EFFECT OF PHYTIC ACID ADDITION ON STRUCTURAL CHARACTERISTICS OF ACRYLIC POLYMER FILM

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Abstract: *The influence of phytic and citric acids additives on the structure of polymer films formed from the Neoprint PNA/S acrylic polymer was investigated in order to develop finishing compositions for fire protection of textile materials. Standardized methods were used to study the structure formation of acrylic polymer films filled and unfilled with phytic and citric acids in various ratios. The degree of interaction between the components of the polymer system has been estimated and it was found that increasing the concentration of phytic acid enhances the interaction between the filler and the matrix. It was shown, that with an increase in the concentration of phytic and citric acids in the composition of the polymer film, the degree of crosslinking and the fraction of active chains of the acrylic polymer increase. The formation of a significant carbonized residue of the polymer film containing phytic and citric acids after exposure to an open flame is shown. The absence of splashing of the burning polymer melt, in contrast to the film formed from pure polymer, was noted, which excludes the potentially destructive effect in the form of melt dripping, which causes additional hot spots. The results obtained are of practical importance for the development of composite fire retardant finishing compositions for textile materials.*

Keywords: *acrylic polymer, phytic acid, citric acid, polymer film, structure formation, coke-forming ability, fire retardant finishing compounds.*

1 INTRODUCTION

The reason for the most active research areas and the introduction of non-halogenated flame retardants into the production cycle of finishing textile materials was the environmental restrictions imposed by many states on the use of organic substances that pose a threat to the environment. One of the most effective substitutions includes phosphorus-containing materials in inorganic or polymeric form, or in the form of low-molecular-weight additives to synthetic or natural polymers [1].

The advantages of phosphorus-containing fire retardants include the fact that phosphorus can act both in the vapor phase and in the condensed phase, depending on the specific phosphorus compound and the chemical composition of the polymer, in contrast to halogens, which act only in the vapor phase [2]. In the last decade, striving to further design and use products with a lower environmental impact, scientists have shown research on products of biological origin, such as proteins, nucleic acids, pomegranate peel extracts, banana pseudostems juice, etc., as effective fire retardants for natural (for example, cellulose) or synthetic (mainly polyester) textile materials [3-8]. These substances have three main advantages. First, their chemical structure and composition are very suitable for imparting fire resistance to fabrics, since biomacromolecules and products of biological origin contain key elements (phosphorus, nitrogen, sulfur) that are responsible for the activation of fire retardant mechanisms [9]. In addition, they tend to be readily dispersed or soluble in water, which is advantageous because the use of organic solvents, which have a strong environmental impact and are highly toxic, is prohibited in many countries. Also, the processing of fabrics can be carried out using existing finishing devices, for example, industrial impregnation / pressing / drying equipment.

Phosphorus-containing substances based on bioorganic compounds of phytic acid have attracted wide interest in the processing of textiles, especially as a fire retardant. Phytic acid (PA), known as inositol-hexakisphosphate acid or phytate in the form of a salt, is regarded as a “green” molecule and is found in abundance in plant tissues such as beans, grains and oilseeds [10, 11]. As a biocompatible, environmentally friendly, non-toxic and easily obtained organic acid, phytic acid is already widely used in antioxidant, antitumor, biosensor, cation exchange, nanomaterial and other fields due to its special structure of inositol hexaphosphate [12].

Phytic acid contains 28 wt.% phosphorus in terms of molecular weight and is promising as one of the effective fire retardants. Phytic acid was used as a doping acid to significantly improve the flame retardant characteristics of composite paper deposited with polyaniline [13]. PA/chitosan and

PA/nitrogen-modified silane hybrids were used by layer-by-layer assembly to make thin fire-resistant films on cotton fabric [14]. The potential fire protection effect of various metal phytates was assessed as a biosource of phosphorus additives for polylactic acid-based composites [15].

One of the significant disadvantages of processing textile materials with bioorganic molecules, limiting their use in the production of textiles, is the instability of the finish to water treatments.

