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COMPOSITE POLYMER COMPOUNDS FOR FLAME RETARDANT FINISHING OF COTTON FABRICS

Monograph

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The monograph is devoted to the development of environmentally friendly compositions for the processing of cotton textile materials in order to impart flame retardant properties.

The monograph scientifically substantiates the use of composite preparations for flame retardant finishing of textile materials, which include a polymer, a flame retardant, an intumescent additive and a nanofiller. Complex studies of the structural, physicomechanical, and chemical properties of polymer films with montmorillonite nanoparticles have been carried out. Based on the analysis of the synergistic effect of montmorillonite nanoparticles and ammonium polyphosphate on the flame retardant properties of textile materials, a composition has been developed for treating cotton and mixed fabrics.

The monograph is of scientific and practical interest for scientists and specialists in finishing production, lecturers, graduate students and students studying the chemical technology of fibrous materials.

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LIST OF CONDITIONAL ABBREVIATIONS

ACA – azadicarbamide;
GKM – Gurevich-Kubelka-Munk function;
DEL – double electric layer;
DSC – differential scanning calorimetry;
IR – infrared spectroscopy;
LOI – limiting oxygen index;
MEL – melamine;
MMT – montmorillonite;
POSS – polyhedral oligomeric silsesquioxane;
APP – ammonium polyphosphate;
PES – polyester;
SA – styrene-acrylic;
TGA – thermogravimetric analysis method;
CNT – carbon nanotubes;
PDSPB – poly-4,4-diaminodiphenylmethanespyrocyclic pentaerythritol bisphosphonate.

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INTRODUCTION

The problem of imparting flame retardant properties to textile materials of different nature and purpose in recent years is becoming increasingly important. This is due to the fact that they are a serious source of danger during fires, they easily ignite, contribute to the spread of the flame and emit large amounts of toxic smoke and gases during combustion that adversely affect the human body, the ozone layer of the atmosphere and the ecological situation in general.

In a number of countries, regulations and legislation have been developed prohibiting the use of products made of flammable fabrics (primarily, working clothes, decorative, upholstery and wallpaper, curtain fabrics, nonwovens).

Much attention is paid to the safety of fire protection. Thus, the efforts of researchers are aimed at developing flame retardant systems that do not contain halogens, as well as formaldehyde-containing preparations, the burning of which is accompanied by the release of toxic products and an increase in smoke formation.

These requirements are met by phosphorus and phosphoazo-containing flame retardants, the presence of phosphoramide groups of which contributes to synergy – enhancing the flame retardant effect due to the process of cellulose degradation, increasing the yield of non-volatile carbonated residue, reducing the volatile pyrolysis products and forming a surface glass layer of polyphosphoric acids, which is a physical barrier to heat transfer.

The issue of fire protection of textile materials is widely studied, but there are still a number of unsolved problems in this area: modern means are not effective enough, do not correspond to performance indicators, in particular, have low resistance to washing and destructive loads, are treated with formaldehyde-containing preparations in high concentrations (100 – 200 g/l), the total concentration of flame retardants exceeds 400 – 500 g/l.

The use of formaldehyde-containing preparations in such quantities is problematic, since the presence of formaldehyde on both fabric and the environment in sufficiently large quantities is currently not allowed by environmental regulations.

A promising method of improving the flame retardant properties is the introduction of fillers, the purpose of which is to increase the effectiveness of the flame retardant action due to the release of carbonized residue, reducing the thermophysical properties, as well as creating a mechanical barrier to flame propagation and oxygen penetration.

Of particular interest are nanoscale fillers, such as nanoclays, nanotubes, ultrafine metal powders, metal oxides, and other reinforcing composites, as well as providing additional functions – thermal and barrier.

Thus, the relevance of scientific work is determined by the need to expand the range of fire-protected textile materials and improve their consumer properties through the development of environmentally friendly compositions, the synergistic effect of the components of which provides an improvement in the quality of flame retardant finish.

1. State of the problem of obtaining textile materials of low flammability

Textile materials and products based on them are among the most flammable among combustible polymeric materials.

According to statistics, in case of fires in residential areas, more than 70% of deaths are directly related to the burning of textile materials. Every year, about 5 thousand people in Europe and more than 4 thousand people in the USA die on fires [1].

Analysis of the fires [2] that occurred in residential buildings (in 2012 in the Kherson region occurred 1952 fires) and caused the death of 73 people, shows that the source of ignition was matches, cigarettes, careless handling of fire, short circuit. At the initial stage of fire development, clothing, bedding, curtains and upholstery fabrics caught fire in 12% of cases, causing death. In this regard, the release of fabrics and fibers with reduced flammability is relevant.

In the global market of flame retardant and heat-resistant materials, there are 4 main ways to obtain low-flammability textile materials:

1. synthesis of highly heat-resistant fiber-forming organic polymers;
2. the creation of inorganic fibers obtained by modifying the "classical" types of chemical fibers of general purpose with the introduction of phosphorus, nitrogen or halogen-substituted monomers, less commonly used the method of graft copolymerization;
3. modification of the fiber at the stage of its formation with stabilizers and flame retardants of the reactive and additive type;
4. surface or bulk processing of fibers, fabrics or finished products.

The range of manufactured heat-resistant and slow-burning fibers and yarns is quite wide [3]. The slow-burning fibers are aromatic heavy-duty and ultra-high modulus fibers. They have a limiting oxygen index (LOI) in the range of 27–45% and have high thermal and thermal-oxidative resistance (decomposition temperature above 400–500°C). The disadvantage of their use is that in the conditions of "forced" burning in the air of these fibers, toxic products of their thermal decomposition and burning can be released.

Oxidized polyacrylonitrile fibers (PANOX and others) are a relatively new inexpensive type of heat-resistant fibers [4]. Fibers and nonwoven materials based on them are heat resistant in air to a temperature of 300°C. The disadvantage is the natural black color, which limits their use.

Textiles based on aramid fiber [5, 6] have high flame retardant characteristics. The advantage of the fiber "Arlan" is a higher LOI, equal to 36%, while the foreign counterpart of LOI is 28%. It is also important that this fiber has high hygienic properties (moisture absorption at 65% relative humidity of the fiber – 11–12%, while at the fiber "Nomex" – 5–6%).

Quite often, aramid fibers are used in hybrid compositions in combination with carbon fiber. The high level of carbon fiber consumption, which grows from year to year, is determined by their specific properties and cost.

The cost of aromatic heat-resistant and slow-burning fibers is higher compared to general-purpose fibers, mainly due to the high cost of the initial monomers and polymers. But their use in a number of areas is justified by operational necessity or economic advantages.

A fundamentally new type of fluorine fibers [7] has been developed based on fully fluorinated polymers with a unique set of properties for use in extreme conditions. These materials are characterized by: ultrahigh chemical resistance; incombustibility when exposed to an open flame, even in oxygen-containing environments; full bioinertness and biostability; low friction performance and high dielectric properties.

Fluorocarbon fibers are record holders among slow-burning fibers [8], which do not burn even in an atmosphere with a high oxygen content. Due to the high cost, these fibers are used only in particularly important cases.

The currently available assortment of heat-resistant fibers (Phenylone, Terlon, Tverlana, Rusar, superhigh-modulus fibers) cannot satisfy the demand for fire-resistant fibrous materials. The area of their use is limited to the technical sector, since the production of such fibers requires large capital investments and their cost is very high.

The vast majority of textile materials belong to the group of combustible materials due to their easy flammability, the potential for flame spread, and the ability to melt and produce burning droplets [9]. “Reaction to fire” is mainly determined by the chemical basis of the raw materials, regardless of whether they are of natural or synthetic origin. In this regard, the burning dynamics of raw textiles can vary greatly, as evidenced by the data Table 1.

Table 1

Flammability of fibers

Fiber	LOI, %	Melting temperature, °C	Ignition from an external source, °C	Self ignition, °C
Acrylic	18	215–260	225	515
Polypropylene	19	160-175	–	430–450
Cotton	19	–	350	400
Viscose	20	–	350	420
Polyamide	20	215–220	430	530
Polyester	21	255	390	510
Wool	25	–	325	590
Modacril	27	130–170	–	650–700

Combustible synthetic and natural textile materials have a wide range of applications: in everyday life, technology, public buildings, transport, and as special protective equipment. Textile materials are also used as curtains, draperies, curtains, materials in the manufacture of upholstered furniture, bedding, special protective clothing and products, and decorative finishing of various functional premises [10].

For the manufacture of upholstery, decorative fabrics and non-woven materials developed fire-resistant synthetic and artificial fibers. As for the textile materials used for the manufacture of workwear, they must possess not only low flammability, but also sufficient strength and high hygienic indices. These requirements are met by fabrics made from a mixture of cellulose fibers or wool yarn with synthetic fibers, in particular polyester fibers, treated with flame retardants.

Giving the flame retardant properties to cellulose materials and fabrics from a mixture of cellulose and synthetic fibers is carried out using the following methods:

– impregnation of fabrics with solutions of flame retardants;

– graft copolymerization of flame retardants with the fiber surface directly or with the use of crosslinking agents. This technology is limited by the reactivity of the fibers or the structure of the additives;

– formation of functional fire retardant coatings on the fabric surface. This method is multipurpose, in many cases quite independent of the type of fabric.

The choice of a method in each case is determined by the required degree of fire protection and by how firmly the flame retardant properties are maintained after multiple water treatments (washes), the level of physical and mechanical properties of the fibers and fabrics obtained, and the process and equipment design capabilities.

There are no universal fire retardants (components added to materials of organic origin to provide fire protection) that are suitable for reducing the flammability of any type of fabric. However, there is a search for multifunctional fire retardants, which, in addition to the main purpose, should serve as plasticizers, structure-forming agents, fillers [11].

Comparing the action of various fire retardants, they can be divided into three groups:

1) primary (phosphorus and halogen-containing compounds), which prevent the material from heating to decomposition temperatures;

2) synergists or activators (compounds containing nitrogen and antimony) inhibit the processes of destruction of the material, directing them towards structuring, coking;

3) additives that change the physical nature of the action of flame retardants (aluminum hydroxide, boron compounds, silicates, carbonates) interfere with the interaction of active radicals with the polymer or products of its destruction, reduce the concentration of combustible gases in the pre-flame zone

Much attention is paid to the environmental safety of fire protection. Currently, the efforts of researchers are focused on the development of flame retardant systems that do not contain halogens, as well as formaldehyde-containing preparations, the operation and combustion of which is accompanied by the release of toxic products and an increase in smoke generation.

Taking into account the environmental requirements, the safest flame retardants include phosphorus-containing compounds, both organic and inorganic. The effective action of phosphorus compounds as flame retardants is to ensure the following factors:

– specific effect of phosphorus compounds on the processes occurring in the condensed phase during polymer combustion: chemical transformations of polymers are carried out in the direction of increasing the yield of non-volatile carbonized residue and reducing volatile pyrolysis products;

– formation of a surface glassy or viscous molten layer of polyphosphoric acids, which serves as a physical barrier to the transfer of heat from the flame to the polymer and the diffusion of reagents;

– inhibition of gas-phase flame reactions;

– effect on the heterogeneous oxidation of the carbonized residue formed during the pyrolysis of polymers.

The adding of phosphorus-containing flame retardants into textile materials can be carried out using the methods listed above. The composition for the fire retardant finish, in addition to the primary flame retardants, may include synergists and activators, dispersants, dyes, latexes, etc.

2. Effect of nanofillers on the barrier and thermophysical properties of polymer composites

Materials [12], consisting of a polymer and a nano-dispersed mineral phase, are called “hybrid nanocomposites”, “nanohybrids”, “nanostructured composites”, due to the combination of organic and inorganic substances. As a result of adsorption phenomena, chemical and physical interaction of the surface of inorganic fillers, including inert fillers, with the film-forming substance, the film-forming agent is modified near the surface of the filler particles, which causes a significant change in the flame retardant properties in several directions:

– reduction of volatile products;

– the change in thermal conductivity of the material obtained and all its thermophysical properties;

– the change the viscosity of the material obtained.

Minerals are often used as flame retardants due to the physical nature of their flame retardant exposure at high temperatures. With a rise in temperature, endothermic decomposition of mineral fillers occurs with energy absorption, release of non-combustible molecules (water, carbon dioxide), which dilute combustible gases, and also a protective ceramic or glassy layer is formed.

The use of nanoscale additives to enhance the flame retardant properties represents a new direction in this area. There are two features that distinguish this type of materials from macroscopic composites (or microcomposites): nanoparticles in at least one dimension <100 nm and their mass fraction in the polymer matrix is from 1 to 10%. Nanoparticles (Fig. 1) are used in polymer nanocomposites and are characterized by nanoscales:

- spherical or colloidal solids (0D) – metal oxides and POSS-additives (polyhedral oligomeric silsesquioxane);
- tubes or rods (1D) – carbon nanotubes (CNT);
- layered materials (2D) – montmorillonite (MMT), layered double hydroxides, layered zirconium phosphate.

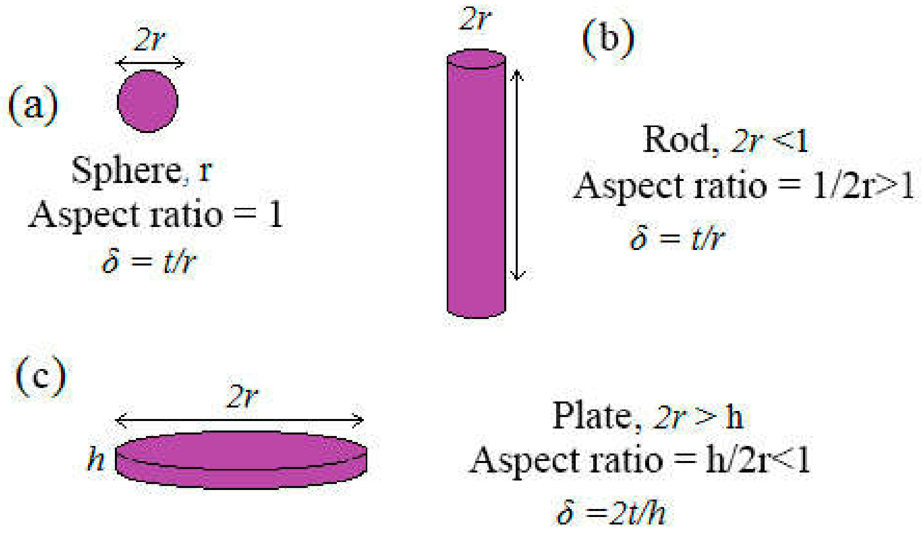


Fig. 1. Forms of nanoparticles:
a) 0D – spherical; b) 1D – rod; c) 2D – plate.

The interfacial interaction between the polymer and the particle strongly affects the degradation of nanocomposites. The strong interaction allows the particles to participate as restriction zones for the movement of the polymer chain, which makes breaking the chain more difficult at low temperatures and moves the temperature of destruction of the material to higher temperatures.

Since nanoparticles have a high surface area to volume ratio, with the same concentration of particles, they have a larger surface area than microparticles. The increase in the interfacial surface area of the section leads to a significant change in the properties of the nanocomposite, for example, a high modulus of elasticity and strength, a decrease in gas permeability, an increase in resistance to solvents, an increase in thermal stability and high transparency [13].

Polyhedral oligomeric silsesquioxane (POSS) of different chemical composition is used as polymer fillers to improve mechanical properties, thermal stability, low dielectric constant, as well as reducing the flammability of the material.

POSS is one example of a zero-dimensional nanoparticle, the general structure of which is shown in Fig. 2.

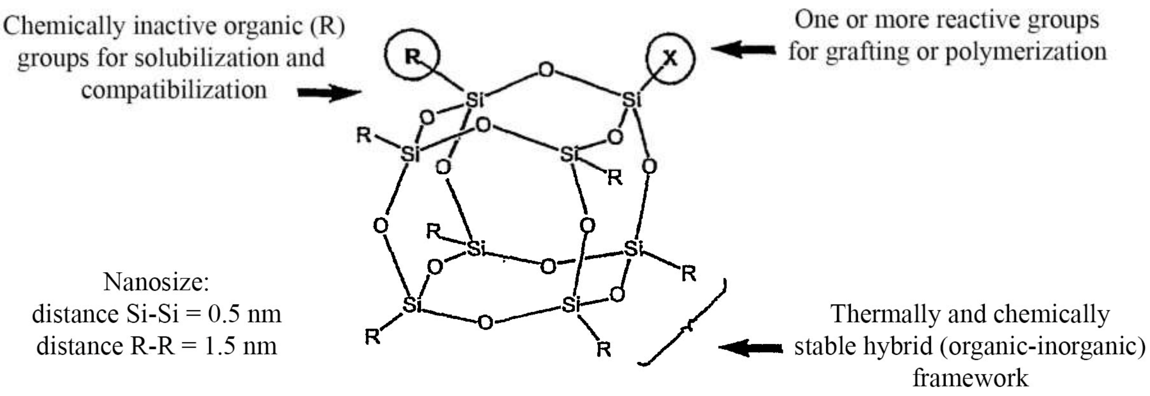


Fig. 2. The internal structure of nanostructured POSS^{TM}.

POSS refers to inorganic-organic hybrids containing a core of inorganic siloxane (Si_8O_{12}) and organic substitutes that can be modified by different groups. When POSS molecules/particles are introduced into the polymer matrix, they reinforce the polymer chain segments due to the large surface area and interaction with the polymers in the composites.

The fire retardant mechanism, similar to POSS, is characterized by nanoparticles of metal dioxides (Si, Ti, Al, Fe, Zn), which is associated with coagulation of particles near the sample surface, which form a protective barrier for the propagation of thermal degradation products. Using the method of conical calorimetry (irradiation of 30 kW/m^2) Laachachi et al. [14] found that in the presence of 20% nano-TiO_2, the heat release rate of a polymethylmethacrylate-based nanocomposite decreases by 50%, and the ignition time is significantly increased (more than 20 s). This phenomenon is explained by the heat exchange between nanoparticles of metal oxides and polymer chains due to an increase in the contact surface of the nanofiller-polymer interface.

CNTs have unique mechanical, electrical, and thermal properties that allowed them to be used to make refractory nanocomposites. Due to the high attractive forces of Van der Waals and, as a result, aggregation of nanoparticles, as a rule, CNTs require surface treatment by functionalization or grafting on the surface, which leads to improved dispersion. Accordingly, the flame retardant performance of the nanocomposite increases with an increase in the content and surface area of the nanofiller-polymer contact.

CNTs are long cylinders of covalently bonded carbon atoms that have a very high aspect ratio (>1000). There are two main types of CNTs: single-layer and multi-layer (Fig. 3).

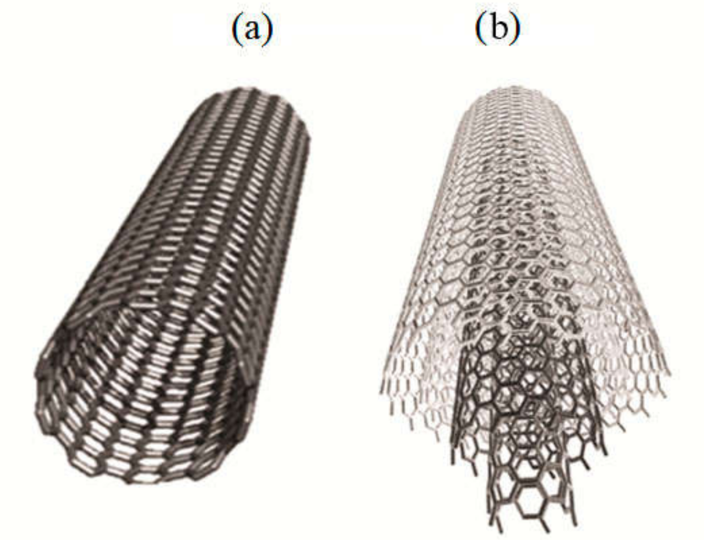


Fig. 3. Schematic illustration of CNTs:
a) single layer; b) multilayer.

