

Elena S. Bokova ¹,
*Grigory M. Kovalenko ¹,
Bogusław Woźniak ²,
Maria Pawłowa ³,
Kseniya S. Bokova ¹,
Edyta Grzesiak ²

¹ Moscow State University
of Design and Technology,
Faculty of Chemical Technology
and Industrial Ecology,
Department of Polymeric Film Materials and
Synthetic Leather
Sadovnicheskaya 33-1, 117997, Moscow,
The Russian Federation
*E-mail: gregoryi84@mail.ru

² Institute of Leather Industry
ul. Zgierska 73, 91-462 Łódź, Poland

³ Kazimierz Pulaski University of Technology
and Humanities in Radom
Radom, Poland

Interpolymer Complexes as Modifying Compounds for Reducing Cotton Blended Fabric Flammability

DOI: 10.5604/12303666.1221750

Abstract

In this study modifying compounds on the basis of interpolymer complexes (IPC) of polyacrylic acid with nonionic polymers (polyvinyl alcohol, polyethylene oxide, polyacrylamide) were obtained. The conditions for formation of polymer-polymer complexes in aqueous media were studied. The method of impregnation of cotton blended fabrics with different surface mass of compositions based on interpolymer complexes of stoichiometric and non-stoichiometric composition is presented. The possibility of adjusting the gain of IPC in tissue structure was also determined. The impact of IPC was proved to increase the oxygen index of tissues, reducing their flammability, with an almost complete reduction of the self-combustion time.

Key words: textiles, interpolymer complexes, oxygen index, fire safety, laying the grain.

The fire safety of textiles can be achieved in two ways: If textile is obtained from fire resistant textile fibres and if processed (modified) by flame retardants in the final production stages or in the finished product. In the first case fire resistance depends on the chemical structure of the polymer (such as polyaramides or their derivatives) as well as on the presence of flame retardants in the production of synthetic fibres (e.g., FR viscose). In the second case the modification comprises functional surface-treating of fibres and/or textiles.

The fire sizing effect of flame retardant fibre is stronger, whereas if textiles are processed the resistance of the modifier and its effectiveness depends primarily on the adhesion to the surface of the fibres, as well as on the structure of textile materials (porosity, specific surface area, presence of defects, etc.). The stability of the flame retardant additives to external influences is limited by specific usage of products, which typically must be subjected to localised cleaning [1].

One of the urgent tasks in the field of reducing the flammability of polymeric textiles is the search for new eco-friendly, high-performance modifiers.

Demand for such a modifier has significantly increased over the past twenty-five years. This is a consequence of increasing commercial demands for polymer (including textile materials) from the point of view of economic efficiency combined with reduced environmental

risks for environment and general toxicological properties of these materials.

The survey in [2] presents questions regarding fibre-forming polymer modification by functional nanoclays, with the aim of reducing the flammability of fibrous structures by increasing the intumescent effect. The authors attempted to replace textile flame retardants containing bromine and antimony with modifiers based on various phosphorus compounds.

It is promising to use textile products of citric acid and 1,2,3,4-butanetetracarboxylic acid (BTCA) as flame retardants, as shown in work [3]. Both modifiers were used as binders in cleaner reactions with N-hydroxymethyl-3-dimethylfosfinpropionamidom. The results were compared with the antipiriruyuschim effect of additives based on melamine-formaldehyde resins [4, 5]. The authors found that the best catalyst for use in mixtures of different carboxylic acids as a flame retardant is sodium hypophosphite monohydrate (SHP) [6, 7].

In [8] the high effectiveness of ammonium polyphosphate, brand EXFLAM APP-201, in combination with the flame retardant metazin for granting fire-retardant properties to cellulosic and synthetic textile fabrics is established.

Based on the theoretical assumptions, particular interest for reducing fire hazard has been shown in interpolymer complexes (IPC) based on polycarboxylic acids and non-ionic polymers stabilised by hydrogen bonds [9, 10].

Introduction

A generally accepted scientific approach aimed at reducing the fire hazard of polymeric materials is the introduction of modifying additives of purposeful action - retardants, smoke suppressants, adsorbing toxic substances, etc. into their structure. Typically these additives are effective in sufficiently high concentrations, thus hampering the processing of polymeric compositions and, in most cases, leading to the deterioration of other operational parameters of the finished product.