2 THE GOAL OF THE STUDY

For many applications, the wash resistance of flame retardant fabrics is an important issue that can significantly limit their practical use. The high solubility of phytic acid in water causes an almost complete loss of the flame retardant coating after rinsing, resulting in significant weight loss for all flame retardant systems. To increase the resistance to washing, compositions are being developed using organosilicon substances, deposition by the sol-gel method, layer-by-layer assembly, etc. To increase adhesion to the fiber, textile materials are treated with polymer compositions. In this regard, it is relevant to study the effect of phytic acid on the spatial characteristics of the polymer in order to use it as a matrix for obtaining fire retardant coatings on textile materials.

3 MATERIALS AND METHODS

The 30 wt.% aqueous acrylic dispersion Neoprint PNA/S (LAMBERTI IBERIA S.A.U., Spain) was studied as a polymer matrix capable of providing a set of required properties. Phytic acid (Xi'an virgin Biological Technology Co.Ltd., China) was studied as a fire retardant. A tribasic carboxylic acid – citric acid (CA) (Ukraine) – was used as a carbon source.

An initial polymer film was formed on a glass substrate, as well as films with the addition of phytic and citric acids in a ratio of 1/1 and 3/2, respectively, followed by drying of the studied compositions at a temperature of 80°C.

To study the structural characteristics of acrylic polymer films filled and unfilled with phytic and citric acids in various ratios, we used methods based on the properties of crosslinked polymer systems to swell limitedly in various solvents.

4 RESULTS AND DISCUSSION

Most often in the finishing industry, aqueous dispersions of acrylic polymers are used, which is dictated by the requirements of environmental friendliness, as well as high adhesion properties, mechanical strength and availability.

Considering that most organic polymers are highly flammable objects, it was of interest to study the effect of phytic acid additives on the fire resistance of the polymer formation.

The selected ratios of phytic and citric acids are dictated by obtaining the most possible options for providing fire retardant properties to textile substrates, as well as by solubility in water. An increase in phytic acid in the composition leads to the formation of an insoluble precipitate, which during the processing of textile materials can adhere to the shafts of finishing machines and textile materials, leading to products defect.

Phosphorus-based biomacromolecules, as fire retardants, usually use the condensed phase mechanism, contributing to the formation of stable aromatic coke [3, 4]. This is possible due to the formation of phosphoric acid species during the activation of the biomacromolecule, which promotes dehydration reactions on the underlying textile substrate, significantly limiting the formation of organic combustible gases, which can additionally fuel the combustion process. This mechanism is further enhanced when phosphorus-containing biomacromolecules are combined with a carbon source [16].

The nature of intermolecular bonds (crosslinks) largely determines the properties of the polymer network. To obtain information about the crosslinked polymer matrix, the number of crosslinks in the volume of the polymer matrix is determined and the kinetics of swelling, as well as the relationship between the degree of crosslinking and the properties of the composition, are studied. The efficiency of the studied polymer films crosslinking was evaluated by the amount of acetone-insoluble fractions of the formed polymer films during the extraction of samples in a solvent. The polymer films were extracted with acetone in a Soxhlet apparatus for 24 hours. After removing and drying the films to constant weight, the degree of their curing was calculated using the formula:

$$C = \frac{W_1}{W_0} \times 100\% \quad (1)$$

where: W_0 - initial film weight [g]; W_1 - film weight after extraction [g].

The results of determining the degree of polymer films curing are shown in Figure 1. Analysis of the acetone-insoluble fraction of polymers shows that the individual polymer film Neoprint PNA/S is slightly soluble in acetone and is capable of providing a high-quality polymer coating. In Figure 1 shows a diagram characterizing the effect of different ratios of phytic and citric acids on the resistance of polymer films to the action of an organic solvent, which depends on the degree of their curing. As a result of the study, it was found that the film with the addition of phytic and citric acids in a ratio of 1/1 is characterized by the highest degree of curing of 90.38%. The cure rate of the individual polymer film is 83.48%. The degree of curing of the polymer film with the addition of phytic and citric acids, taken in a 3/2 ratio, is 75.02%.