The mechanism of the fire retardant action of CNT consists in the formation of a continuous charred lattice layer acting as a heat shield.

Of greater interest is the study of polymer nanocomposites based on layered silicates, which are widely distributed and well known as various rocks of clay. To create polymer nanocomposites based on clays use layered natural inorganic structures [15–18], such as montmorillonite, hectorite, vermiculite, kaolin, saponin, etc.

The most studied lamellar filler for polymer nanocomposites used to improve mechanical properties, reduce gas permeability and improve flame retardant characteristics, today is MMT.

MMT plates [19] are capable of spontaneously dispersing in water to elementary packages with a thickness of 1 nm with a distance between the packages from 3 to 14 nm. Clay belongs to the 2: 1 family of layered silicates and consists of one central layer of $Al(OH)_{6-3}$ or $Mg(OH)_{6-4}$ octahedra, sandwiched between two layers of Si_2O_5 tetrahedra, as shown in Fig. 4.

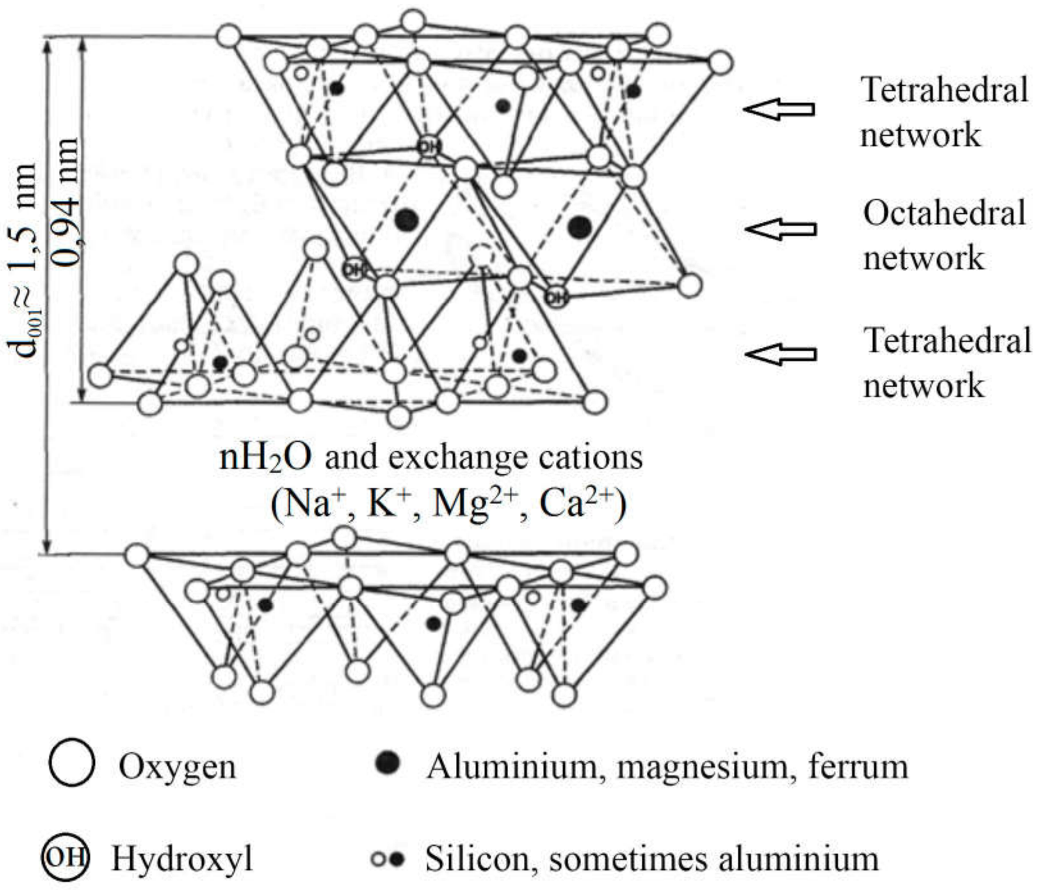


Fig. 4. The structure of the unit of montmorillonite.

The negative surface charge of MMT plates is balanced by Na$^+$ or K$^+$ cations in the gallery space between the layers, which can be replaced by various organic cations.

The most significant problem with the use of nanoparticles is the tendency to aggregation, which complicates their uniform distribution in the polymer matrix [20]. The final structure depends on the technology of the composite. The properties of polymer composites and organic/inorganic nanoparticles are determined by the nature of the blend components and the structure of the resulting composites.

Three main morphological structures of nanocomposites are distinguished (Fig. 5) [21]: separate phases of the polymer and nanoparticles (Fig. 5a); with intercalation – by introducing the polymer phase into the nanoparticle phase (Fig. 5b); with the phase separation of nanoparticles by the polymer phase (Fig. 5c).

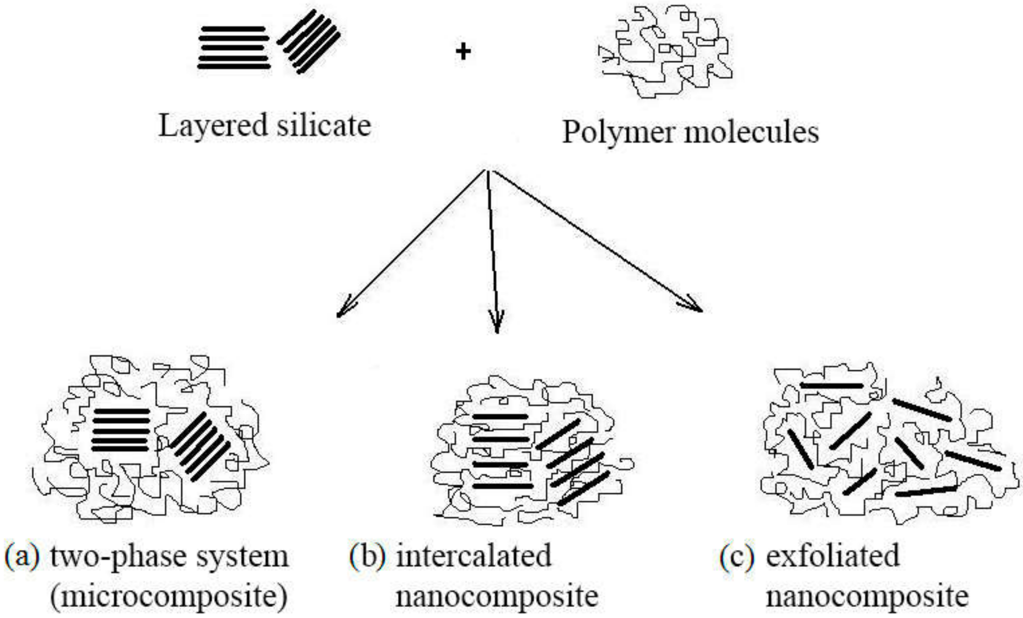


Fig. 5. Structuring scheme of MMT plates in polymers.

In the absence of polymer penetration (intercalation) between silicate plates, a common composite material is obtained. Intercalated structures are formed under the condition of separation of the silicate layers by polymer chains, which results in an ordered nanostructure.

When clay plates are completely dispersed in the polymer matrix, exfoliated nanocomposites are formed. The formation of an exfoliated structure is most preferable for enhancing many properties of nanocomposites due to its isotropic behavior.

More than ten years ago, Toyota used commercial nanocomposites for the first time in the manufacture of automobiles, having developed nylon-6 composite with nanoclay for hard and heat-resistant coating of nylon toothed belts. Later, Unitika used MMT in the manufacture of nanonylon-6 with a high heat distortion temperature for engine covers. With the introduction of 4% w/w of layered silicate deformation heat resistance (at 1.8 MPa) increased from 70°C for pure nylon-6 to 152°C. The Belgian company Kabelwerk Eupen introduces organoclays in combination with aluminum trihydrate or magnesium hydroxide in a copolymer of ethylene and vinyl acetate and obtains compounds for wires and cables. Tests using a conical calorimeter showed that the addition of 3–5% organoclay reduces the heat release of the polymer by 50–60%.

It is known that adding of nanofillers also reduces the level of mass loss of the composite and slows down the rate of polymer pyrolysis. In fig. 6 shows a diagram summarizing the various stages of degradation of a polymer filled with clay and characterizing the process of formation of a barrier [22].

It is shown that under the action of an open flame, catalytic carbonization of the nanocomposite occurs, in which MMT flakes migrate to the surface of the polymer matrix as a result of the formation of decomposition products and layered together. When exposed to fire, plates with a high ratio of length to width, are sintered and form a shielding layer that limits heat transfer, the evaporation of combustible decomposition products and the diffusion of oxygen into the material.

Also, the active acid sites of clay nanoparticles can accept electrons from single donor molecules and form free radicals, which leads to dehydrogenation, physical and chemical crosslinking of the polymer chain. Improving thermo-oxidative stabilization and the formation of a barrier to volatile substances and heat causes a decrease in the rate of mass loss and heat generation of the nanocomposite.

Another proposed flame retardant mechanism for nanocomposites includes the formation of a three-dimensional nanofiller structure, which is formed when the critical concentration of the filler is reached. Formed lattice structure limits the movement of polymer chains and as a result increases the viscosity of the melt polymer nanocomposites. In addition, the structure of the grid can reduce the access of oxygen to the composite and to combustible volatile substances. With poor dispersion, the particles form separate domains that are too far apart from each other to form an effective mesh. When exposed to fire, the polymer [23] between the domains burns very quickly, since the areas between the isolated “islands” are subjected to constant heat flow, as shown in Fig. 7.

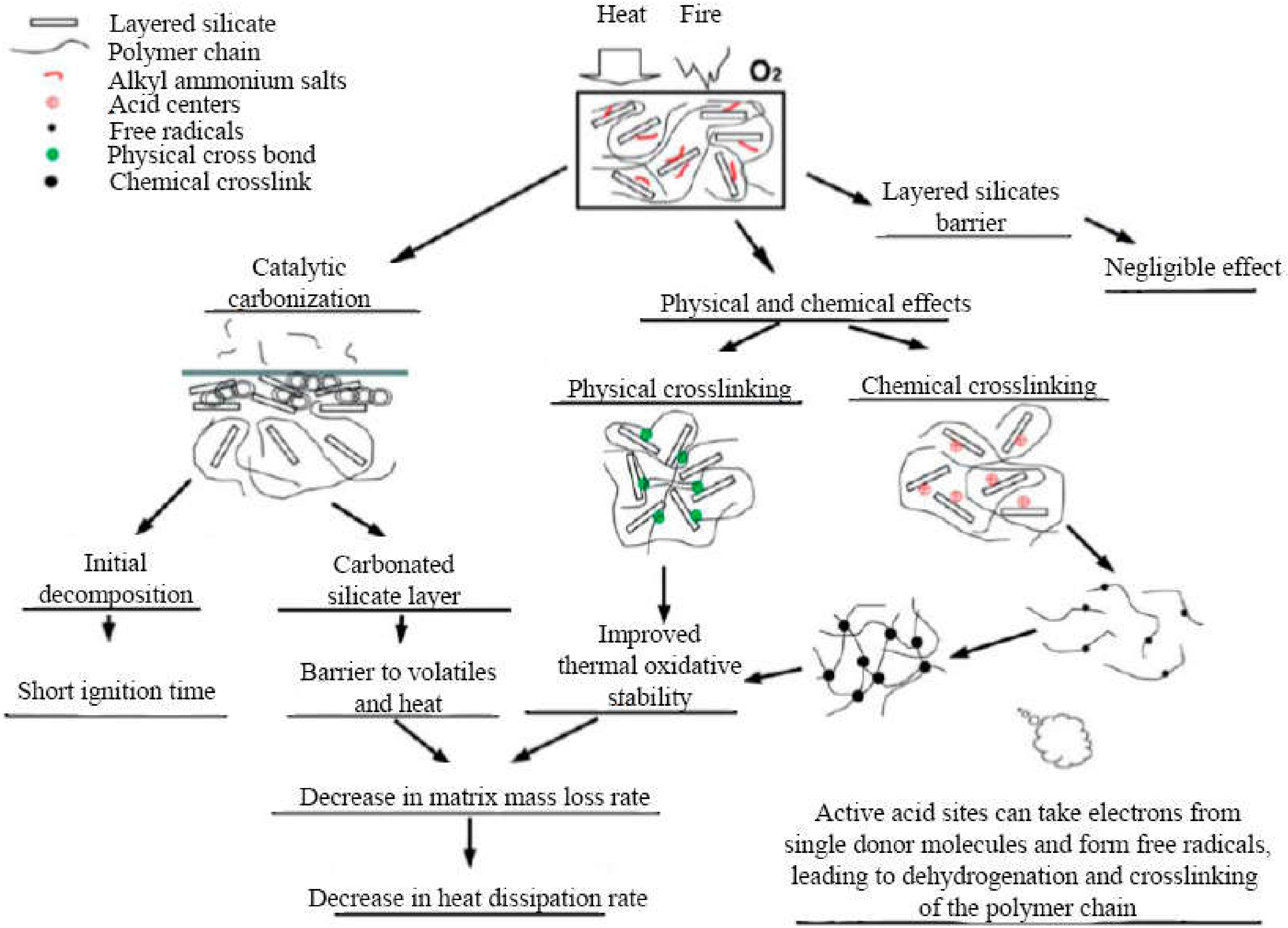


Fig. 6. Fireproof mechanism of polymer/clay nanocomposites.

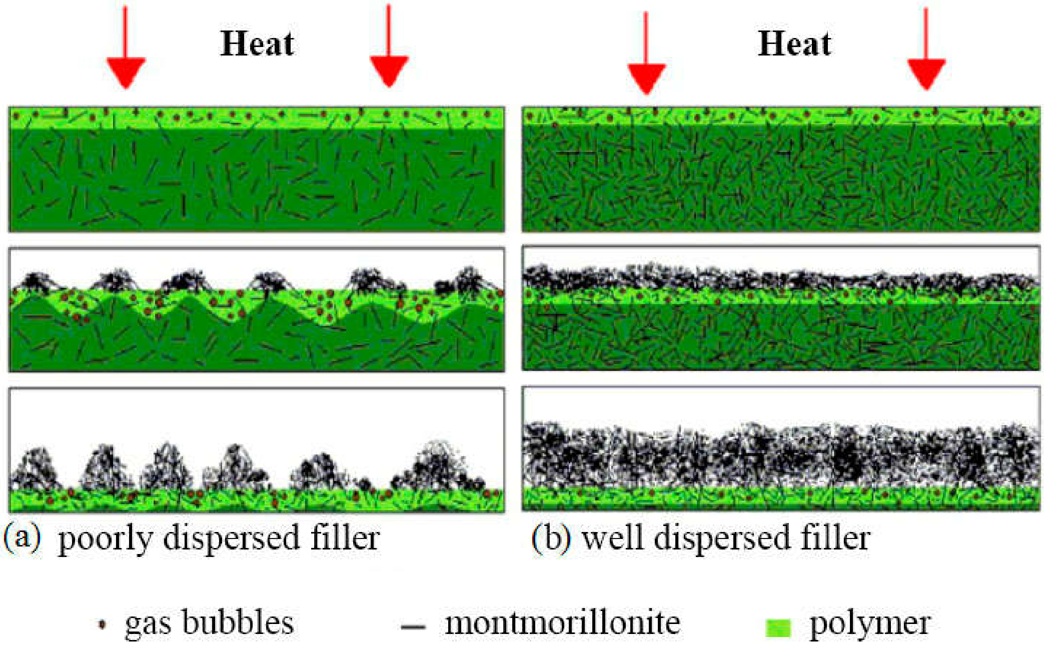


Fig. 7. Schematic representation of the composite (a) with a poorly dispersed filler and (b) a continuous filler structure.

2D and 1D nanoparticles, such as clays and carbon nanotubes, provide a denser coke-like layer than spherical 0D nanoparticles. In this case, spherical particles can also prevent thermal movement of the polymer chains. Physical cross-linking between nanoparticles allows the nanocomposite to retain its original shape during combustion.

The problem of imparting flame retardant properties to textile materials of different nature and purpose in recent years is becoming increasingly important. This is due to the fact that they are a serious source of danger during the occurrence of fires, they easily ignite, contribute to the spread of the flame and emit large amounts of smoke and gases during combustion.

In a number of countries, regulations and legislation have been developed prohibiting the use of products made of flammable fabrics (primarily, overalls, decorative, upholstery and wallpaper, curtain fabrics, nonwovens).

The issue of fire protection of textile materials is widely studied, but there are still a number of unsolved problems in this area: modern means are not effective enough, do not correspond to performance indicators, in particular, have low resistance to washing and mechanical loads, are treated with formaldehyde-containing preparations in high concentrations (100–200 g/l), the total concentration of flame retardants exceeds 400–500 g/l.

The modern textile industry, and in particular, the Global Organic Textile Standard (GOTS), Oeko-Tex Standard 100, Fair Trade, excludes the use of halogen- and formaldehyde-containing preparations, the exploitation and burning of which is accompanied by the release of toxic products and an increase in smoke formation. Taking into account environmental requirements, the safest are phosphorus-containing and phosphorus-nitrogen-containing flame retardants.

To increase the resistance of the fire retardant finish to washing and breaking load, polymers are added to the composition, the structuring of which determines the final result of the finish. Polymer binders are usually combustible, if it is not a flame retardant by its chemical nature, given this, the amount of flame retardant agent introduced into the composition is higher than is necessary when using pure flame retardant.

To increase the barrier properties to the action of the flame, at present, non-combustible fillers are introduced into the composition, which, in addition to the strengthening effect, perform barrier functions for the penetration of fire and oxygen, due to which they can act as synergistic flame retardants.

Based on the above, the work is planned to be carried out in the following areas:

– develop environmentally friendly compositions for flame retardant finishing of textile materials based on montmorillonite;

– to obtain an aggregately stable suspension of montmorillonite, which provides exfoliated structure of the composite;

– to establish the synergistic effect of montmorillonite and phosphorus-nitrogen-containing flame retardant on the structure, physical and mechanical properties and flammability indexes of textile materials;

– to investigate the processes of formation of the screening foam-coke layer, induced by decomposition of the phosphorus-nitrogen-containing flame retardant and the migration of plates of montmorillonite to the surface of the textile material.

3. Characteristics of textile materials and chemicals used in the work

3.1. Textile materials. We used cotton fabric, diagonal art. 0-166, produced by OAO Donetskiy Tekstil' and fabric of mixed fibers (78% cotton, 22% polyester), raincoat art. 3070, produced by PAO Cherkasskiy Shelkovyy Kombinat. Technical characteristics of the used textile materials are given in Table 2.

Table 2

Characteristics of textile materials

Fabric, article	Width, cm	Surface weight, g/m^2	Cloth construction
Diagonal art. 0-166	150±2.0	230±14	serge 2/2
Whipcord art. 3070	150±2.0	262±13	serge 2/2

3.2. Film-forming substances. As a film-forming substances included in the composition for fire protection of textile materials, the aqueous dispersion of polyurethane (produced by OOO Macromer, Russia, Vladimir) and water dispersions of styrene-acrylic (SA) polymers (produced by OOO Polimer-lak, Ukraine, Kherson region, Belozersky district, Kiselevka) are investigated. Basic data on film-forming polymers are given in Table 3.

Table 3

Characteristics of film-forming substances

Title	Chemical composition	Dry residue, %	pH	Particle size, µm	Viscosity at 25°C mPa·s
Aquapol 14	aliphatic polyurethane	35	7.36	≈ 0.1	20,1
Lacrytex 430	aqueous dispersion of copolymer of acrylic ester and styrene	50	7.5–8.5	≈ 0.1	5000–15000
Lacrytex 640	water dispersion of acrylic copolymer modified by additive of adhesion promoter	55–57	2.0–3.0	≈ 0.2	not less 5000

3.3. Crosslinking agents. Triglycidyl ester of trimethylolpropane and triglycidyl ester of polyoxypropylene triol (produced by OOO Macromer, Russia, Vladimir), were used as cross-linking agents (Table 4).