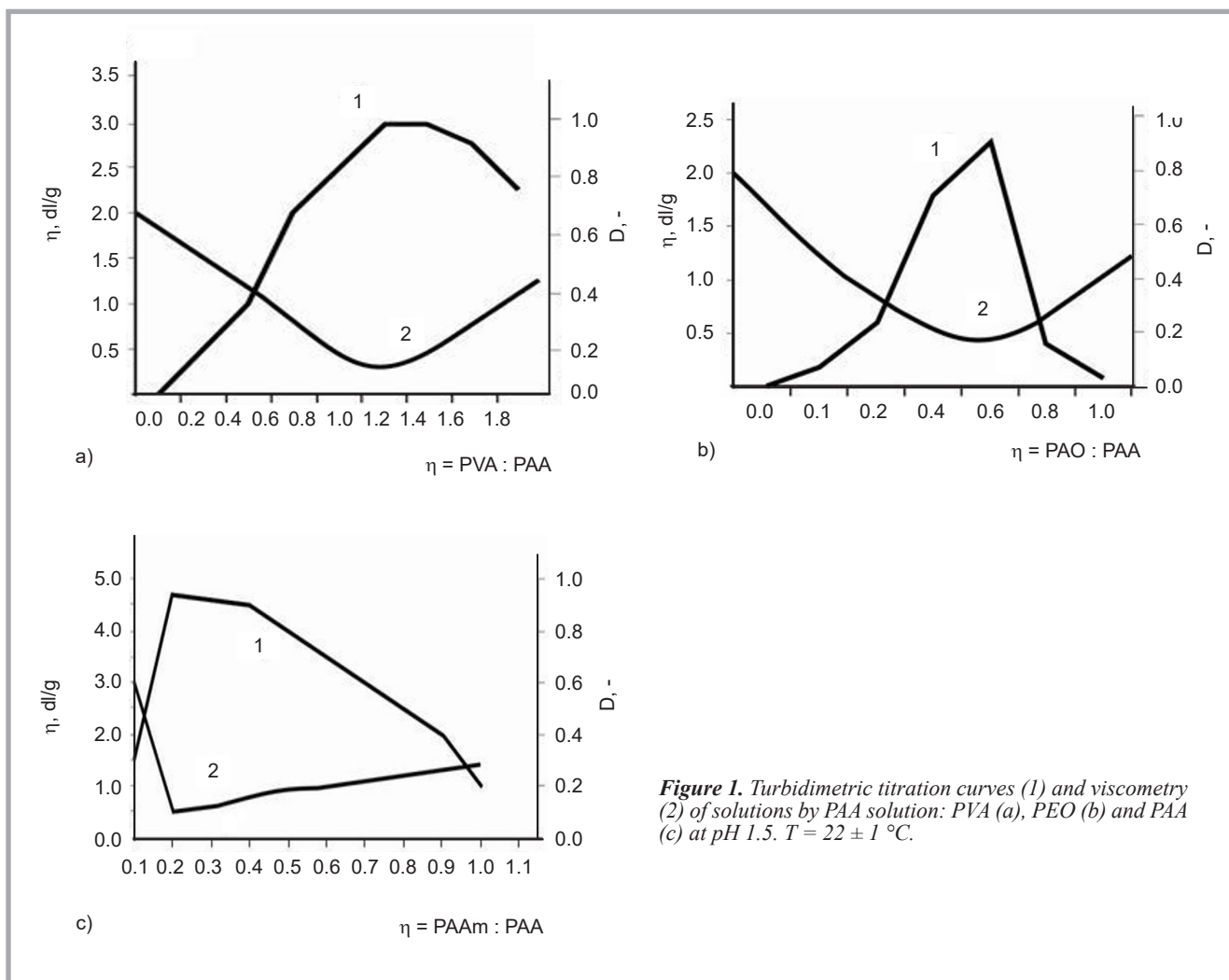


Figure 1. Turbidimetric titration curves (1) and viscometry (2) of solutions by PAA solution: PVA (a), PEO (b) and PAA (c) at pH 1.5. $T = 22 \pm 1$ °C.