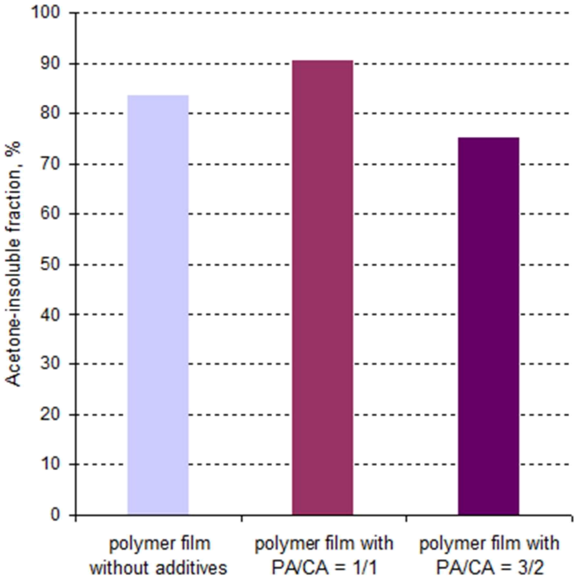

Figure 1 Degree of polymer films curing

Thus, it can be concluded that the presence of phytic acid in low concentrations contributes to an increase in the degree of polymer cure by 7.64%. However, an increase in the concentration of acids in the polymer film negatively affects the amount of the acetone-insoluble fraction, and the degree of cure decreases by 16.99%, which will contribute to the washout of the polymer during the operation of the textile product.

The efficiency of polymer-filler interaction was determined by the equilibrium swelling method and calculated using the Lorentz and Parks equation [17].

The ratio Q_f/Q_g characterizes the degree of interaction between the filler and the matrix, moreover, the higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix. The subscripts *f* and *g* refer to filled and unfilled polymer films, respectively.

Q is defined as grams of solvent per gram of polymer which is calculated by the formula:

$$Q = \frac{M_s - M_d}{M_d} \qquad (2)$$

where: M_s - the swollen weight [g]; M_d - the dried weight [g].

The results of determining the polymer-filler interaction are shown in Table 1.

Analysis of the results of the Table 1 shows that polymer films with the addition of phytic and citric acids in a ratio of 3/2 have the highest interaction between the filler and the matrix.

To calculate changes in the structural parameters of the network of acrylic polymer, individual and with additives of phytic and citric acids, the sol content was determined by sol-gel analysis. A polymer sample weighing 1 g was first extracted with acetone to remove soluble products, then with benzene in an inert atmosphere. The weights of the samples were calculated before and after extraction with benzene. The degree of gel crosslinking was determined from the equilibrium degree of the studied polymer systems swelling. The data obtained are presented in Table 2.

The data obtained (Table 2) indicate that the structural characteristics of polymer films change depending on their filling with acids. When phytic and citric acids are added in equal amounts, the density of the polymer cross-link network is reduced by 37% compared to the unfilled film. In this case, the fraction of active polymer chains decreases to 0.59, in comparison with a film without additives, the fraction of active chains of which is 0.74. With an increase in the concentration of acids in the polymer film, the degree of crosslinking slightly increases by 5.79%, and the fraction of active chains increases to 0.76.

Table 1 The extent of interaction between the filler and the matrix

Index	Polymer film without additives	Polymer film with PA/CA=1/1	Polymer film with PA/CA=3/2
Degree of polymer-filler interaction Q_f/Q_g	6.74	5.04	1.26

Table 2 Structural characteristics of the formed polymer films

Crosslinking agent	Sol fraction *S* [%]	Equilibrium degree of polymer swelling *a* [%]	Degree of polymer crosslinking *j*	Fraction of active polymer chains V_c
Without additives	3.29	16.16	4.66	0.74
PA/CA=1/1	7.36	0.17	2.90	0.59
PA/CA=3/2	2.99	3.66	4.93	0.76

Figure 2 demonstrates the dependence of the formation of the fraction of active chains of unfilled and acid-filled acrylic polymer films on the change in the degree of polymer crosslinking.