Table 4

Characteristics of crosslinking agents

Title	Chemical composition	Mass fraction of epoxy groups, %	Viscosity at 25°C mPa·s
Laproxide TMP	triglycidyl ester of trimethylolpropane	27.0–31.0	150–250
Laproxide 703	triglycidyl ester of polyoxypropylene triol	13.5–16.5	90–160

3.4. Nanodisperse filler. Cherkassy montmorillonite with a dimension of 50–300 nm and a plate thickness of 0.94 nm was used as a nanodisperse filler.

3.5. Flame retardants. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) – GOST 3771-74, diammonium phosphate ($(NH_4)_2HPO_4$) – GOST 3772-74, triammonium phosphate ($(NH_4)_3PO_4$) – GOST 10651-75, ammonium pyrophosphate ($(NH_4)_4P_2O_7$) – TU 6-09-1288, melamine – GOST 7579-76 were investigated as flame retardants.

4. Characteristics of the main research methods

4.1. Measurement of ξ-potential. Measurements of the ξ-potential of MMT Na^+-form suspensions were carried out by introducing a small part of the suspension into cells of Malvern Instruments Technical Note MRK 654-01 (Malvern, United Kingdom) at room temperature in the pH range from 2 to 10. Electrophoretic mobility of charged colloidal particles in the electric field is transformed in the ξ-potential at the interface using the Smoluchowski equation:

$$\xi = \frac{4\pi\eta}{\varepsilon} \times 100, \quad (1)$$

where ζ is ξ-potential, mV;

η — liquid viscosity;

ε is the dielectric constant.

4.2. X-ray analysis method. X-ray diffraction analysis was used to assess the intercalation/exfoliation of the Na^+ form of MMT in the polymer matrix. The study was carried out at room temperature using a X'Pert PRO PANalytical diffractometer (45 kV, 40 mA) in CuKα1 radiation at a wavelength λ = 1.54 Å in the range 2θ = 2–10° and in increments of 0.013°. The distance between the clay layers in the composition is calculated according to the Bragg equation:

$$n\lambda = 2d \sin\theta, \quad (2)$$

where λ is the X-ray wavelength, d is the lattice spacing, θ is the angle between the incident radiation and the scattering plane, n is the diffraction order.

4.3. Thermogravimetric Analysis Method (TGA). The change in mass, the rate of change in mass, and the magnitude of thermal effects upon exposure to polymers and composites the elevated temperatures were studied by the method of thermogravimetric analysis on TGA 7 (Perkin Elmer, USA). Samples weighing 15 mg were heated in air from 40 to 800°C with a constant heating rate of 10°C/min.

4.4. Method of differential scanning calorimetry (DSC). DSC graphics of polymers and polymer composites were recorded on DSC1 (Mettler-Toledo, Switzerland) using closed aluminum crucibles (cells) having a hole in the lid. Thermal scans of the samples weighing about 9 mg were carried out in air at a temperature of from 90 to 300°C at a heating rate of 10°C/min.

4.5. Determination of limiting oxygen index (LOI). The determination of the flammability index with limited oxygen content is aimed at measuring the relative flammability of materials when burning them in a controlled environment. LOI is defined as the minimum oxygen concentration at which a material can burn for 3 minutes or it can keep the spread of the burning sample at a distance of 50 mm. The higher LOI, the lower the probability of combustion.

The fixed sample (Fig. 8) is set on fire with an auxiliary flame, which is then quenched. With successive test cycles, the oxygen concentration is reduced until the sample can no longer sustain combustion.

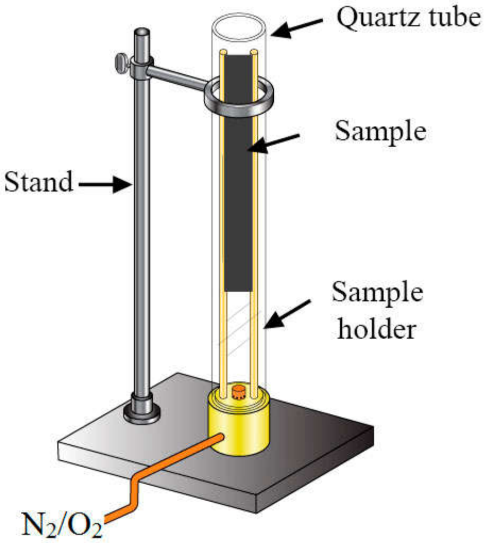


Fig. 8. Test for determining LOI.

The value of LOI is calculated by the formula:

$$LOI = \frac{V_k}{V_k + V_a} \times 100, \qquad (3)$$

where V_k is the volume flow rate of oxygen, l/min or cm^3/s;

V_a is the volume flow rate of nitrogen, l/min or cm^3/s.

For the result of the tests take the arithmetic average of at least three determinations of the limiting oxygen index.

4.6. Flame retardancy testing of polymers. A UL-94 vertical burning test (Fig. 9) was conducted to determine the flammability of a polymer sample by measuring the self-extinguishing time in a vertical position in accordance with ASTM D-3801.

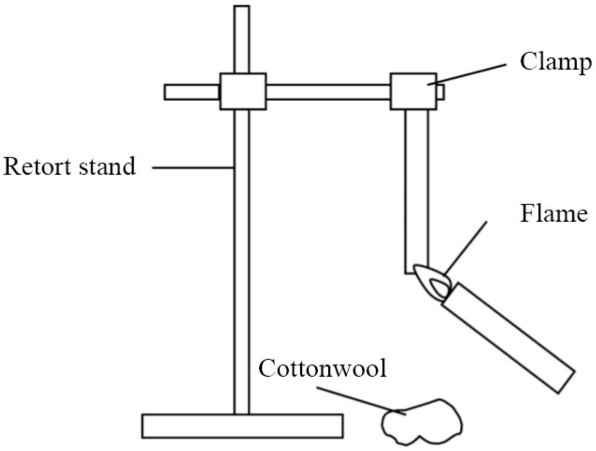


Fig. 9. Vertical UL-94 burning test.

Surgical cotton is placed 300 mm below the specimen to detect flammable droplets that will ignite the cotton. The flame of a Bunsen burner is applied to the sample twice (10 seconds each). For testing used a series of samples with a size of 125 mm×13 mm×2 mm.

After each experiment, the ignition time is recorded and after another 10 seconds the flame is re-supplied to the sample, which is then removed from the flame. The self-extinguishing time of the polymer sample and the formation of droplets are estimated as follows:

– V-0 – self-extinguishing for 10 s on a vertically mounted sample, the formation of droplets from non-burning particles is allowed;

– V-1 – self-extinguishing for 30 s on a vertically mounted sample, the formation of droplets from non-burning particles is allowed;

– V-2 – self-extinguishing for 30 s on a vertically installed sample, the formation of droplets from non-burning particles is allowed.

4.7. Test method of textile materials for flame retardancy. To determine the flame retardant properties of cotton and mixed materials (GOST 19297-2003) a test strip of 5×10 cm is cut out, which is kept in a flame of a gas or alcohol burner for 15 seconds. The height of the flame should be 4–5 cm and test strip is introduced into the flame at a distance of 0.5 cm from its top. Material is considered flame retardant if does not burn or not smolder after removal from the flame.

The height of the charred area of the fabric is defined as the distance from the edge exposed to the flame to the extreme visible point of damage to the sample.

4.8. Infrared spectroscopy. Infrared (IR) spectra of polymer films and coated textile materials were obtained on a Nicolet-iS10 FTIR spectrometer (Thermo Fisher Scientific, USA) using a DTGS detector, a KBr beam splitter and a Smart Performer attachment equipped with a ZnSe crystal. The measurement was carried out at a resolution of 4 cm^{-1}; spectrum area 4000–650 cm^{-1}. Spectra were processed using the OMNIC-7.0 software.

4.9. Preparation and analysis of the physicomechanical properties of polymer films. Polymer films were obtained in accordance with GOST 14243-78 (methods for producing free films). The conditional strength of the samples and the relative elongation at break of the films were determined according to GOST 2580-87 on a tearing machine RT-250M, at a speed of 300 mm/min. The strength of the films (MPa) at break was estimated by the formula:

$$\sigma_y = \frac{F_y}{A_0}, \tag{4}$$

where F_y is the maximum load in the tensile test, N;

A_0 is the initial cross section of the sample, mm^2.

Relative elongation at break was determined by the formula:

$$\varepsilon = \frac{l_p}{l_0} \times 100, \tag{5}$$

where ε is the relative elongation at break,%;

l_p – absolute breaking elongation, mm;

l_0 – initial length, mm.

4.10. Spatial network definition. The density of the chains of the network was investigated according to the equilibrium swelling of the polymer in isopropanol [24]. Rectangular samples with dimensions of 20×10×2 mm and a mass of about 0.3 g were cut out from the central part of the polymer film and immersed in isopropanol for 24 hours. The outer surface of the swollen sample was dried, the sample was weighed, and then placed in an oven for 24 hours at 60°C to remove the solvent. The dried sample was weighed. The molecular mass of the chains of the grid was determined by the Flory-Renera equation:

$$\frac{1}{M_c} = \frac{V_r + \chi V_r^2 + \ln(1 - V_r)}{\rho_k V_0 \left(V_r^{1/3} - 0{,}5V_r\right)}, \tag{6}$$

where V_0 is the partial molar volume of the solvent ($V_0 = m/\rho = 60/0.785 = 76.4$ cm^3/mol (for isopropanol));

V_r is the volume fraction of polymer in the swollen sample;

χ is the polymer-solvent interaction constant (Huggins constant);

ρ_k – polymer density, g/cm^3.

Crosslinking density (v), mol/cm^3:

$$\nu = \frac{1}{2M_c}. \tag{7}$$

The efficiency of the interaction of the polymer-filler was determined by the method of equilibrium swelling and was calculated by the Lorentz and Parks equation [25]. The ratio Qf/Qg characterizes the degree of interaction between the filler and the matrix, and, the higher the value, the lower the interaction between the filler and the matrix. Q is determined in grams of solvent per gram of polymer and is calculated by the formula:

$$Q = \frac{M_s - M_d}{M_d}, \tag{8}$$

where M_s is the mass of the swollen sample, g;

M_d is the mass of the dry sample, g.

4.11. Study of the rheological characteristics of polymer compositions. The rheological properties of polymer compositions were studied on a Rheotest-2 rotational viscometer designed to measure the rheological properties of “non-Newtonian liquids” in a system of coaxial cylinders at 20°C in the speed range 3–1312 s^{-1}.

4.12. Determination of the turbidity of the polymer system. The determination of the turbidity of the system was carried out as follows: to find the turbidity windows, the optical density (D) of the free film was measured in the wavelength range (λ) using a photoelectric concentration colorimeter KFK-2MP. The turbidity windows correspond to straight-line parts of the spectrum and are described by a power dependence of the form:

$$D = B\lambda^{-n}. \quad (9)$$

The turbidity of the system (τ) is also expressed by a power function λ and does not correspond to the formula given for D, since τ is proportional to D:

$$\tau = 2{,}3 \cdot D/l, \quad (10)$$

where l is the film thickness.

Turbidity is calculated at a wavelength $\lambda = 540$ nm.

4.13. Determination of color intensity. The color intensity was estimated by the reflection coefficient R, % of the colored samples and by the magnitude of the Gurevich-Kubelka-Munk function (GKM) values.

The determination of the reflection coefficients R of fabrics was performed on a Spekol-11 spectrophotometer with an appropriate attachment. First, a reflection spectrum of a textile material dyed with a specific dye is obtained, then the wavelength at which a pronounced minimum of the reflection coefficient is observed is selected, and at that wavelength, the reflection coefficient for this dye is then determined.

The reflection coefficient is not linearly related to the concentration of the dye on the textile material, therefore, the color intensity is better characterized by the function of GKM, which was determined by the formula:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R^o)^2}{2R^o}. \quad (11)$$

where K/S is the function of the GKM;

R and R^o are the spectral reflection coefficients of the dyed and non-dyed textile materials, respectively.

In accordance with the goal of the work, the methods of conducting theoretical and experimental studies are defined, which allow you to: select textiles, chemicals, equipment and instruments for the implementation of practical testing of the theoretical concepts outlined in the work; justify the use of the basic theoretical principles of the fundamental sciences in relation to the accepted object of study; to ensure the specified reliability of the research results for the formulation of evidence-based conclusions and recommendations.

5. Investigation of the effect of montmorillonite on the properties of composite materials

Textiles and textile products are widely used in various fields, starting with the furniture industry, food packaging, protective and automotive textiles, and ending with aerospace and medical textiles. In order to increase the efficiency of functional fabrics, nanotechnology is considered a futuristic approach that can replace conventional chemical, physical or physico-chemical modifications [26].

The textile industry is a small part of global research in new areas of nanotechnology, but fiber and textile manufacturers were the first to successfully introduce the latest advances for consumer use. In the textile field, research focuses mainly on the use of nano-sized substances and the creation of nanostructures in the production and finishing process in order to impart anti-bacterial, water-repellent, dirt-repellent, antistatic, fireproof properties and improve dyeability of textile materials.

The nanotechnological approach starts with the production of nanofibers or nanocomposite fibers before the formation of nanostructures and nanoelectronics embedded in clothing to produce a wide range of “smart” textiles and textiles with elements of artificial intelligence [27]. This work mainly focuses on the applicability of nanotechnology in the surface treatment of textiles, covering nano-finishing, nano-coating and nanocomposite coatings, as well as in the development of materials with flame retardant properties that may find application in various fields.

5.1. Preparation of montmorillonite Na^+-form and investigation of the tendency of nanoparticles to aggregate. As one of the methods for enhancing the flame retardant properties of textile materials, the introduction of fillers can be considered, which increase the yield of carbonizing residue and reduce the thermophysical properties, as well as create a mechanical barrier during flame propagation.

Of particular interest is the use of nanoscale fillers. Laminated plate materials, tubular and spherical solids are used. Among water-dispersible commercially available nanofillers, lamellar natural and synthetic layered silicates should be noted [28]. Unlike fillers with a tubular or spherical shape, when exposed to fire, plates with a high ratio of length to width are sintered and form a shielding layer that limits heat transfer, evaporation of combustible decomposition products and diffusion of oxygen into the material.

The most significant problem with the use of nanoparticles is their ability to aggregate as a result of a developed area and high uncompensated energy. Plates of layered silicates (Fig. 10) have negatively charged surfaces and positively charged edges [29]. This complicates their uniform distribution in the polymer matrix. Thus, a double electric layer (DEL) is formed around the particle.

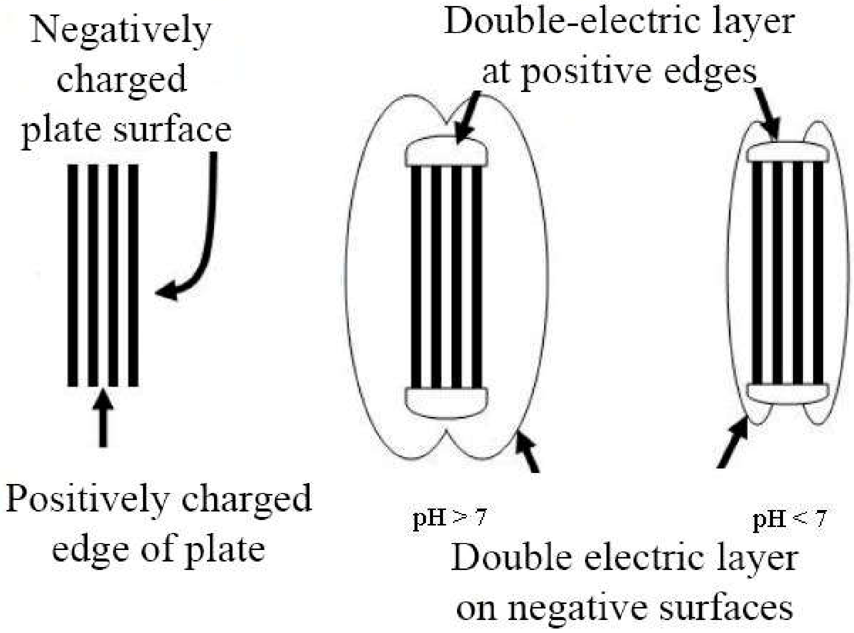


Fig. 10. Schematic representation of the DEL around the clay particle.

In an alkaline solution of DEL, the negatively charged surfaces of the plates can mask the positively charged edges, which causes the particles to repel. However, in an acidic environment, the DEL decreases and the positively charged edges become more active. Electrostatic repulsion decreases, resulting in aggregation of clay particles.

The divalent cations of calcium and magnesium allow the plates to come closer to each other than monovalent cations, which leads to coagulation into domains and, ultimately, the formation of aggregates. Since Na^+ ions have lower electric charges than Ca^{2+} ions, they are adsorbed less consistently to the surface of clay particles. When the clay particles are wetted, the radius of the hydrated Na^+ ion causes the clay plates to repel each other (swell) and the attractive forces between them weaken. This process destroys the structural units, leading to deflocculation and dispersion of particles. Therefore, natural MMT, as a rule, is pre-modified [30] to reduce the surface energy of clay layers, i.e. interlayer cations (for example, Ca^{2+}, Mg^{2+}, K^+) found in natural MMT are mainly replaced by sodium ions, which improve its ability to swell in polar solvents. Using water as a solvent instead of an organic solvent eliminates environmental problems.

In order to obtain the Na^+ form, MMT clay was previously treated with an aqueous solution of NaCl to replace the Ca^{2+}, Mg^{2+} and other exchange cations in the MMT interlayer galleries with Na^+ cations [31].

The process was carried out as follows: 100 g of clay was suspended in 4 dm^3 of 1M NaCl solution with constant stirring at 70°C for 24 hours, and then the solid was separated by filtration and washed several times with distilled water (centrifuged) until Cl^- ions have not been completely removed. The presence of chlorine anions was controlled by adding a solution of $AgNO_3$ (0.1 M). The resulting material, designated hereinafter as Na^+-MMT, was dried at 60°C.

Measurement of the ξ-potential, which characterizes the electrokinetic properties of suspended colloids and aggregates [32–34], was carried out for suspended Na^+ –MMT particles with a concentration of 0.02% in water at a pH in the range from 2 to 10. Colloids with high ξ-potential (more than ± 30 mV) are electrically stabilized systems, while colloids with low ξ-potential tend to coagulate or flocculate. Diagram on Fig. 11 is describing the effect of the pH of the solution on the ξ-potential of Na^+-MMT nanoparticles.

Data on Fig. 11 indicate that Na^+-MMT nanoparticles have a high negative ξ-potential (from ~ -34 to -53 mV) in the pH range from 2 to 10, with the result that the clay is well dispersed and resistant to aggregation [35].

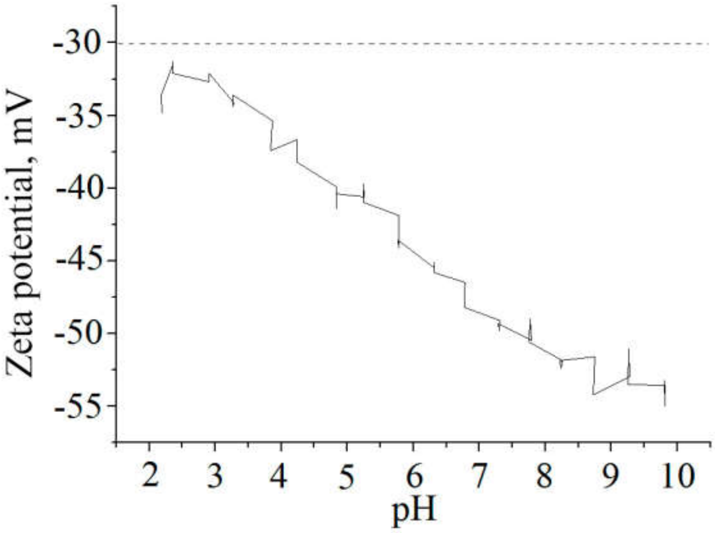


Fig. 11. Dependence of the ξ-potential of Na^+-MMT nanoparticles on the pH of the medium.