The scientific goal of the work was to develop conditions for obtaining interpolymer complexes stabilised by hydrogen bonds as modifier compositions to improve the flame retardant properties of cotton blended fabrics.

Experimental

Materials

The object of study was polyacrylic acid (PAA) with a molecular weight of $2 \cdot 10^5$ (Russia), polyvinyl alcohol (PVA) with a molecular weight of $8.4 \cdot 10^4$ and content of acetate groups of 10% (Celvol, USA), polyethylene oxide (PEO) with a molecular weight of $1 \cdot 10^6$ (Sigma Aldrich, USA), and polyacrylamide (PAA) with a molecular weight of $7 \cdot 10^6$, FA 920 (SNF Floeger, France).

As objects for modification, samples of cotton blended fabrics were used:

- Canvas (sample № 1) - the number of threads per 10 cm - 214 (cotton yarn), weft 63 (312 tex yarns, linen),

and the surface mass of the fabric $315 \text{ g/m}^2 \pm 7\%$,

- Canvas (sample № 2) - the number of threads per 10 cm - 280 (cotton yarn), 83 weft (jute yarn), the surface mass of the fabric - $440 \text{ g/m}^2 \pm 7\%$. Tissue samples were produced by LLC Sharkom, (Russia).

Methods

Turbidimetric titration methods (method of analysis of turbid media) were used for analysis of complex formation techniques and viscometry. The absorbance of the reaction mixture was determined with a spectrophotometer - KFK-3-01 (TECHNOCOM, Russia) in glass cuvettes with an optical path length of 20 mm, with respect to the optical density of distilled water. The viscosity was measured on a viscometer - VNZH 0.45 EKROS (EKOHIM, Russia).

To determine the transition temperature and thermal stability of the polycomplexes under study, the method of differential

scanning calorimetry was used. The research was performed on DSC Q 100 (Intertech, USA) at 5 K/min heating rate.

IPC flammability was determined according to ISO 4589 84, 5438 BS tissues, and tissue oxygen index according to ISO 4589-2.

Interpolymer complexes were obtained by mixing aqueous solutions of polyacrylic acid and nonionic polymers with equal concentrations of 0.3 mol/l at 25 ± 0.1 °C. The conversion depth of the complexation reaction was regulated by changing the pH of 0.2 N by hydrochloric acid.

Results and discussion

Results of turbidimetric titration and viscometer

Interpolymer complexes are a special class of high-molecular compounds, formed by reacting chemically dissimilar complementary macromolecules [11].