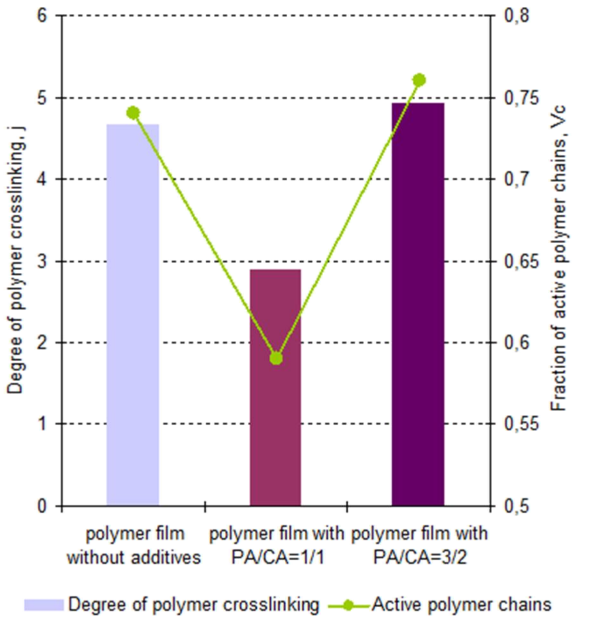

Figure 2 Influence of phytic and citric acids additives on the degree of crosslinking and the fraction of active polymer chains

Graphical dependencies in Figure 3 show that with an increase in the concentration of phytic and citric acids in the composition of the polymer film, the degree of crosslinking and the fraction of active chains of the acrylic polymer increase.

The supposed mechanism for the interaction of phytic acid with an acrylic polymer is via hydrogen bonds. To confirm this hypothesis, it is necessary to further study the nature of the chemical interaction using IR spectroscopy.

Based on the comprehensive studies carried out, it can be concluded that the use of phytic acid as a phosphorus-containing product that acts as a fire retardant, and citric acid as an additional source of carbon to increase coke formation, without deteriorating of the structural parameters of the acrylic polymer film is recommended in a ratio of 3/2, respectively.

At the next stage of work, the formed samples of unfilled and acid-filled acrylic polymer films were tested for resistance to open flame. The experimental results are shown in Figure 3.

Photo in Figure 3 demonstrates the results of exposure to flame on polymer films. The unfilled sample is characterized by fast ignition and high burning rate. In addition, the polymer film melted, burning droplets were formed, which could potentially cause the formation of new hot spots, as well as an increased risk of burns.

Figure 3 Resistance of polymer films to open flame: 1 - residue after splashing the polymer film melt without additives; 2 - carbonized residue of the polymer film with the addition of phytic and citric acids in a ratio of 1/1; 3 - carbonized residue of the polymer film with the addition of phytic and citric acids in a ratio of 3/2

5 CONCLUSIONS

Samples of polymer films with additives of phytic and citric acids showed the presence of a significant charred residue after combustion compared to unfilled film. It was also noted that there was no dripping of the polymer melt, which eliminated the potentially destructive effect that could cause additional hot spots.

Further research will be directed towards the development of composite environmentally friendly fire-protective finishing compositions for textile materials.

6 REFERENCES

1. Hörold S.: Chapter 6 – Phosphorus-based and Intumescent Flame Retardants, Polymer Green Flame Retardants, Elsevier, 2014, pp. 221-254, ISBN 9780444538086, https://doi.org/10.1016/B978-0-444-53808-6.00006-8
2. Green J.: Mechanisms for flame retardancy and smoke suppression - a review, Journal of Fire Sciences 14(6), 1996, pp. 426-442, https://doi.org/10.1177/073490419601400602
3. Basak S., Ali S.W.: Sustainable fire retardancy of textiles using bio-macromolecules, Polymer Degradation and Stability 133, 2016, pp. 47-64, https://doi.org/10.1016/j.polymdegradstab.2016.07.019
4. Basak S., Samanta K.K., Chattopadhyay S.K. et al.: Flame retardant cellulosic textile using bannana pseudostem sap, International Journal of Clothing Science and Technology 27(2), 2015, pp. 247-261, https://doi.org/10.1108/IJCST-12-2013-0135
5. Basak S., Ali S.W.: Leveraging flame retardant efficacy of pomegranate rind extract, a novel biomolecule, on ligno-cellulosic materials, Polymer Degradation and Stability 144, 2017, pp. 83-92, https://doi.org/10.1016/j.polymdegradstab.2017.07.025