The decrease in the absolute value of the ξ-potential with decreasing pH is probably due to a shift in the equilibrium between the hydrogen in solution and the hydroxyl groups of the edges of the particles according to the schemes: $SO^- + H^+ \leftrightarrow SOH$; $SOH + H^+ \leftrightarrow SOH_2^+$, where S denotes any surface center.

The offset increases the variable positive charge of the edges of the particles, as the concentration of protons in the volume of the solution increases. Delgado et al. [35] also noted that the positive charge that occurred at the edges of the particles is less in absolute value than the constant negative charge on the surface. Therefore, the resulting particle charge remains negative.

Thus, we can conclude that Na^+-MMT nanoparticles have a ξ-potential below -30 mV over the entire pH range, as a result of which they are well dispersed and resistant to aggregation.

5.2. Obtaining and using nanocomposite materials. Nanocomposites belong to the class of composites containing dispersed particles in the nanometer range in at least one dimension. In the adjacent field, thermoplastic polymer nanocomposites have attracted considerable interest since they often show significant improvement in properties compared to individual polymers or conventional microcomposites.

It has long been noted that the technology of preparation of nanocomposites has a significant effect on the dispersion of nanoparticles [36]. The preparation of polymer matrix nanocomposites can be classified as follows: *in situ* polymerization, solution mixing method, melt compounding (mixing) method, and latex method [37].

All methods except latex use organically modified clay, in which long-chain alkyl ammonium ions are inserted into the structure of a layered silicate. With this dissolution method, clay is mixed with a polymer solution, after which the organic solvent is evaporated to obtain the final product. Nevertheless, the intercalation of polymer chains in the form of an organic solution into silicate layers is a difficult task, and the process of solvent removal is rather difficult. Thus, this method is not promising for industrial applications.

A promising way to obtain nanocomposite materials is latex polymerization and mixing. In an aqueous polymer dispersion, solid polymer particles of submicron sizes are suspended in water. In combination with a nanoscale filler, polymer particles can create a specific segregated network. The corresponding material after drying and "hot pressing" can exhibit excellent properties at a very low concentration of filler compared to the melt mixing method containing the same polymer and filler. The advantage of this compounding process with dispersion of the polymer is that expensive chemical modification of the fillers can be avoided, since the filler itself swells or disperses in water.

Dispersed clay particles in water have a higher gallery space and, with an increase in the water content in the dispersion, clay exfoliates/stratifies into separate plates, which leads to the formation of nanoscale dispersions [38–40]. A hydrated layer of polymer particles can attract clay plates and probably interact with them. At this time, the stratified layers of silicate are re-aggregated into several layers of silicates of nanometer thickness, and the polymer is located between several layers of silicates in the process of co-coagulation.

This is a huge advantage of the latex method, because the polymer molecule with a high molecular weight does not need to penetrate into the galleries of silicates. Most of the plates remain separated, and those that are in close proximity to each other can aggregate, in particular, at a high concentration of MMT. In some cases, polymer chains prevent the re-aggregation of nanoplates, which leads to the formation of nanocomposites, which are a mixture of exfoliated, intercalated and aggregated MMT in a dried film.

Fig. 12 is a diagram of the formation of a nanocomposite polymer dispersion/clay.

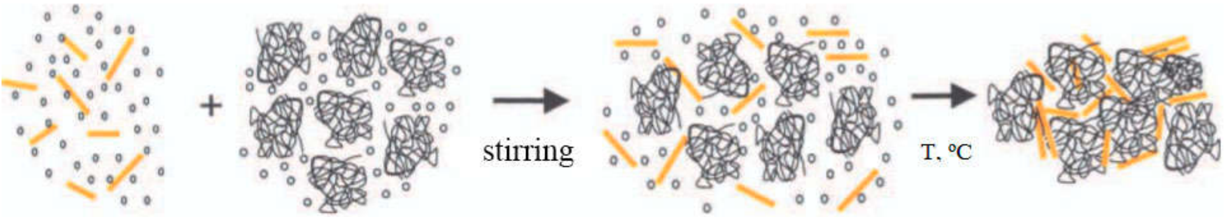


Fig. 12. The scheme for producing nanocomposites based on clay and polymer dispersion.

Analyzing the foregoing, it was concluded that the preparation of the studied nanocomposites from an aqueous suspension of Na$^+$-MMT and an aqueous polymer dispersion should be carried out as follows. Na$^+$-MMT was dispersed in water with vigorous stirring for 24 hours. An aqueous polymer dispersion was added and mixed using a magnetic stirrer at 600 rpm. to obtain a homogeneous aqueous dispersion. Then the water was slowly removed to avoid the formation of bubbles in the solid mixture.

5.3. Effect of Na$^+$-MMT nanoparticles on the rheological properties of polymer dispersions. The rheological properties of polymer nanocomposites have been studied by several researchers [41], since this indicator is important for the processing of polymers and obtaining finished products. The study of dynamic vibrations and rheology at a constant shear stress of polymer nanocomposites showed an increase in viscosity compared with the original polymer, which is explained by the formation of clay intercalated or exfoliated network structures.

The rheological properties of the styrene-acrylic dispersions Lacrytex 430, Lacrytex 640, modified by Laproxide 703, and polyurethane dispersion Aquapol 14, modified by Laproxide TMP, at a dry matter content of 35%, were analyzed with respect to the shear rate and the amount of Na$^+$-MMT filler (Fig. 13–15).

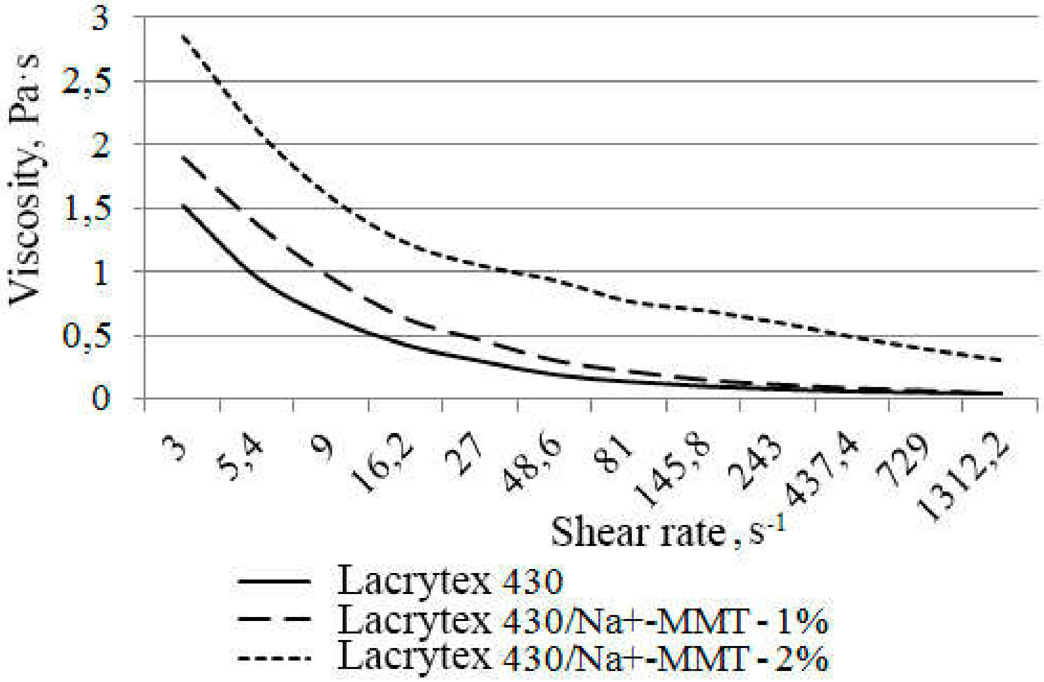


Fig. 13. The dependence of viscosity on shear rate of nanocomposites based on Lacrytex 430.

In all systems, the viscosity of polymer dispersions reinforced with layered silicate decreases with increasing shear rate, reflecting a pseudoplastic nature, i.e., shear thinning.

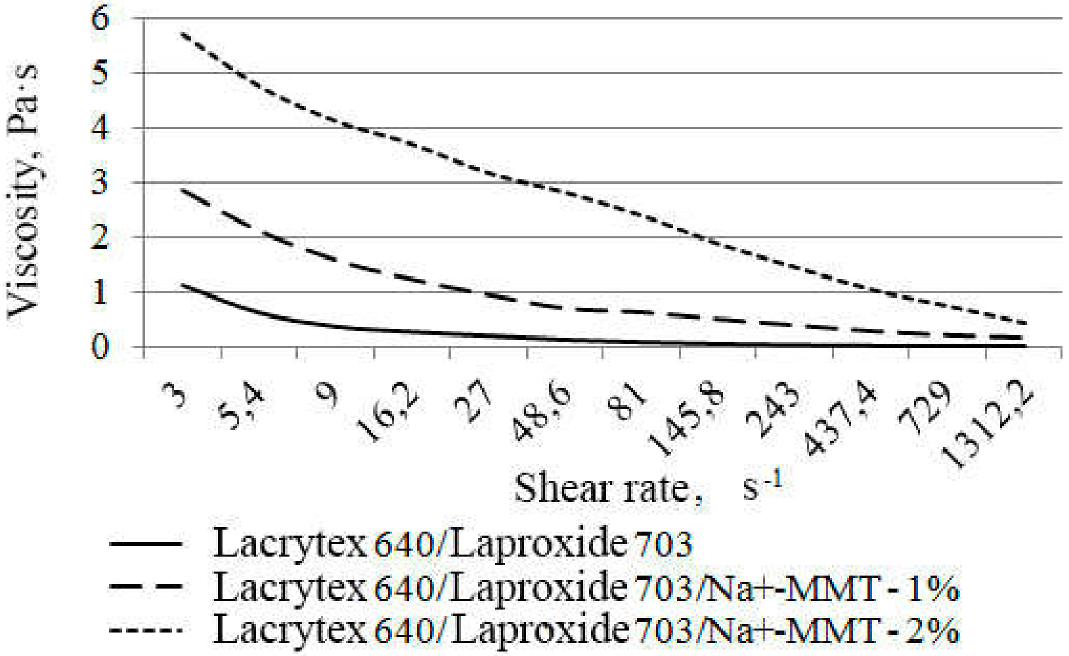


Fig. 14. The dependence of viscosity on shear rate of nanocomposites based on Lacrytex 640 / Laproxide 703.

The rheological behavior of the compositions depends on the degree of compatibility between the polymer matrix and clay. In addition, the interlayer distance of clay plays an important role in the distribution of layered silicates in the polymer dispersion, and hence the viscosity.

As expected, the viscosity of all nanocomposites increases with the addition of layered silicate. The rheological properties of polymer dispersions depend on the impregnation of the binder or the mechanism of immobilization. This means that polymers dispersed in an aqueous medium are immobilized inside layers of layered silicates.

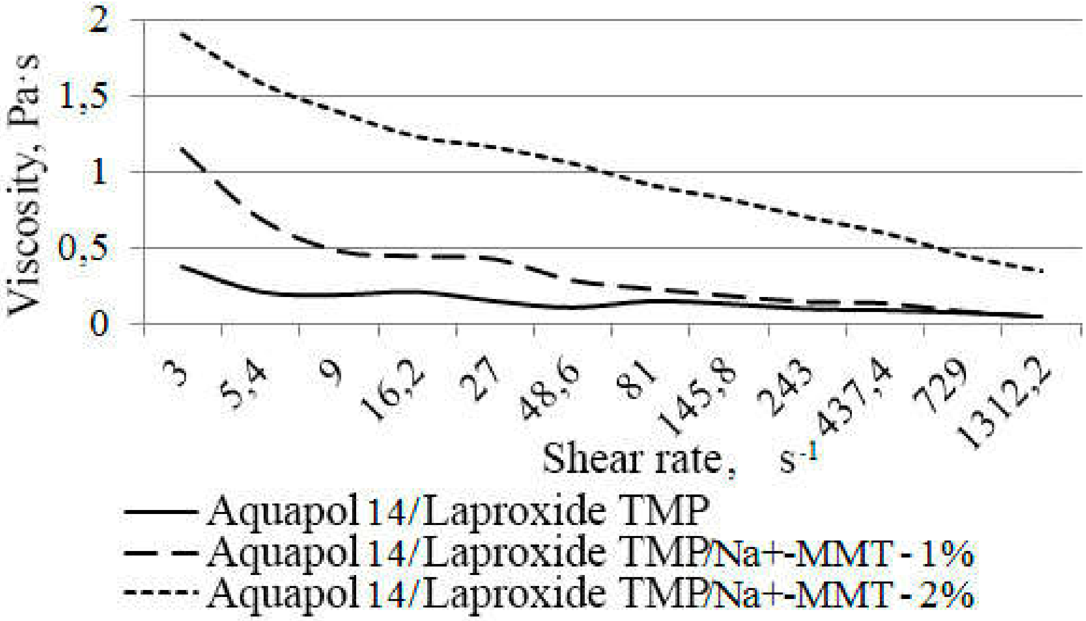


Fig. 15. The dependence of viscosity on shear rate of nanocomposites based on Aquapol 14 / Laproxide TMP.

Layered silicates are known to have the ability to separate layers and intercalate polymers between layers. According to the research of Lazzeri et al., polymer molecules that are immobilized on the surface of the filler are considered as part of the dispersed phase with the effect of increasing the volume fraction of the filler. Since with an increase in the shear rate, a structural equilibrium is observed between the immobilized and the mobilized part, the effective volume fraction is a function of the shear rate. This causes a decrease in shear viscosity of polymer dispersions reinforced with layered silicates.

The change in the networks of nanocomposites based on polymer dispersion and layered filler as a function of shear rate [42] is shown schematically in Fig. 16.

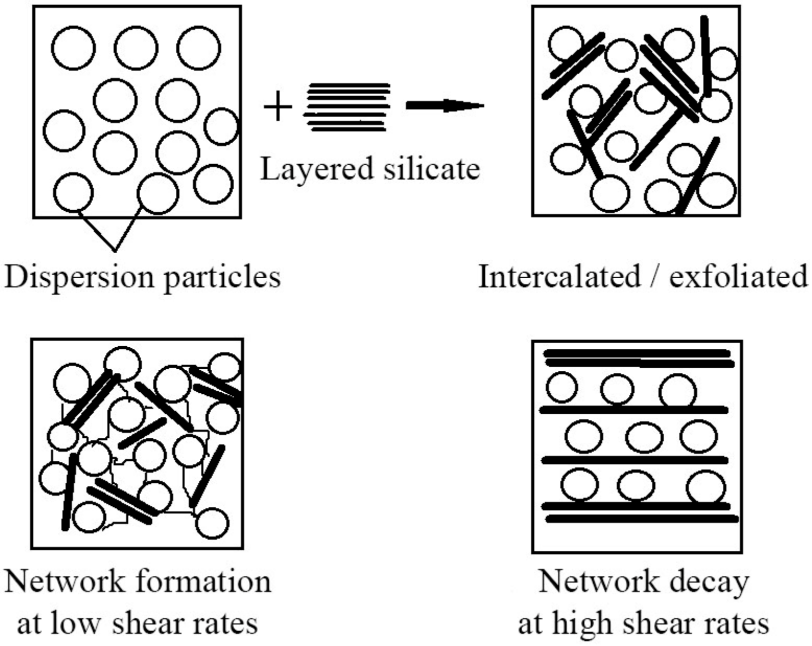


Fig. 16. Schematic representation of the influence of shear rate on the formation and decay of the network.

Thus, with an increase in the shear rate, the viscosity of the samples decreases. This is a non-Newtonian behavior of both the initial polymer dispersions and compositions with Na^+-MMT. Shear thinning increases with increasing nanofiller content, which indicates the formation of a network at a low shear rate and the gradual restructuring of clay flakes linearly to the shear direction at high speeds.

It is known that the bond between particles is reversible, that is, sticky particles can be separated, for example, by intensively mixing the suspension, and after the cessation of mixing, the bond is restored again. The process of reversible isothermal destruction and restoration of bonds between particles in structured dispersed systems is called thixotropy, and dispersed systems with such properties are called thixotropic. This is one of the most important properties of structured systems [43].

The degree of thixotropic viscosity recovery was calculated by the formula:

$$S = \frac{\Sigma \eta_{1i}}{\Sigma \eta_{0i}} \cdot 100\%, \qquad (12)$$

where S is the degree of thixotropic viscosity recovery;

η_{1i} is the viscosity at the i-th shear rate, measured in the shear rate gradient mode, which decreases;

η_{0i} is the viscosity at the i-th shear rate, measured in the shear rate gradient mode, which increases.

The data of the degree of thixotropic reduction of polymer nanocomposites with Na^+-MMT are presented in Table 5.

Table 5

The degree of thixotropic reduction of nanocomposite compositions

Polymer composition	Viscosity η, Pa·s		S, %
	η_{1i}	η_{0i}	
Lacrytex 430	0.37	0.32	87%
Lacrytex 430 / Na^+-MMT – 1%	0.52	0.48	92%
Lacrytex 430 / Na^+-MMT – 2%	1.08	0.96	91%
Lacrytex 640 / Laproxide 703	0.26	0.21	82%
Lacrytex 640 / Laproxide 703 / Na^+-MMT – 1%	0.96	0.80	83%
Lacrytex 640 / Laproxide 703 / Na^+-MMT – 2%	2.69	2.31	86%
Aquapol 14/ Laproxide TMP	0.21	0.19	91%
Aquapol 14/ Laproxide TMP / Na^+-MMT – 1%	0.35	0.32	91%
Aquapol 14 / Laproxide TMP / Na^+-MMT – 2%	1.01	0.94	93%

It was found that with the introduction of nanoclay in an amount of 2%, the degree of thixotropic reduction of the styrene-acrylic dispersion Lacrytex 430 increases from 87 to 91%, Lacrytex 640 / Laproxide 703 – from 82 to 86%, and the composition Aquapol 14 / Laproxide TMP – from 91 to 93 %

After analyzing the data in Table 5, we can conclude that the introduction of layered silicate increases the degree of thixotropic recovery of the initial dispersions, which is explained by the hydrophilicity of montmorillonite clays with reversible isothermal destruction.

5.4. Study of clay morphology in nanocomposites. IR spectra are widely used to characterize polymer-clay nanocomposites in order to prove the presence of all components of the composition. However, modern studies use this method to assess clay exfoliation [44, 45]. The object of the study was to research the morphology of the distribution of Na^+-MMT particles in the matrix of the SA polymer. The IR spectra of Na^+-MMT, SA polymer, and nanocomposite are shown in Fig. 17, 18.

A typical peak for montmorillonite corresponds to a wide range between 1100 cm^{-1} to 1000 cm^{-1}, related to vibrations of various Si–O bonds in the clay structure [44]. The Si–O spectrum region is rather complex and consists of several overlapping spectral features. One silicate layer contains two types of Si–O bonds/orientations. The first refers to the basal oxygen atoms included in the silicon-oxygen tetrahedron, and has its own moment of transition located in the plane of the layer, this type of oscillation is called "in the plane". The second corresponds to the silicon–oxygen bond directed to the octahedrally coordinated aluminum ions and has its moment of transition perpendicular to the layer; this view is called " outside the plane". Layered silicates exhibit four intersecting bands in the Si–O region: three in the plane (1120 cm^{-1}, 1048 cm^{-1}, and 1025 cm^{-1}) and one outside the plane (1080 cm^{-1}).

