sources of ignition of the blended cotton-polyester fabric.

5. Conclusion

The presence of compositions containing phytic acid on the fiber surface significantly outpaces the degradation of cotton. Despite the apparent contradiction, as a result of the tests carried out, it was proved that it is the carbonization and dehydration of phytic acid that is a necessary condition for increasing the resistance of the textile material to the effects of flame, due to the activation of its decomposition before the decomposition of the main substrate.

An increase in textile residues at T_{max1} indicates the formation of a sufficiently thermally stable product as a result of the first decomposition step. At the same time, the carbonated residue formed at the first stage acts as a barrier that prevents the diffusion of decomposition products into the flame zone and oxidizer, primarily air oxygen. It further decomposes at higher temperatures, which is confirmed by the T_{max2} values, in addition, the final residues at 600°C are slightly higher than that of untreated cotton. The use of thiourea in the finishing composition allows an increase in the bulk foamed carbonated layer, which acts as a physical barrier to protect the surface of textile materials. A significant advantage of such processing is also the absence of splashing of the synthetic component of the mixed fabric, which makes it possible to reduce the threat of additional sources of ignition in the event of a fire.

References

1. Mohd Yu. A Review on Flame Retardant Textile Finishing: Current and Future Trends. *Current Smart Materials*, 2018, Vol. 3, No. 2, pp. 99-108. DOI: 10.2174/2405465803666180703110858

2. Guan, J.; Yang, C.Q.; Chen, G. Formaldehyde-free flame retardant finishing of silk using a hydroxyl-functional organophosphorus oligomer. *Polym. Degrad. Stab.*, 2009, 94(3), 450-455.

3. Duskova D., Marounek M., Brezina P. Determination of phytic acid in feeds and faeces of pigs and poultry capillary isotachophoresis. *J. Sci. Food Agric.* 2000, 81(1), 36–41. DOI:10.1002/1097-0010(20010101)81:1<36::AID-JSFA776>3.0.CO;2-A

4. Moccelini S.K., Fernandes S.C., Vieira I.C. Bean sprout peroxidase biosensor based on l-cysteine self-assembled monolayer for the determination of dopamine. *Sensors & Actuators: B. Chemical.* 2008, 133, 364–369.

5. Laufer G., Kirkland Ch., Morgan A.B., Grunlan J.C. Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton. *Biomacromolecules,* 2012, *13*, 9, 2843–2848. DOI:10.1021/bm300873b

6. Zhou Y., Ding Ch., Qian X., An X. Further improvement of flame retardancy of polyaniline-deposited paper composite through using phytic acid as dopant or co-dopant. *Carbohyd. Polym.* 2015, 115, 670–676. DOI:10.1016/j.carbpol.2014.09.025

7. Wang X., Romero M.Q., Zhang X.-Q., Wangc R., Wang D.-Y. Intumescent multilayer hybrid coating for flame retardant cotton fabrics based on layer-by-layer assembly and sol–gel process. *RSC Adv.* 2015, 5, 10647–10655. DOI:10.1039/C4RA14943B

8. Costes L., Laoutid F., Dumazert L., Lopez-Cuesta J.-M., et al. Metallic phytates as efficient bio-based phosphorous flame retardant additives for poly(lactic acid). *Polym. Degrad. Stabil.,* 2015, 119, 217–227. DOI:10.1016/j.polymdegradstab.2015.05.014

9. Cheng X.-W., Guan J., Chen G., Yang X.-H., et al. Adsorption and Flame Retardant Properties of Bio-Based Phytic Acid on Wool Fabric. *Polymers.* 2016, 8(4):122. DOI:10.3390/polym8040122

10. Yang L., Liu H., Hu N. Assembly of electroactive layer-by-layer films of myoglobin and small-molecular phytic acid. *Electrochem. Commun.* 2007, 9, 1057–1061.

11. Chen Y., Zhao Sh., Liu B., Chen M., et al. Corrosion-controlling and osteo-compatible Mg ion-integrated phytic acid (Mg-PA) coating on magnesium substrate for biodegradable implants application. *ACS Appl Mater Interfaces,* 2014, 6, 19531–19543. DOI: 10.1021/am506741d

12. Shang Sh., Yuan B., Sun Y., Chen G., et al. Facile preparation of layered melamine-phytate flame retardant via supramolecular self-assembly technology. *J. Colloid Interface Sci.,* 2019, 553, 364–371. DOI: 10.1016/j.jcis.2019.06.015

13. Peng H., Wang D., Li M., Zhang L., et al. N-P-Zn-containing 2D supermolecular networks grown on MoS2 nanosheets for mechanical and flame-retardant reinforcements of polyacrylonitrile fiber. *Chemical Engineering Journal,* 2019, 372, 873–885. DOI:10.1016/j.cej.2019.04.209

14. Malucelli G. Biomacromolecules and Bio-Sourced Products for the Design of Flame Retarded Fabrics: Current State of the Art and Future Perspectives. *Molecules*, 2019. 24(20):3774. DOI: 10.3390/molecules24203774.

15. Tiwari A., Raj B. (2015) Reactions and Mechanisms in Thermal Analysis of Advanced Materials. DOI:10.1002/9781119117711

16. Liu L., Xu Yu., Xu M., Li Z. Economical and facile synthesis of a highly efficient flame retardant for simultaneous improvement of fire retardancy, smoke suppression and moisture resistance of epoxy resins. *Composites Part B: Engineering,* 2019, 167, 422–433. DOI: 10.1016/j.compositesb.2019.03.017

17. Levitt M., Perutz M.F. Aromatic Rings Act as Hydrogen Bond Acceptors. *J. Mol. Biol.*, 1988, 201, 751-754.

18. Malucelli G., Bosco F., Alongi J., Carosio F., et al. Biomacromolecules as novel green flame retardant systems for textiles: an overview. RSC Adv., 2014, 86, 46024–46039. DOI:10.1039/C4RA06771A

19. Jagdale P., Ziegler D., Rovere M., Tulliani J.M., et al. Waste Coffee Ground Biochar: A Material for Humidity Sensors. *Sensors*, 2019, 19(4), 801. DOI:10.3390/s19040801

20. Daneluti A.L.M., Matos J.doR. Study of thermal behavior of phytic acid. *Brazilian Journal of Pharmaceutical Sciences*, 2013. Vol. 49, No. 2, 275-283.