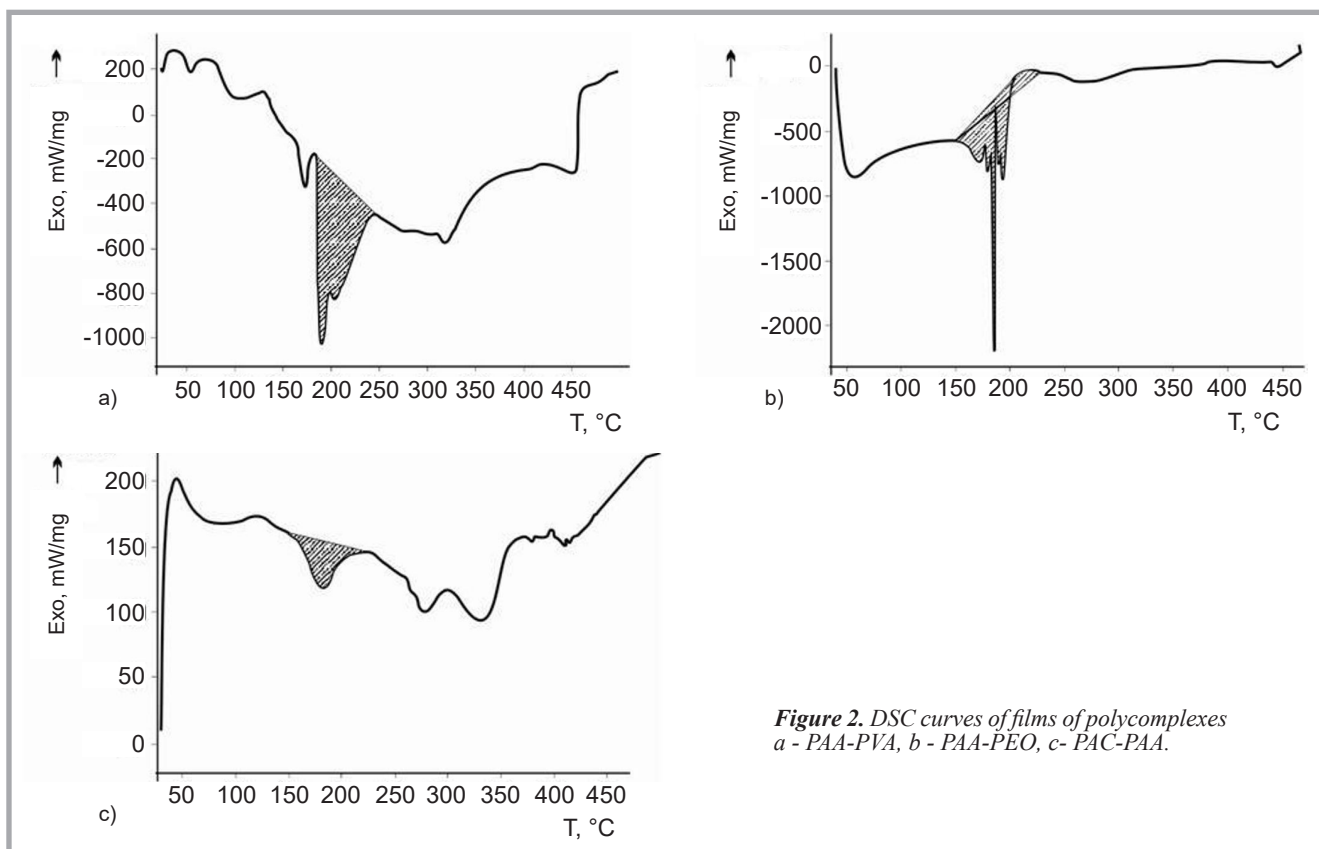


Figure 2. DSC curves of films of polycomplexes
a - PAA-PVA, b - PAA-PEO, c- PAC-PAA.

Under macromolecules, we understand complementary functional groups which are capable of specific interactions, and their geometric structure does not prevent the formation of a large number of intermolecular links based on the polymer chain [12].

From the above, it was necessary to demonstrate that mixing aqueous solutions of polyacrylic acid and non-ionic polymer compounds indeed produce interpolymer complexes, rather than a mechanical mixture of raw complexing components.

To study the processes of complexation, we used a classic approach that includes a set of methods and turbidimetric titration viscometers.

The curves of turbidimetric titration (Figure 1), in the acidic sphere (pH 1.5)

Table 1. Polymer temperature ignition.

Ser. No.	Polymer	Flash point, °C
1.	IPC PAA-PVA	390
2.	IPC PAA-PEO	370
3.	IPC PAA-PAA	393
4.	PAA	340
5.	PVA	205
6.	PEO	303
7.	PAA	Non-flammable

of reaction show characteristic peaks (Figures 1.a, 1.b, 1.c - Cr 1), the position of which coincides with the minimum in the curves of viscometry (Figures 1.a, 1.b, 1.c - Cr 2). According to the generally accepted laws of complexation, it indicates the formation of a stoichiometric (1 : 1) polycomplex PAA-PVA as well as a non-stoichiometric (1 : 0.6 and 1 : 0.2) PAA-PEO and PAA PAA-stabilized cooperative system of hydrogen bonds.

DSC method

The availability of endopicks on DSC grams (Figures 2.a - 2.c) characterised by a high melting enthalpy indicates the formation of stable macromolecular compounds stabilized with a solid system of hydrogen bonds. Differences in the value of melting enthalpy, which ranges from 30 to 57 kJ/g among polycomplexes PAA-PAA → PAA-PEO → PAA-PVA, are due to their chemical composition and structural features. In general, based on the high melting enthalpy, characteristic of all IPC received, we can make an assumption about their potential heat resistance, fire resistance and thermal stability during combustion.

Flame retardant properties

A study of thermal stability was carried out on model films prepared by the meth-

od of irrigation on plastic substrate solutions of initial complexing polymers, as well as ready-made polycomplexes. Drying was carried out at $T = 20 \pm 5$ °C.