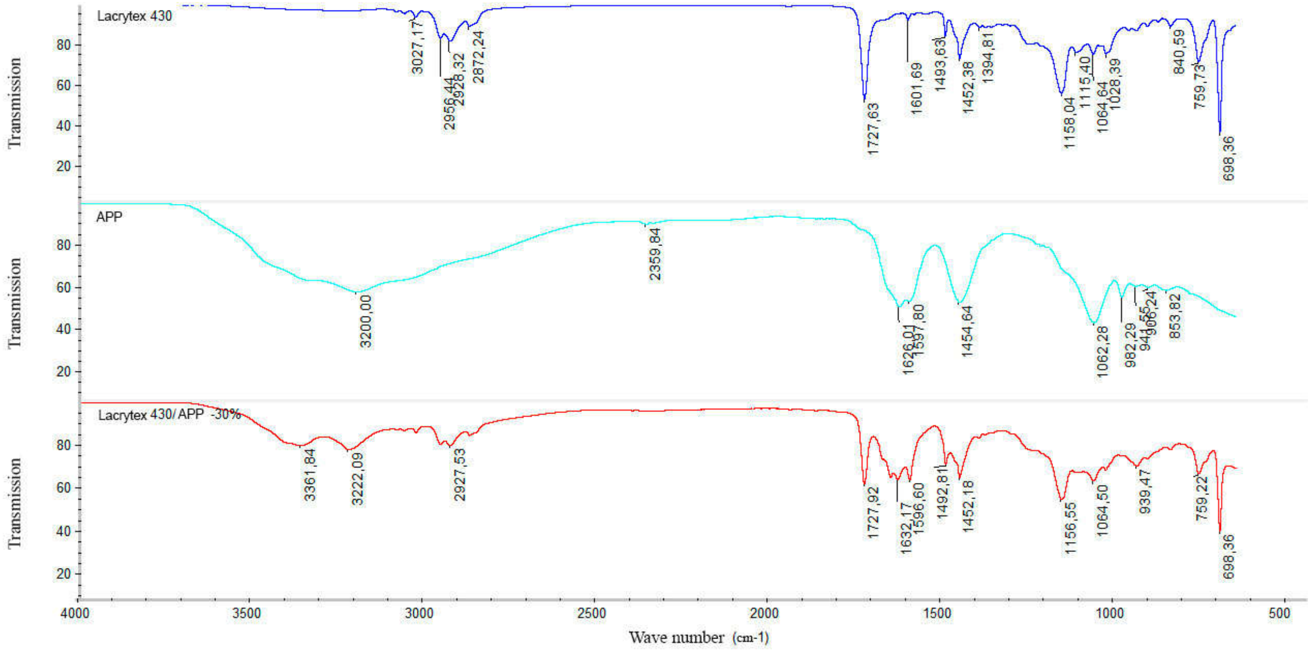


Fig. 17. The IR spectra of the SA polymer Lacrytex 430, APP and composition Lacrytex 430 / APP – 30 wt %.

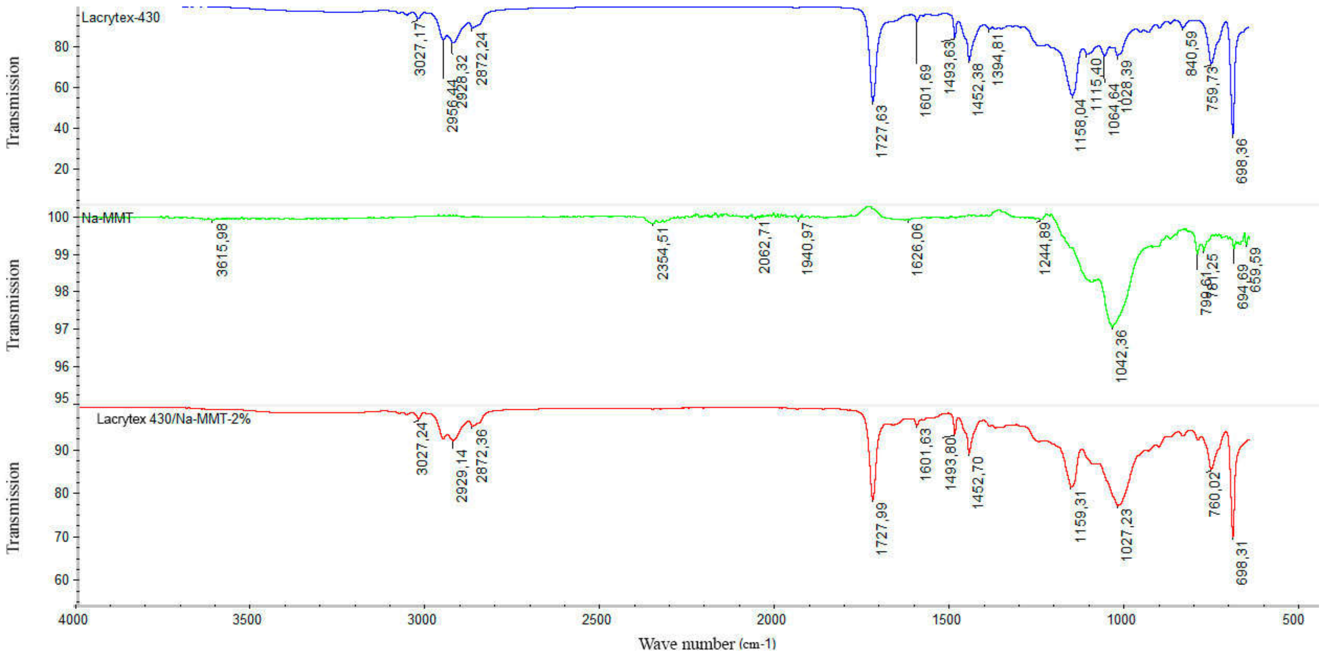


Fig. 18. The IR spectra of the SA polymer Lacrytex 430, Na$^+$-MMT and the composition Lacrytex 430 / Na$^+$-MMT – 2 wt %.

When filling the styrene-acrylic polymer, one can observe the appearance of peaks in the Si–O stretching range corresponding to the spectra of pure Na$^+$-MMT. In the nanocomposite, the peaks of 1100 cm^{-1} and 1018 cm^{-1}, which correspond to Si–O vibrations "in the plane", are strong enough, while a peak "outside the plane" is not detected in the absorption spectra. The intensity of Si–O vibrations increased relatively intensively with an increase in the nanosilicate content in the styrene-acrylic polymer; however, a shift toward higher frequencies was not observed. Accordingly, no clear evidence of clay exfoliation in the polymer was found by IR spectroscopy.

The morphology of composites filled with Na$^+$-MMT was studied using X-ray diffraction analysis. The study of X-ray diffraction patterns of clay water dispersions by the authors of [45–48] showed the complete exfoliation of clay particles at a low concentration due to clay swelling and subsequent separation of its particles into separate layers in an aqueous medium. Exfoliated clay plates [49] in an aqueous medium retain a layered state when mixed with a polymer dispersion or form an ordered distance between clay plates at a concentration of less than 10%.

By X-ray diffraction analysis of composite films, X-ray diffraction patterns were obtained showing the positions of the diffraction peak and corresponding to the interlayer distance of Na^+-MMT particles in each nanocomposite film, as shown in Fig. 19.

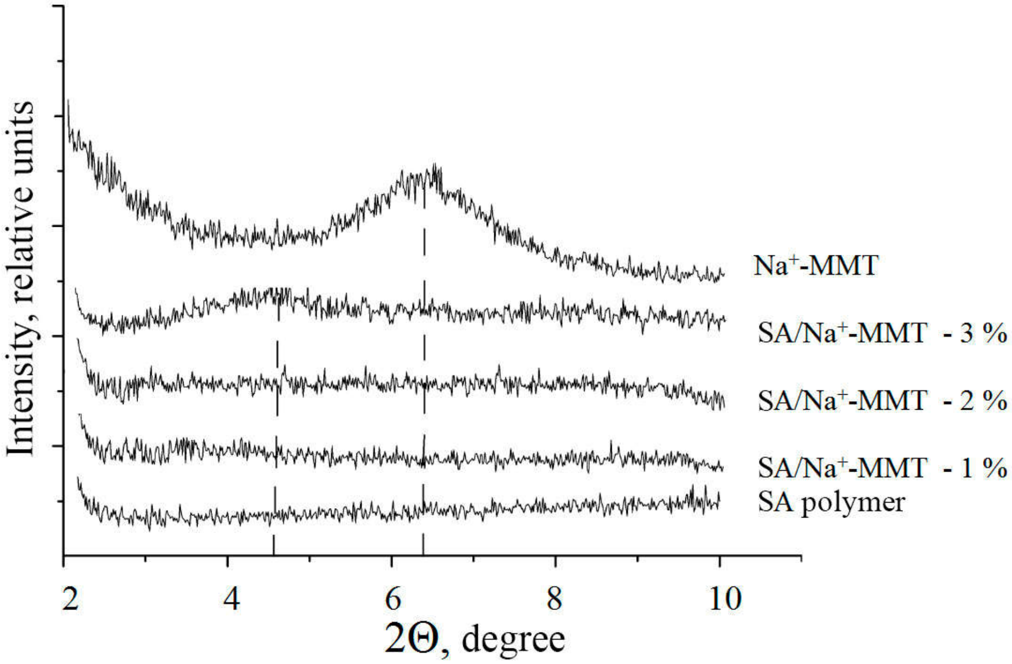


Fig. 19. X-ray diffraction analysis of nanocomposite films.

X-ray diffraction patterns of Na^+-MMT samples showed a first-order peak in the region <10°, which corresponds to the basal distance of the clay. The characteristic diffraction peak of (d_{001}) Na^+-MMT clay is 6.45° with an interlayer distance of 1.37 nm, corresponding to 2–3 layers of intercalated water between the particles of layered silicate. It was found that there is no diffraction peak for an unfilled styrene-acrylic film and composites containing Na^+-MMT from 1 to 2%.

According to the data obtained, nanocomposites have an exfoliated, that is, a layered silicate structure in composite films with a uniform distribution of Na^+-MMT particles in the polymer matrix when filled up to 2%. With an increase in the amount of clay to 3%, a wide diffraction peak appeared in the 4.44° region, which indicates the aggregation of clay structures in packs with an increase in the interlayer space to 1.98 nm.

Based on the studies, we can conclude that the obtained nanocomposites have an exfoliated structure with a Na^+-MMT content of up to 2%. When a 3% aqueous suspension of Na^+-MMT, which is already exfoliated, is introduced into the styrene-acrylic dispersion, an intercalated structure is formed in the polymer matrix.

5.5. Effect of Na^+-MMT on the structural parameters and physicomechanical properties of nanocomposite films. In accordance with the concept of free volume, chain mobility provides a driving force for the diffusion of small molecules. In a nanocomposite, molecular mobility is greatly reduced in the immediate vicinity of clay plates as a result of the formation of an interface between the clay and the polymer matrix. Thus, the diffusion of solvent molecules (or gas) deep into the material is significantly reduced due to the formation of a "winding path" [40], shown in Fig. 20, which increases the barrier properties of polymer composites.

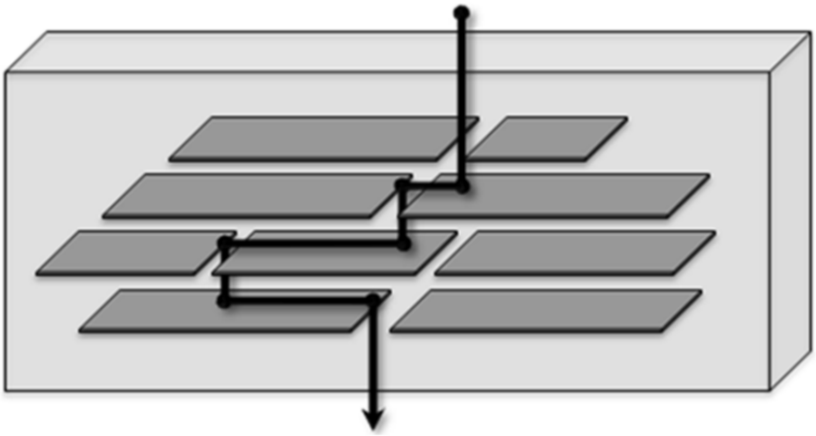


Fig. 20. A model of a winding path for diffusion of molecules in a polymer matrix containing plates.

Various models of continuous media were developed and applied to polymer/clay nanocomposites, providing in most cases a random distribution of plates parallel to each other and located perpendicular to the direction of diffusion of molecules, as shown in [50, 51]. According to the presented model, the decrease in permeability increases due to an increase in the ratio of the width to the thickness of the plates.

From the data presented in Table 6, it can be seen that the introduction of Na^+-MMT up to 5% leads to low values of the Q_f/Q_g index, which characterizes the appearance of a rather high degree of polymer–filler interaction [52].

Table 6

Structural parameters of Na^+-MMT-filled polymers

Na^+-MMT, %	Lacrytex 430			Lacrytex 640/ Laproxide 703 (8%)			Aquapol 14/ Laproxide TMP (6%)		
	Q_f/Q_g	M_c, g/mol	$v\times10^{-3}$, mol/m^3	Q_f/Q_g	M_c, g/mol	$v\times10^{-3}$, mol/m^3	Q_f/Q_g	M_c, g/mol	$v\times10^{-3}$, mol/m^3
–	–	52	9.6	–	50	10	–	1240	0.40
1%	0.65	47	10.6	0.57	42	11.9	0.73	909	0.51
2%	0.65	45	11.1	0.57	42	11.9	0.70	982	0.55
3%	0.65	45	11.1	0.60	44	11.4	0.65	867	0.58
4%	0.66	45	11.1	0.65	45	11.1	0.65	867	0.58
5%	0.68	47	10.6	0.68	47	10.6	0.67	982	0.51
10%	0.71	51	9.8	0.91	56	8.9	1.11	1118	0.45
20%	0.71	54	9.3	0.99	60	8.3	1.17	1212	0.41
30%	0.77	56	8.9	1.03	60	8.3	1.25	1319	0.38

Note: Q_f/Q_g is an indicator of the interaction of the polymer–filler; M_c is the average molecular length of the polymer chain; v is the density of crosslinking.

The change in the density of the crosslinking of nanocomposite films depends on the filling of the polymer matrix with Na^+-MMT particles. Thus, the optimal nanofiller concentration for Lacrytex 430 and Lacrytex 640 / Laproxide 703 is 2%, while the average molecular chain length decreases from 52 to 45 g/mol and from 50 to 42 g/mol, and the crosslink density increases by 16 and 19% respectively.

When the Aquapol 14 / Laproxide TMP matrix is filled, the average molecular chain length of which is 1240 g/mol, Na^+-MMT nanoparticles from 3 to 4% can reduce the average molecular length of the chain to 867 g/mol and increase the crosslink density by 28%. An increase in the content of silicate filler above the indicated concentrations negatively affects the structural characteristics of the spatial network of nanocomposites.

This is probably due to the fact that with an increase in the amount of filler in the polymer composition and as a result of high surface activity, the nanoparticles begin to aggregate, therefore, the number of available active sites for the formation of crosslinks decreases [25].

The data presented are a clear evidence of the emergence of a barrier to the migration of the solvent into nanocomposite films. In the studies of Aprem et al. [53], a decrease in the solvent absorption coefficient with MMT containing nanocomposites was explained by the fact that layered clay plates, having scaly structures, form physical cross-links that prevent solvent sorption by the polymer matrix. Later Valdares et al. [54] showed that the delaminated and intercalated silicate structures in the composition of the polymer matrix act as synergetics.

A feature of polymer-clay nanocomposites is their greatly improved physical and mechanical properties. There are several factors that affect the strength characteristics of polymer nanocomposites, such as the interaction of clay and a polymer matrix, the method of preparation and the amount of filler. The complete dispersion of clay nanolayers in the polymer optimizes the number of available reinforcing elements that prevent cracking.

The determination of mechanical properties, such as conditional tensile strength (σ_p) and elongation at break (ε_p), was carried out on a tensile testing machine RT-150M, at a speed of 300 mm/min in accordance with GOST 14236-81.

Diagram 21 shows the results of the effect of the filler on elongation at break (ε_p) of nanocomposite materials.

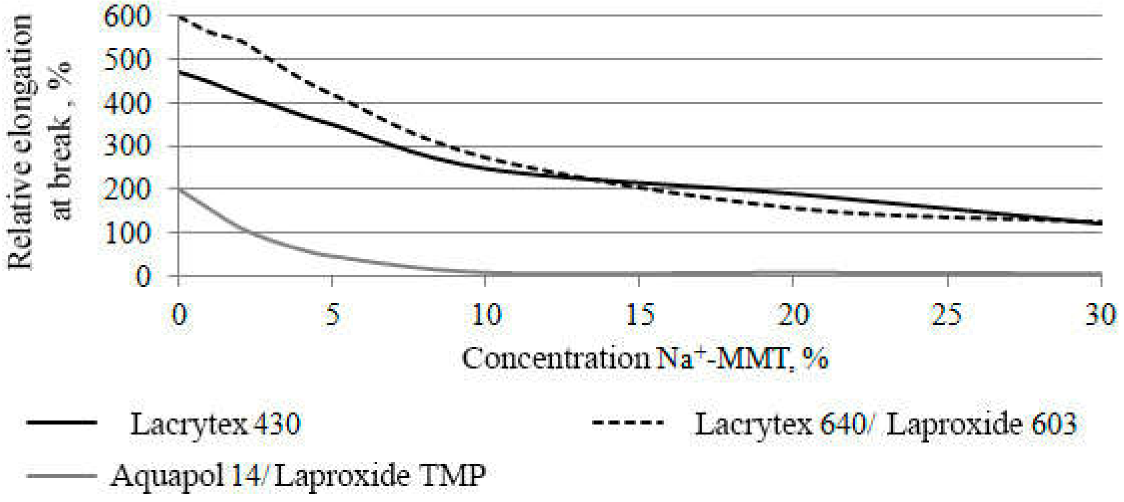


Fig. 21. Effect of Na^+-MMT concentration on elongation at break of nanocomposites.

The introduction of clay into the polymer matrix to 5% leads to a decrease in the elongation at break of the nanocomposite films due to the formation of polymer sections immobilized by Na^+-MMT plates. When a nanofiller is introduced into the polymer matrix above 5%, the elongation at break of the nanocomposite films decreases 2 times Lacrytex 430 and Lacrytex 640 / Laproxide 703 and 20 times for Aquapol 14 / Laproxide TMP compared to the starting polymers.

The chart data presented in Fig. 22, indicate a significant reinforcing effect of nanocomposites containing Na^+-MMT up to 4%.