6. Alongi J., Carletto R.A., Blasio A.D. et al.: DNA: a novel, green, natural flame retardant and suppressant for cotton, J. Mater. Chem. A 1, 2013, pp. 4779-4785, https://doi.org/10.1039/C3TA00107E
7. Malucelli G.: Biomacromolecules and bio-sourced products for the design of flame retarded fabrics: Current state of the art and future perspectives, Molecules 24(20), 2019, p. 3774, https://doi.org/10.3390/molecules24203774
8. Costes L., Laoutid F., Brohez S., Dubois P.: Bio-based flame retardants: When nature meets fire protection, Materials Science and Engineering: R: Reports 117, 2017, pp. 1-25, https://doi.org/10.1016/j.mser.2017.04.001
9. Malucelli G.: 9 - Textile Finishing with Biomacromolecules: A Low Environmental Impact Approach in Flame Retardancy, In The Textile Institute Book Series, The Impact and Prospects of Green Chemistry for Textile Technology, Woodhead Publishing, 2019, pp. 251-279, ISBN 9780081024911, https://doi.org/10.1016/B978-0-08-102491-1.00009-5
10. Dušková D., Marounek M., Březina P.: Determination of phytic acid in feeds and faeces of pigs and poultry by capillary isotachophoresis, Journal of the Science of Food and Agriculture 81(1), pp. 36-41, https://doi.org/10.1002/1097-0010(20010101)81:1<36::AID-JSFA776>3.0.CO;2-A
11. Katiuce M.S., Fernandes S.C., Vieira I.C.: Bean sprout peroxidase biosensor based on l-cysteine self-assembled monolayer for the determination of dopamine, Sensors and Actuators B: Chemical 133(2), 2008, pp. 364-369, https://doi.org/10.1016/j.snb.2008.02.039
12. Laufer G., Kirkland C., Morgan A.B., Grunlan J.C.: Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton, Biomacromolecules 13(9), 2012, pp. 2843-2848, https://doi.org/10.1021/bm300873b
13. Zhou Ya., 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, Carbohydrate Polymers 115, 2015, pp. 670-676, https://doi.org/10.1016/j.carbpol.2014.09.025
14. Wang X, Romero M.Q., Zhang X.-Q.: Intumescent multilayer hybrid coating for flame retardant cotton fabrics based on layer-by-layer assembly and sol–gel process, RSC Adv. 5, 2015, pp. 10647-10655, https://doi.org/10.1039/C4RA14943B
15. Costes L., Laoutid F., Dumazert L. et al.: Metallic phytates as efficient bio-based phosphorous flame retardant additives for poly(lactic acid), Polymer Degradation and Stability 119, 2015, pp. 217-227, https://doi.org/10.1016/j.polymdegradstab.2015.05.014
16. Yang W., Tawiah B., Yu Ch. et al.: Manufacturing, mechanical and flame retardant properties of poly(lactic acid) biocomposites based on calcium magnesium phytate and carbon nanotubes, Composites Part A: Applied Science and Manufacturing 110, 2018, pp. 227-236, https://doi.org/10.1016/j.compositesa.2018.04.027
17. Halim S.F., Lawandy S.N.: Effect of in-situ bonding system and surface modification of montmorillonite on the properties of butyl rubber/MMT composites, AIP Conference Proceedings 1459(1), 2012, p. 148, https://doi.org/10.1063/1.4738426