Analysis of flame retardant properties of the polycomplexes was carried out on samples of textile fabrics. Interpolymer complexes were formed in tissue structures by placing them in a solution containing complexing polymers with subsequent acidification to a critical pH, which is required for IPC formation. The number of polycomplex tissues was adjusted by impregnated canvases passing through padding shafts with a 1 mm gap. The samples were dried at $T = 20 \pm 5$ °C.

Data on the weight gain of IPC tissue structures show a high weight increase of the binding on the fabric fibres before agglomeration of polycomplexes particles. Hence for canvas №1 the gain of IPC PAA-PVA amounted to - 4.6 g/g PEO PAF and PAA-PAA - 1.5 g/g. For canvas №2 when impregnated with any polycomplexes the gain averaged 1 g/g.

It is obvious that the ignition temperature of interpolymer complexes is higher than the initial complexing polymers (Table 1). The increase in the IPC ignition temperature as compared to PVA,

Table 2. Determination of flammability of fabrics according to ISO 4589 84. * - burning out of the sample to the edge.

Parameters recorded (Test along the basis)	Material							
	Canvas (sample No. 1)				Canvas (sample No. 2)			
	Without treatment	IPC PAA-PVA	IPC PAA-PEO	IPC PAA-PAA	Without treatment	IPC PAA-PAA	IPC PAA-PEO	IPC PAA-PVA
	1	2	3	4	5	6	7	8
Surface ignition time, s	15	15	-	15	15	15	-	15
Ignition time from the edge, s	15	15	15	15	15	15	15	15
Independent burning time, s	143	-	150	-	-	10	83	5
Burn-up edge	+	-	+	-	-	-	-	-
Inflammation of c/b wool	-	-	-	-	-	-	-	-
Length of the charred area, mm	*	77	*	73	59	80	135	37
Surface flash	-	-	-	-	-	-	-	-

PEO and PAA is caused by the presence of a strong system of hydrogen bonds between the non-ionic polymers, PAA and water as part of the polycomplexes.

Tests of fabric flammability showed that the most fire-resistant materials are 5 and 8 (Table 2).

If sample № 5 (canvas № 2) shows a short self-combustion period (5 seconds), which then stops, fabric 8 (canvas № 2 further treated with complex PAA-PVA) does not support combustion and has a small length of char bases. This is due to the modifying effect of IPC, in the processing of which the charred length is reduced from 59 to 37 mm.

The exception is sample 3 (canvas № 1, treated by IPC PAA-PEO), which burned up to the edge. Low combustion stability is apparently due to the poor impregnation tissue of the PAA-PEO complex.

Ambiguous results show that apparently IPC effectiveness as flame retardants is largely dependent on their chemical composition and structure. Since highly viscous non-stoichiometric polycomplexes PAA-PEO and PAC-PAA, despite greater hydrophilicity if compared to the PAA-PVA complex, penetrate into the tissue worse their gain is smaller and there is an increase in the char length of the section from 59 to 135 mm, and in sample 3 comes to the edge of the burn-out.

According to the results of the experiments, tissues 1 & 3 are flammable and tissues № 2, 4, 5, 6, 7 and 8 are inflammable materials. These characteristics are retained after repeated washings, indicating permanent fixation on polycomplexes tissue fibres.

For further confirmation of the properties of IPC as a flame retardant, the oxygen

index of the initial and modified samples of canvases was determined.

According to the research conducted, the original canvases #1 and #2 are classified as easily flammable materials (oxygen index 19.9 and 23.7%, respectively). Canvas № 2 modified by PAA-PAA IPC fell into the category of hard flammable materials with an oxygen index of 31.7%, and canvas № 1 also has a high oxygen index (OI 27 to 32%).

Conclusions

After carrying out systematic research of conditions for obtaining interpolymer complexes of polyacrylic acids and non-ionic polymers for use as modifiers of textile fabrics in order to reduce their flammability, it was proved that the processing of canvas #1 by polycomplexes PVA-PAA and PAA-PAA independent combustion is lacking, and that the length of the charred section of canvas № 2 is reduced from 59 to 37 mm. All fabrics treated by polycomplexes PAA-PVA and PAA are flame-retardant materials.

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Received 08.12.2015 Reviewed 26.07.2016