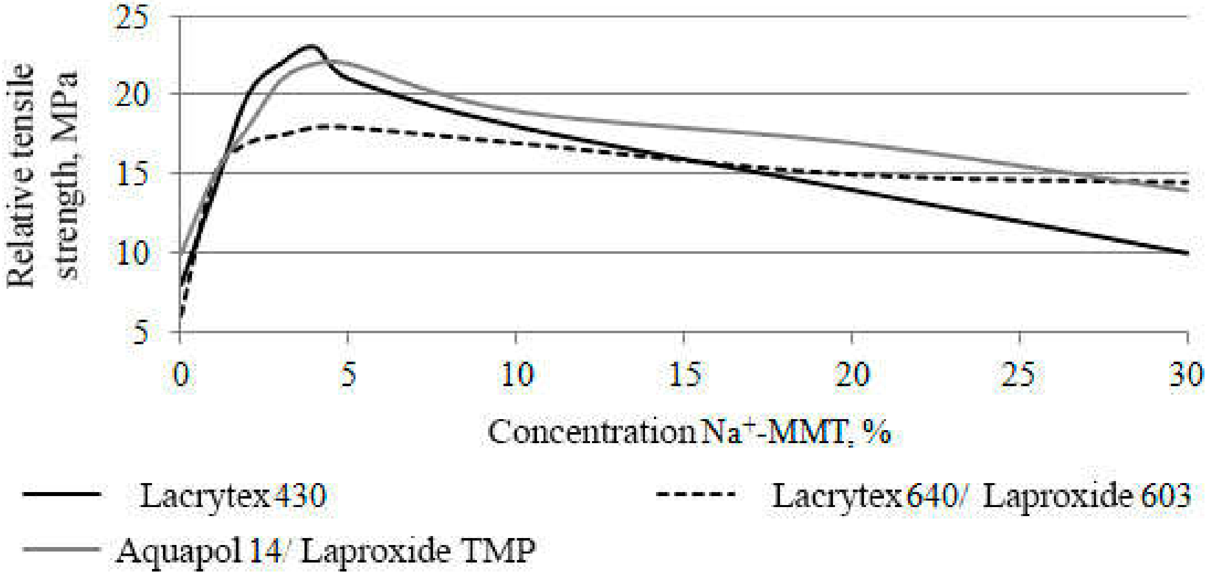


Fig. 22. Effect of Na^+-MMT concentration on conditional tensile strength of nanocomposites.

So, for Lacrytex 430 and Lacrytex 640 / Laproxide 703, the relative tensile strength increases 3 times, and for Aquapol 14 / Laproxide TMP 2 times compared to the original polymers.

Studies [55, 56] also report a gradual decrease in elongation at break in polymer-clay nanocomposites, which is explained by the introduction of nanoclay. The authors of [57] believe that silicate layers can contribute to the formation of immobilized or partially immobilized polymer phases, which also increases the strength. In addition, it is possible that the orientation of the silicate layers contributes to the reinforcing action. Nanosized fillers with a high length to width ratio, such as Na^+-MMT, are of interest due to the high contact area between the filler and the polymer matrix. In fact, the strength of the polymer / Na^+-MMT nanocomposites studied in this work depends on the increase in the content of Na^+-MMT, which indicates the presence of a strong interaction between the two types of substances and part of the network structure in the material. In this case, the exfoliated layers of Na^+- MMT interact with polymer chains to form a physical crosslink in which Na^+-MMT acts as a physically crosslinking compound.

The tensile strength of the nanocomposite is also improved due to the presence of the nanodispersed filler Na^+-MMT. When the content of Na^+-MMT in the polymer matrix is increased to 4%, the tensile strength of styrene-acrylic polymers and polyurethane does not increase, and the elongation at break is significantly reduced. Two reasons lead to this phenomenon. Firstly, the introduction of a larger number of Na^+-MMT plates prevents crystallization under the action of stresses of the pure polymer. Secondly, a high content of Na^+-MMT easily causes an increase in the size of the dispersed phase (non-exfoliated structures) in nanocomposites as a result of co-coagulation.

A study of the physicomechanical properties of individual polymers and nanocomposites with Na^+-MMT allows us to conclude that an increase in the cross-linking strength at the polymer / layered silicate interface occurs due to the formation of a physical network of polymer macromolecules with filler nanoparticles, which reduces the diffusion of solvent molecules, gases or flame into the polymer matrix by increasing the barrier properties of polymer composites.

5.6. Assessment of the optical properties of nanocomposite films with Na^+-MMT. The study of the optical properties of the obtained polymer nanocomposites with Na^+-MMT is of practical interest, since the thickness of the stratified MMT plates is 0.94 nm, which is less than the wavelengths of visible light, and therefore they are transparent particles [58, 59].

To determine the turbidity of the polymer system, the optical density of the free film was measured on a KFK-2MP photoelectric concentration colorimeter (Table 7).

Table 7

Turbidity indicators of polymers and nanocomposites with Na^+-MMT

Na^+-MMT, %	Optical density, D			Turbidity coefficient, τ		
	Lacrytex 430	Lacrytex 640/ Laproxide 703	Aquapol 14/ Laproxide TMP	Lacrytex 430	Lacrytex 640/ Laproxide 703	Aquapol 14/ Laproxide TMP
–	0.53	0.46	0.39	0.76	0.65	0.55
1%	0.50	0.44	0.38	0.72	0.63	0.55
2%	0.50	0.42	0.35	0.72	0.60	0.50
3%	0.55	0.47	0.38	0.79	0.68	0.55
4%	0.67	0.53	0.44	0.96	0.76	0.78

A decrease in the turbidity coefficient is observed in all the studied polymers with a Na^+-MMT content of 1–2%. An increase in the content of nanofiller impairs the optical properties of nanocomposites, which limits the use of this concentration of nanofiller in the finishing of textile materials.

The results obtained confirm that the clay content affects the transparency of nanocomposites [60, 61]. Maximum efficiency is achieved when the concentration of the plate nanofiller up to 2%.

5.7. Study of thermal decomposition of nanocomposite films. It is generally accepted that the formation of a nanocomposite allows one to achieve good flame retardant properties. Using conical calorimetry, it was shown that the peak in the rate of heat release of the ethylene vinyl acetate / Na^+-MMT–5% microcomposite decreases by only 25%, and in the case of the nanocomposite, by 50% compared to an unfilled polymer [62].

Considering that the introduction of layered silicate in an amount of 1–2% does not provide the necessary fire retardant properties for both the SA film and the textile material, we studied the effect of a higher nanofiller content on the thermal degradation of the SA polymer.

The thermal decomposition of the unfilled SA Lacrytex 430 polymer and nanocomposite materials based on it, containing 10, 20 and 30% Na$^+$-MMT, was studied by thermogravimetric analysis (TGA). The results of the study are presented in Fig. 23.

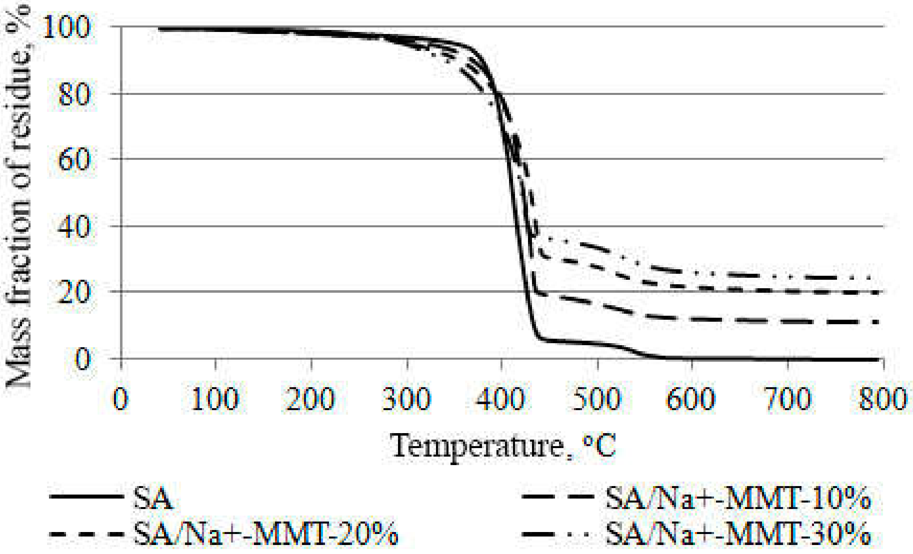


Fig. 23. Thermogravimetric analysis of SA film with Na$^+$-MMT.

It is noted that thermal stability is significantly increased when filling the polymer matrix with Na$^+$-MMT. The results show (Table 8) that the SA polymer is stable up to 200°C, and thermal decomposition begins at a maximum temperature of destruction of 370°C.

Table 8

Effect of Na$^+$-MMT on the change in the mass of styrene acrylic film depending on temperature

Nano-composite films	The main stage of destruction		Mass fraction of residue with increasing temperature, %							
	$T_d^{0,1}$, °C	$T_d^{0,5}$ °C	100	200	300	400	500	600	700	800
SA	379	411	99.9	99.0	97.1	70.7	4.6	0.1	0	0
SA/ Na$^+$-MMT – 10%	364	423	99.5	98.3	96.0	78.4	16.8	12.2	11.5	11.3
SA/ Na$^+$-MMT – 20%	349	421	99.6	98.2	95.5	77.3	27.9	21.8	20.6	20.1
SA/ Na$^+$-MMT – 30%	342	422	99.5	98.3	95.0	70.8	33.3	25.8	24.5	24.2

Comparative analysis of the data given in Table 8, indicates that the main mass loss of the films was observed in the range of ~ 300–400°C for both unfilled SA polymer and nanocomposites. As a measure of thermal decomposition, we studied the temperature at which 10% ($T_d^{0,1}$) and 50% ($T_d^{0,5}$) thermal decomposition occurs.

For an unfilled SA polymer, $T_d^{0,1}$ is 379°C. The introduction of 30% Na^+-MMT reduces $T_d^{0,1}$ to 342°C. However, $T_d^{0,5}$ of all the studied nanocomposites occurs at a temperature higher than that of the unfilled polymer and amounts to 422°C. At temperatures above 600°C, all the curves are aligned, which is explained by the formation of an inorganic residue, which is absent in the unfilled SA polymer. So, the coke residue of a nanocopositite containing 30% Na^+-MMT is 25.8%, which is 2.5 times higher than when a similar amount of ammonium polyphosphate (APP) was introduced.

The main fire retardant mechanism in polymer/clay nanocomposites is obviously the formation of a barrier against heat and volatile flammable substances by migration of a clay nanolayer to the surface of the material, followed by the formation of coke. This mechanism modifies the fire resistant properties of a polymer nanocomposite, sometimes improving them and, in some other cases, worsening, depending on what type of fire test is used and the measurement conditions.

Thus, the introduction of nanoclay into the polymer matrix creates a protective layer during combustion, which should slow down and decrease the peak of the heat release rate and, as a result, can reduce the ignition time of the textile material. When heated, the viscosity of the molten polymer / layered silicate nanocomposite decreases and facilitates the migration of clay nanolayers to the surface, therefore, the accumulation of clay on the surface of the material acts as a protective barrier that limits heat transfer, evaporation of combustible decomposition products and oxygen diffusion deep into the material.

Thus, it can be concluded that the presence of exfoliated nanostructures in the polymer matrix reduces the thermal decomposition of nanocomposite materials, prevents droplet formation and promotes coke formation, however, UL 94 and LOI tests demonstrate insufficient flame retardant properties of the composites when only layered silicate is introduced. The joint use of MMT nanoparticles in a composition with APP is an important technological technique, since the additive plays the role of a synergistic element.

6. Development of a fire retardant composition for finishing textile materials using Na^+-MMT

The limitation of the kinetics of the combustion mechanism is to create on the outer surface of the textile material a glassy or expanded shield, which can at least partially limit the transfer of combustible substances to the gas phase, the transfer of heat from the flame to the condensed phase, and ultimately the diffusion of oxygen in the condensed phase [63].

The combination of hardness, scratch resistance and flexibility in obtaining a fire retardant finish is a necessary property that can be achieved by introducing Na^+-MMT into the polymer matrix and applying the nanocomposite to various textile materials. The inclusion of nanostructures in polymer matrices for flame retardant use limits the toxicity of decomposition products compared to more traditional additives such as halogenated flame retardants.

The main fire retardant mechanisms in polymer/clay nanocomposites is the formation of a barrier against heat and volatile flammable substances by migration of a clay nanolayer to the surface of the material, followed by the formation of coke.

Given that nanoclay really slows down the combustion process and enhances coke formation, they have no effect on ignition trends and material properties after removal of the fire source. The introduction of only nanoclay is not sufficient to provide the fabric with reliable fire retardant properties. In this regard, obtaining an effective nanocomposite composition to ensure the refractory properties of textile materials was not expected. However, an interesting indicator is the structure of the formed protective silicate barrier on the surface of the textile material after exposure to flame.

Finishing of cotton and cotton/PES fabrics was carried out with the compositions shown in Table 9, followed by 80% pressing and drying at 100°C for 5 minutes.

Table 9

Fire retardant composition with Na^+-MMT

№	Composition, g/l	Weight gain, %	
		cotton	cotton/PES
1.	SA – 180, Na^+-MMT – 20	14.42	15.31
2.	SA – 160, Na^+-MMT – 40	14.56	15.34
3.	SA – 140, Na^+-MMT – 60	14.58	15.35

Less energetic ignition occurs on fabric with a nanocomposite finish compared to an untreated sample. In addition, on untreated fabric, prolonged residual decay was observed.

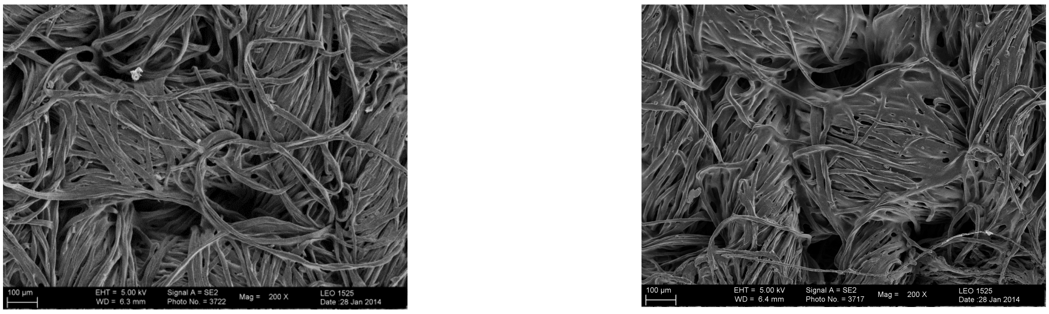
After exposure to the flame, the initial cotton and cotton/PES fabrics and samples treated with compositions with a layered silicate content of less than 10% leave only unstructured ash, and therefore surface micrographs of these samples are not presented.

Micrographs of the surface of cotton and cotton/PES fabric, finished with nanocomposite composition containing 10, 20 and 30% Na^+-MMT, with a magnification of 200 times are shown in Fig. 24.

In fig. 24 (c–e) it is clearly seen that the structure of the interweaving of the coke residue of fabrics with a nanocomposite finish remains relatively untouched. The weave of coke yarn gives a "shrinkage" after the flammability test, leaving gaps between the yarns (Fig. 24c), but increasing the Na^+-MMT content in the nanocomposite composition to 30% leads to the formation of a more reliable protective layer that reduces the thermal decomposition of the textile substrate.

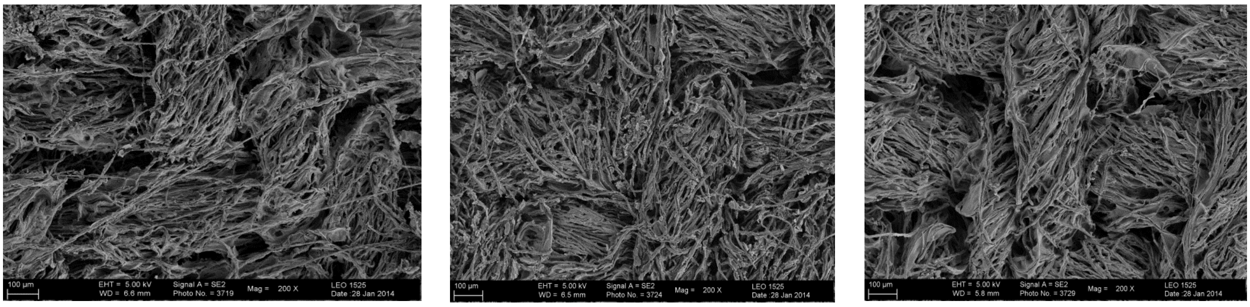
The morphology of the surface of the fire retardant layer on the fibers of cotton and cotton/PES fabrics can only be described after flame exposure on the textile material treated with a nanocomposite composition. With a magnification of 750 times, as shown in Fig. 25 (a, b), each fiber is coated with a coke-like silicate layer.

The formed solid screening layer on the fibers is clearly visible at a magnification of 5000 times in Fig. 25 (c).



a) cotton fabric with SA / Na$^+$-MMT finish – 30% before burning

b) cotton/PES fabric with SA / Na$^+$-MMT finish – 30% before burning

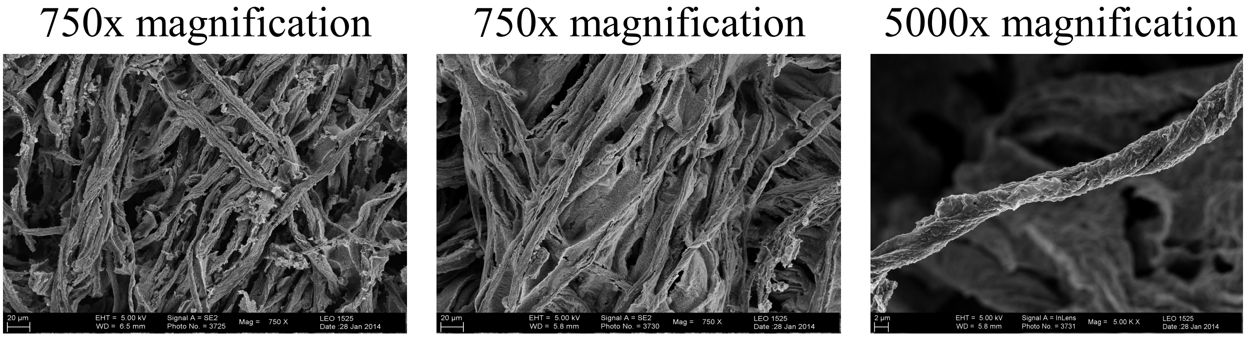


c) cotton fabric with SA / Na$^+$-MMT finish – 10% after burning

d) cotton fabric with SA / Na$^+$-MMT finish – 20% after burning

e) cotton fabric with SA / Na$^+$-MMT finish – 30% after burning

Fig. 24. Micrographs of the surface of cotton and cotton/PES fabrics with 200x magnification: (a, b) before burning; (c–e) after burning.



750x magnification

750x magnification

5000x magnification

a) cotton fabric with SA / Na$^+$-MMT finish – 30%

b) cotton/PES fabric with SA / Na$^+$-MMT finish – 30%

c) elementary fiber with SA / Na$^+$-MMT finish – 30%

Fig. 25. Micrographs of the surface after burning:
a) cotton fabric; b) cotton/PES fabric; c) elementary fiber.

On the micrographs of the surface of the fibers there are no clay aggregates and the edges of the plates are not visible, mainly large solid pieces of coating appear, which occurs as a result of the layering of the clay plates on each other during combustion and sintering together. Similar results were obtained by the authors of [64, 65].

Having analyzed the study of the flammability of nanocomposite compositions and the flammability of textile materials with a nanocomposite finish, we can conclude that adding only nanoparticles of clay to the polymer matrix does not avoid the burning of the fibrous polymer, despite the increase in thermal stability due to the formation of a dense shielding layer on Na^+-MMT plates on the surface of textile fibers. This experiment provides initial evidence that flame suppression for fibers and fabrics with a nanocomposite finish based on polymer/clay composites is an alternative to modern flame retardant technologies. Thus, the joint use of additional flame retardant nanoadditives in compositions with classic flame retardants is an important technological technique, since Na^+-MMT plays the role of a synergistic element.

7. Study of the synergistic effect of Na^+-MMT nanoparticles and APP on the fire retardant properties of textile materials

7.1. Study of the effectiveness of the combined use of APP and Na^+-MMT nanoparticles. To achieve regulatory fire retardant requirements, many commercial combustion inhibitors require the use of additives [66, 67], which activate the flame retardant for the selected polymer system and also act as synergists, allowing the use of less flame retardant.

Metal hydroxides, mainly magnesium hydroxide and aluminum hydroxide, are the most commonly used non-halogenated flame retardants, and the flame retardant process due to endothermic decomposition has been known for many years [68]. However, to obtain the required fire resistance, the content of additives above 50% is necessary, and technological problems arise. The combined use of colloidal silicon dioxide and metal hydroxides is an important way to reduce the content of flame retardants, which avoids the deterioration of the mechanical properties of the polymer. A significant improvement in the fire resistance of EVA in a composition with aluminum hydroxide is caused by the presence of clay and is described by Bayer.

The authors of [69] found a synergistic effect between organomodified MMT, decabromodiphenyl oxide and antimony trioxide (Sb_2O_3) for nanocomposites based on polyamide-6. In the obtained nanocomposite, the peak in the rate of heat release decreases by 42%, which is explained by the possible interaction of Sb_2O_3 / decabromodiphenyl oxide with acidic catalyst centers of clay.

Extruded and injection molded polyamide-6 / red phosphorus / organomodified MMT nanocomposites under pressure exhibit high resistance to ignition according to UL-94 test and demonstrate improved fire retardant properties when organomodified MMT is introduced in an amount of 5–7%. Composites based on polyethylene terephthalate with organomodified MMT and carboxyethyl phenylphosphonic acid show a higher flame retardant effect compared to a polyethylene terephthalate / phosphorus-containing flame retardant composite. It was found that with the introduction of 3% organically modified MMT, the LOI of the composite reaches 32% with a simultaneous improvement in thermal stability and crystallinity of the nanocomposite.

Polymer/intumescent flame retardant composites with improved fire resistance due to the introduction of nanoclay have been extensively studied. Intumescent flame retardants form a foamed carbon shield under the influence of a heat stream, which slows down the transfer of oxygen and heat, and also reduces the release of volatile substances. The combination of intumescent flame retardants with clay leads to an increase in coke formation and, as a result, imparting improved fire resistance to materials. A team of Professor Hu has proposed a new one-step melt blending method for polypropylene with clay, the surfactant cetyltrimethylammonium bromide and APP. It is claimed that APP and MMT lead to a 91% decrease in the peak heat release rate of the polypropylene / APP / MMT / cetyltrimethylammonium bromide sample compared to the original polypropylene. The ratio of APP to MMT plays a key role in reducing flammability, while the increased content of MMT negatively affects the flame retardant properties of the polymer material. It is assumed that the Al–P structure is formed as a result of the reaction between clay and APP, but no evidence has been demonstrated in the work.

The authors of [62] assumed that the combination of organomodified MMT and poly-4,4-diaminodiphenylmethanespyrocyclic pentaerythritol bisphosphonate (PDSPB) increases the thermal stability and fire resistance of acrylonitrile butadiene styrene. The mechanism of the formation of the silicoaluminophosphate structure occurs due to the reaction between phosphoric acid generated from PDSPB and MMT, and also leads to an acceleration of oxidative dehydrogenation and the formation of cross-linked coke induced by MMT acid catalytic centers.

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phosphoric acid generated from PDSPB and MMT, and also leads to an acceleration of oxidative dehydrogenation and the formation of cross-linked coke induced by MMT acid catalytic centers.

Considering the above, on Fig. 26, a probable mechanism for the degradation of the composition of the SA polymer / APP / Na^+-MMT composition is proposed.

When exposed to a flame, thermal oxidation and depolymerization of the styrene-acrylic polymer to monomers occurs. The formation of a silicon-aluminum phosphate structure, as shown in Fig. 26, occurs as a result of the reaction between phosphoric acid generated by ammonium polyphosphate and Na^+-MMT, as well as the esterification of monomers and the formation of foamed cross-linked coke induced by the acid catalytic centers of montmorillonite.

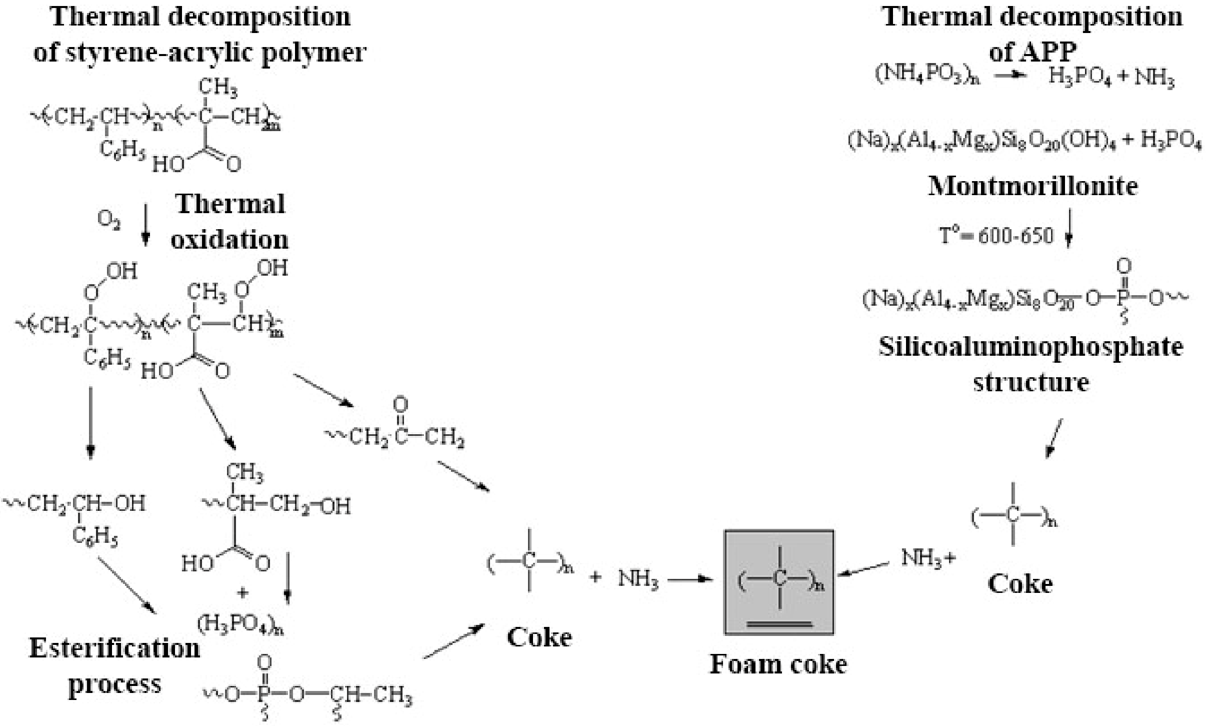


Fig. 26. The likely mechanism of thermal degradation of the composition of SA polymer / APP / Na^+-MMT.

In this work, we studied the effectiveness of the joint use of APP, as an acid source, with Na^+-MMT nanoparticles, as a carbonizing agent to increase the flame retardant properties of textile materials. The effect of Na^+-MMT particles on the fire retardant characteristics of the developed compositions was evaluated by the height of the carbonized area of the cotton and cotton/PES fabrics. The results of the study are presented on Fig. 27.

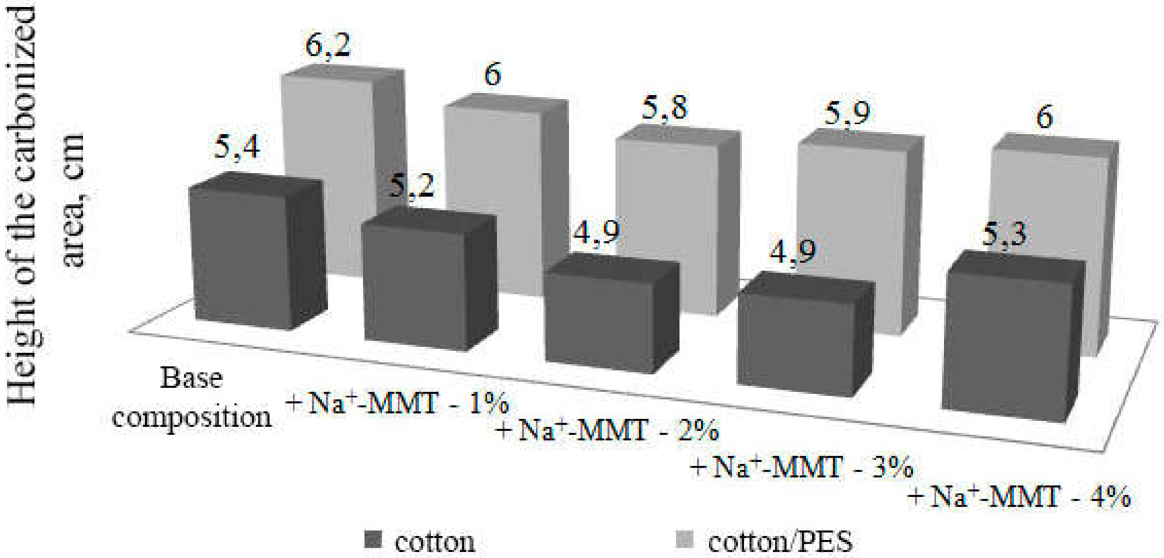


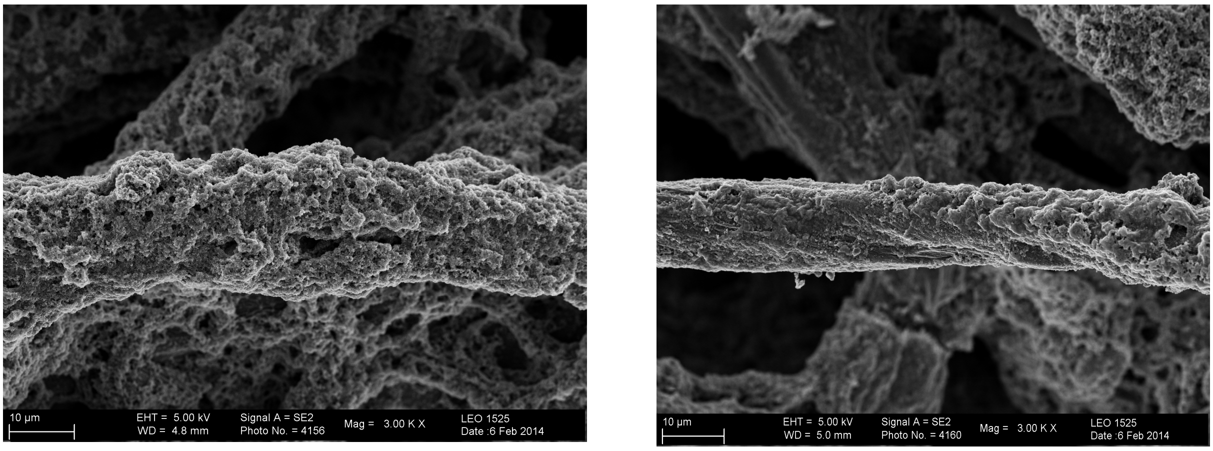
Fig. 27. The height of the carbonized area of cotton and cotton/PES when using polymer compositions containing Na^+-MMT nanoparticles.

According to the data obtained, the introduction of Na^+-MMT to 3% and a corresponding decrease in the amount of APP leads to an improvement in the refractory properties of textile materials, which confirms the synergistic effect of the nanofiller and flame retardant.

Using mathematical modeling, it was found that the optimal content of Na^+-MMT in the composition for flame retardant finish of cotton fabric is 2%, and cotton/PES fabric is 2.3%, while the height of the carbonized area of cotton fabric decreases from 5.4 to 4.9 cm, and cotton/PES fabric – from 6.2 to 5.8 cm.

The Na^+-MMT plates form a physical barrier slowing down the pyrolysis of the decomposing polymer and, as a result, the textile substrate. Clay particles are also likely to cause some chemical crosslinking of the decomposable polymer matrix, which arise due to the long residence time of polymer radicals and the catalytic ability of clay with respect to aromatic hydrocarbons [70].

Micrographs of the surface of the yarns shown on Fig. 28 clearly demonstrate the formation of a carbonized silicate layer.



a) cotton fabric with a basic finish modified with Na$^+$-MMT – 2%

b) cotton/PES fabric with a basic finish modified with Na$^+$-MMT – 2%

Fig. 28. Micrographs of the formation of coke residue on the surface of an elementary fiber after burning.

In addition, the migration of nanoclay on the fiber surface is enhanced by the formation of gas bubbles initiated by the decomposition of both ammonium polyphosphate and polymer chains.

In fact, gas bubbles can serve as the center of transfer of Na$^+$-MMT plates to the surface, forming a barrier against the flame, as shown in Fig. 29.

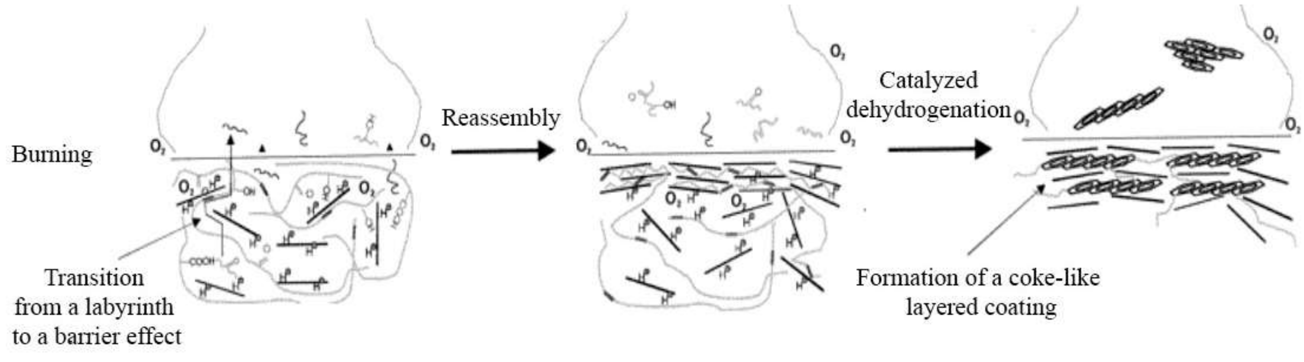


Fig. 29. Scheme of the combustion mechanism of a polymer nanocomposite containing Na$^+$-MMT.

After analyzing the data on the obtained indicators of the height of the carbonized area and micrographs of the surface of the fabric after burning, it was concluded that the formation of a heat-insulating carbonized layer containing a silicon–aluminum–phosphate structure increases the refractory indexes of textile materials and limits the penetration of flame, heat and oxygen into the internal structure of the fiber.

7.2. Assessment of the influence of intumescent agents on the height of the carbonized area of cotton and cotton/PES fabrics. It is known that in combination with phosphorus synergists, intumescent agents (nitrogen-containing compounds) increase the stability of coke by forming nitrogen-phosphorus bonds. Intumescent systems are widely used to protect various building materials such as steel and wood. They require the presence of three components connected to each other by a binder: a carbon source (coke former), an acid source (flame retardant), and an intumescent agent (gas former).

Typical examples of components [71] used for intumescent systems are presented in Table 10.

Table 10

Examples of components of intumescent systems

Sources of acid	**Coke formers**
Source of inorganic acid (phosphoric, sulfuric, boric)	Starch, dextrins, coke-forming polymers
Ammonium salts (phosphates, borates, sulfates, halides)	
Amine or amide phosphates (melamine phosphate)	**Intumescent agent**
Organophosphorus compounds (tricresyl phosphate, alkyl phosphates)	Urea, melamine, dicyandiamide

During foaming, the acid is released and esterifies the carbon-rich components at temperatures above the acid release temperature. This mixture of materials then melts before or during the esterification. The ester is decomposed by dehydration, which leads to the formation of a carbon-inorganic residue. The gases released during the decomposition of the intumescent agent contribute to the foaming of the carbon residue (Fig. 30).

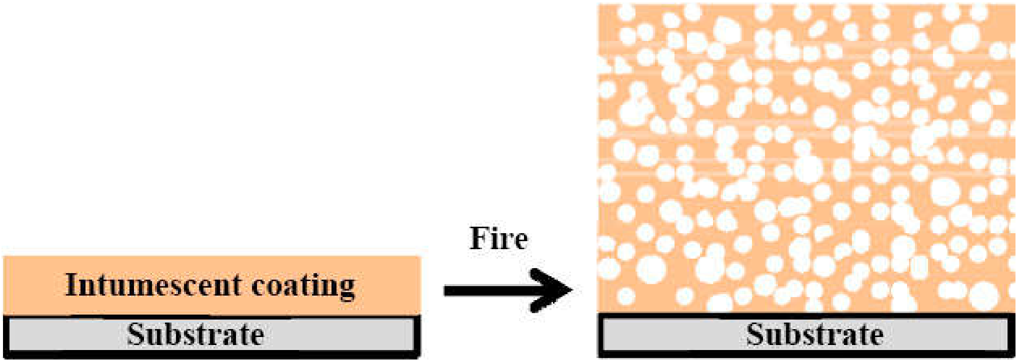


Fig. 30. Scheme foaming coatings with the formation of highly porous structures.

The formation of the foam layer acts as an insulator, protecting the substrate from heat and flame and limiting the diffusion of oxygen into the deeper layers. In this regard, the use of intumescent agents on textile substrates is a promising direction. The most used intumescent agents for composite systems are porophore (azodicarbonamide) and melamine, i.e. chemicals capable of producing abundant gas during thermal decomposition and combustion, which ultimately ensures foaming.

In Fig. 31 presents the results of the influence of melamine (MEL) and azadicarbamide (ACA) on the height of the carbonized area of cotton and cotton/PES fabrics with the introduction of intumescent agents into a polymer composition containing Na^+-MMT and a corresponding decrease in APP.

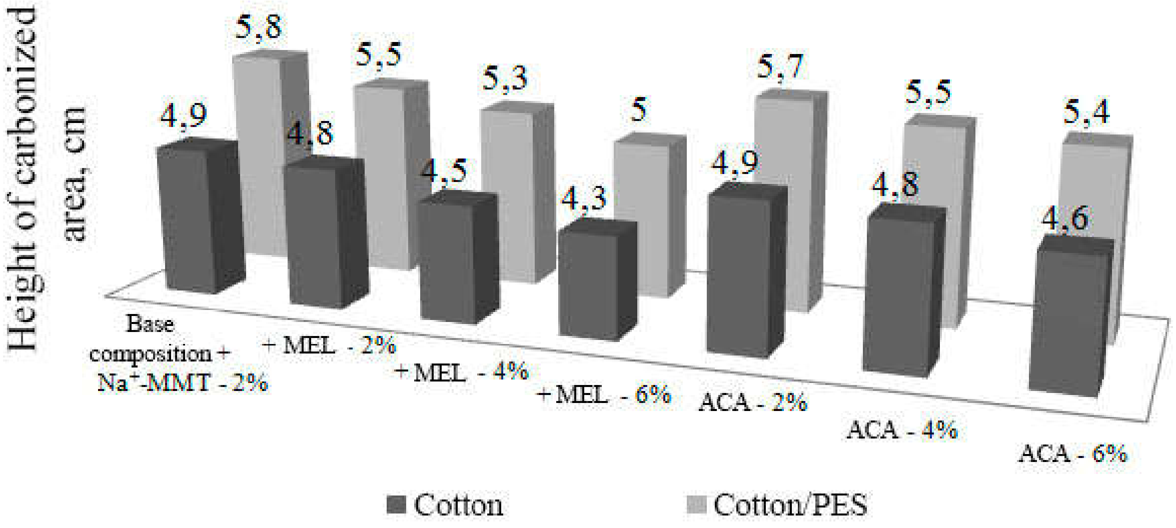


Fig. 31. The effect of intumescent agents on the height of the carbonized area of cotton and cotton/PES fabrics.

According to the data obtained, the introduction of an additional intumescent agent leads to an improvement in the refractory properties of cotton and cotton/PES fabrics, which is likely due to phosphorus-nitrogen synergism.

Phosphorus-nitrogen synergism is explained by the formation of P–N bonds during thermal decomposition, which facilitate phosphorylation and enhance the effect of flame retardants as dehydration catalysts. At elevated temperatures, polyphosphoric acid is released and melts, covering the textile fibers with a protective film, protecting it from smoldering after the cessation of flame combustion. As a result of the decomposition of the nitrogen-containing agent, a gas barrier of ammonia is formed above the surface of the substrate, which impedes the access of oxygen and inhibits the oxidation of carbon in the gas phase. So, with the introduction of 4% melamine, the height of the carbonized section of the cotton sample decreases from 4.9 to 4.5 cm, and cotton/PES – from 5.8 to 5.3 cm. Higher melamine action compared to azadicarbamide can be explained by the formation of a polycyclic structure formed in the process of melamine self-condensation, which affects the formation of stable coke.

In polymer technologies for fire protection of building structures, both concrete and wooden products, intumescent agents are used, the proportion of which can be up to 50% of the total content of flame retardants in the composition. However, the increased content of both melamine and azodicarbamide affects the intensity of the colour of cotton and cotton/PES fabrics, which was characterized by the function of GKM (Table 11).

According to the data obtained, the colour intensity of the initial cotton fabric is 99.0. Finishing the fabric with a APP solution at a concentration of 200 g/l reduces the colour intensity to 82.3. With a basic finish containing SA polymer and APP, and with modification of the basic composition of Na^+-MMT, the colour intensity remains unchanged. However, the colour intensity of cotton fabric with the maintenance of melamine above 4% and azadicarbamide above 2% decreases and is equal to 70.4, respectively, which limits the use of these concentrations of intumescent agents in the decoration of textile materials.

Table 11

Effect of fire retardant finishing on the colour intensity of cotton fabric

Indicator	Initial cotton fabric	APP 200 g/l	basic finish	basic finish + Na^+-MMT – 2%	Basic finish + Na^+-MMT – 2%					
					melamine, %			ACA, %		
					2	4	6	2	4	6
Reflection coefficient, R, %	0.5	0.6	0.6	0.6	0.6	0.6	0.7	0.6	0.7	0.8
GKM function value, K/S	99.0	82.3	82.3	82.3	82,3	82.3	70.4	82.3	70.4	61.5

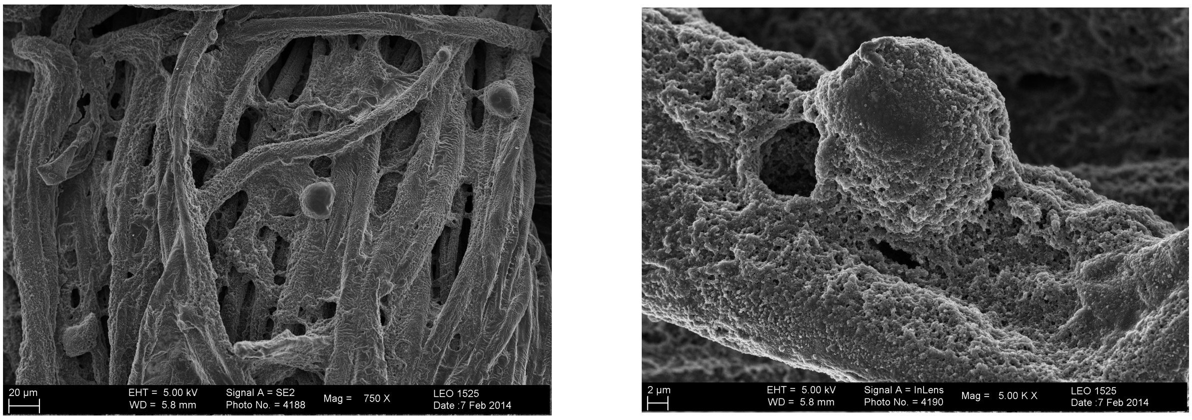
Note: the colour intensity measurement of cotton/PES fabric was not performed because the fabric is dyed in black.

The intumescent effect of nitrogen-containing compounds can be estimated from micrographs of the fabric surface shown in Fig. 32.

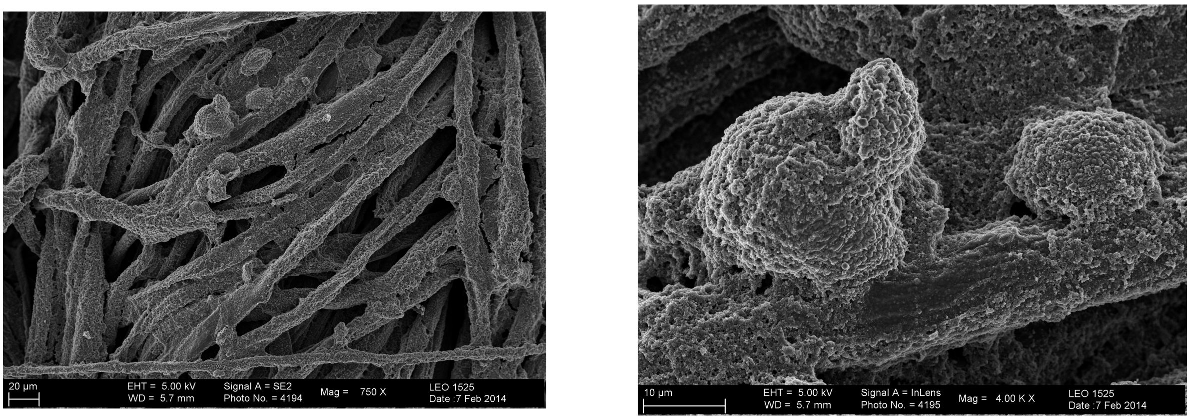
The formation of intumescent bubbles (Fig. 30) is observed on the fibers when using melamine and azocarbonamide, however, the bubbles formed as a result of the decomposition of azocarbonamide are less dense than melamine.

Having studied the height of the carbonized area and micrographs of the fabric surface, we came to the conclusion that the action of melamine, as an intumescent agent, promotes the migration of Na^+-MMT plates during thermal decomposition of the composition with the formation of an insulating foam-coke layer on the surface of textile materials.

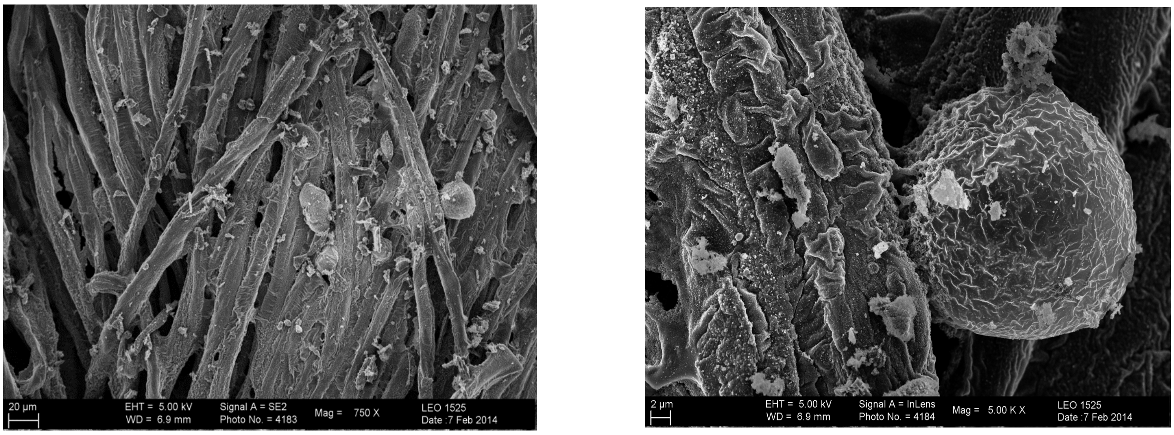
750x magnification 5000x magnification



Cotton fabric with basic finish + Na^+-MMT – 2% / MEL – 4%



Cotton/PES fabric with basic finish + Na^+-MMT – 2% / MEL – 4%



Cotton fabric with basic finish + Na^+-MMT – 2% / ACA – 4%

Fig. 32. Micrographs of the formation of intumescent coke layer on the surface of cotton and cotton/PES fabrics after burning.

7.3. Study of the oxygen index of nanocomposites and nanocomposite textile materials. The most significant characteristic of fabrics fire protection is LOI [72], which for untreated cotton and cotton/PES fabrics, as well as styrene-acrylic polymer used to fix flame retardants on a textile substrate, is 17 and 18%, i.e. samples burn completely.

Table 12

Oxygen index of cotton and cotton/PES fabrics

Substrate	Oxygen index, %			
	initial	basic treatment (SA +APP)	basic treatment + Na^+-MMT	basic treatment + Na^+-MMT + melamine
Cotton	18	28	29	30
Cotton/PES	18	27.5	28	28

The introduction of APP allows increasing the resistance to ignition of the materials used, as evidenced by an increase in the oxygen index of cotton and cotton/PES fabrics up to 28 and 27.5%, respectively. The formation of a protective barrier with the addition of 2% Na^+-MMT and a corresponding decrease in the flame retardant increase the volume percentage of oxygen required to create the combustion conditions of the studied samples to 29 and 28%, respectively.

The additional intumescent effect of melamine leads to an increase in the oxygen index of the cotton fabric up to 30%, however, it will not affect the oxygen index of the cotton/PES fabric. It should be noted that during the vertical combustion of cotton and cotton/PES fabrics, the introduction of melamine contributed to a decrease in the height of the carbonized area (Fig. 31).

According to the quality indicators of fire-retardant finishes, presented in Table 13, it is seen that the developed finishing composition makes it possible to obtain fireproof textile materials having high mechanical properties and resistant to 5 cycles of washing and dry cleaning.

Table 13

Quality indicators of flame retardant finishing

Finishing composition	Substrate	Breaking load, H	Height of carbonized area, cm	Residual burning time, s	Residual smoldering time, s	The height of the carbonized area after 5 washes, cm	The height of the carbonized area after 5 dry cleaners, cm
Classic technology: APP – 300 g/l; thermosetting resin precondensates – 60 g/l;	cotton	449	2.1	0	0	7.3	7.5
	cotton/ PES	831	2.6	0	0	10.9	11.0
Proposed technology: APP – 188 g/l, Na^+-MMT – 4 g/l; melamine – 8 g/l; SA – 150 g/l	cotton	954	4.3	0	0	9.7	10.8
	cotton/ PES	1510	5.0	0	0	11.7	11.9

The effectiveness of the use of montmorillonite nanoparticles and the intumescent agent melamine with ammonium polyphosphate as synergistic flame retardants consists in the migration of nanoplates under the action of decomposition products on the surface of the foamed coke-like layer with the formation of an “insulator” of the textile substrate, which serves as a barrier to the penetration of oxygen, heat and flame into the deeper layers as evidenced by micrographs of the surface of the burned fibers.

7.4. Thermogravimetric analysis of initial fabrics and fabrics treated with flame retardant polymer compositions. The effect of flame retardant compositions on the decomposition of the initial cotton and cotton/PES fabrics under high-temperature exposure was studied using TGA on a Perkin-Elmer TGA 7 device in an air atmosphere at a heating rate of 10°C per min. The dependence of the mass fraction of the residues of the cotton fabric samples on the applied temperature is shown in Fig. 33.

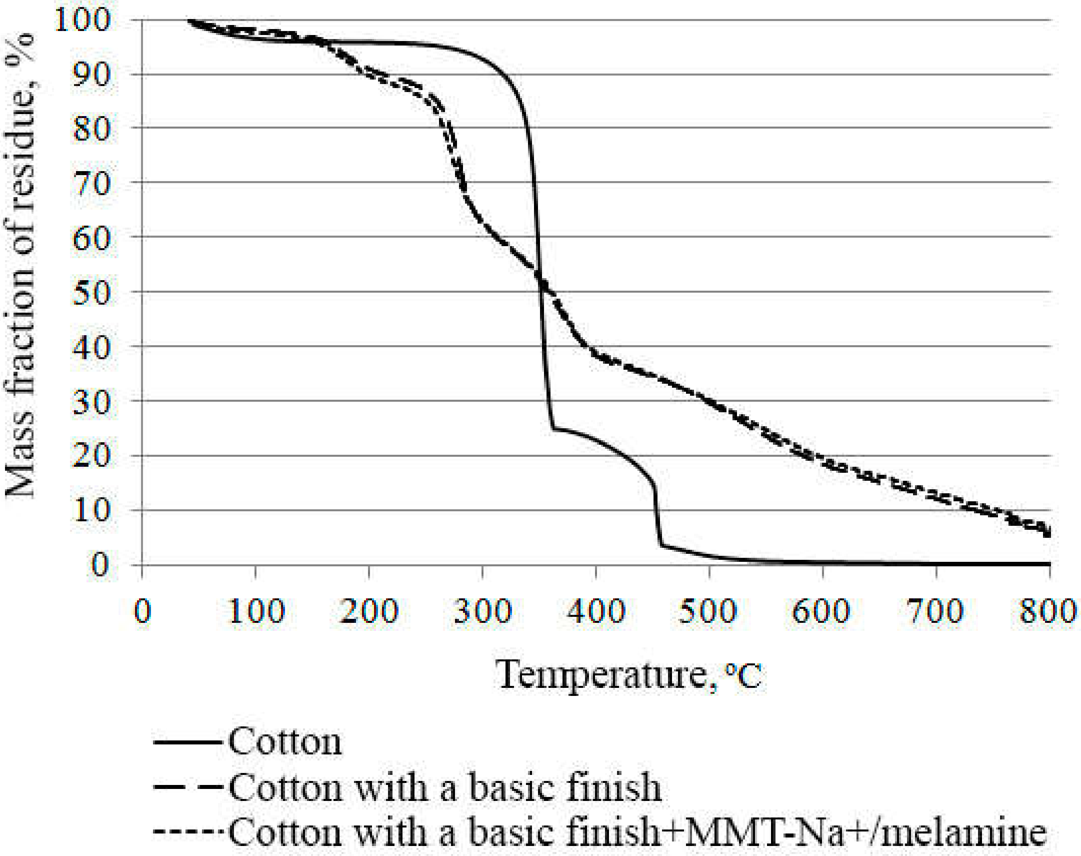


Fig. 33. TGA of cotton fabric.

As can be seen from the thermograms, the initial and treated samples exhibit similar behavior during thermal decomposition. For cotton, weight loss is observed in three temperature ranges [73–75]. The first mass loss region, located between ambient temperature and 150°C, corresponds to the loss of water molecules bound to hydroxyl groups in the cellulose polymer. In this area, the mass loss is less than 4% for all samples studied.

The main stage of destruction is in the second temperature range, which is located between 200 and 400°C. Thus, 10% degradation ($T_d^{0,1}$) of the initial cotton material occurs at 318°C, and 50% ($T_d^{0,5}$) at 355°C. The transition to a lower temperature of destruction is observed in the case of finishing cotton fabric with a basic composition and a composition containing APP, Na^+-MMT and melamine. The use of the basic composition reduces $T_d^{0,1}$ to 210°C, and the composition with APP, Na^+-

MMT and melamine to 199°C. The polyphosphoric acid formed at the second stage of degradation activates the carbonization of the coating and, in combination with Na^+-MMT, acts as a barrier preventing the diffusion of combustible decomposition products into the flame zone and oxidizing agent, primarily air oxygen, into the polymer decomposition zone. In this regard, $T_d^{0,5}$ shifts to higher temperatures and corresponds to 358 and 364°C.

The mass loss of the initial fabric and fabrics with fire retardant finish depending on the applied temperature are given in Table 14.

Table 14

Change in mass of cotton fabric samples depending on temperature

Sample composition	The main stage of destruction		Mass fraction of residue with increasing temperature, %							
	$T_d^{0,1}$, °C	$T_d^{0,5}$ °C	100	200	300	400	500	600	700	800
Initial cotton fabric	318	355	96.29	95.63	92.74	23.09	2.82	1.93	0.37	0.33
Cotton fabric with basic treatment	210	358	97.96	90.83	62.58	38.35	29.76	18.57	12.21	5.38
Cotton fabric with basic treatment+ Na^+-MMT + melamine	199	364	97.57	89.92	62.92	38.97	30.54	19.70	13.36	6.45

Mass losses in the third temperature range occur between 400 and 600°C. At 600°C in an atmosphere of air, the mass fraction of the balance of untreated cotton fabric is 1.93%. The coke residue of a cotton fabric sample treated with a composition containing APP, Na^+-MMT and melamine, under similar temperature conditions, is higher than when treated with the basic composition (18.57%), and is 19.7%.

Loss of mass at temperatures below 150°C for the initial cotton/PES fabric and samples treated with compositions, occurs mainly due to dehydration of the fibers and is 2–3%, as shown in Fig. 34.

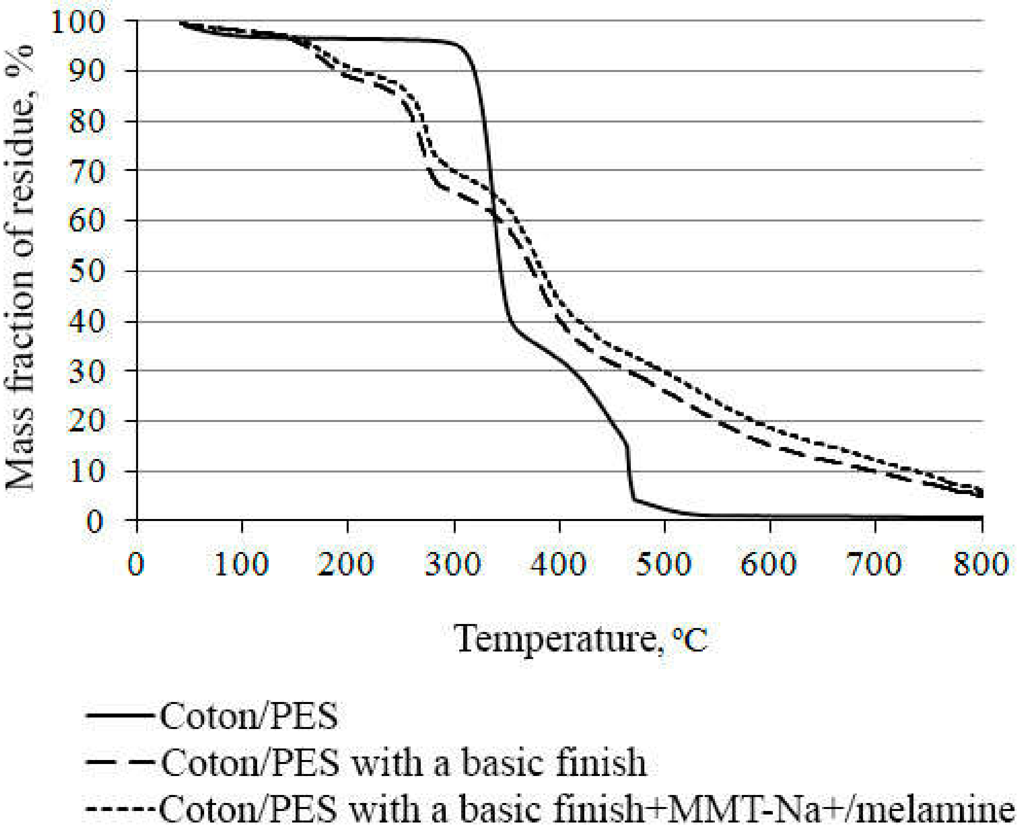


Fig. 34. TGA of cotton/PES fabric.

According to published data [76], thermal degradation of PES fabric is 410°C. However, the relatively low content of PES fibers in the mixed fabric (22%) did not significantly affect the decomposition of the initial cotton/PES sample in the second temperature range, which undergoes $T_d^{0,1}$ at 321°C and $T_d^{0,5}$ at 347°C (Table 15), which actually corresponds to the decomposition temperature of the cotton fabric.

Cotton/PES fabric exhibits a distinctive amount of coke residue in the temperature range 350–450°C, namely 9% higher than that of cotton fabric, which can be explained as follows: thermal decomposition of cotton begins at a temperature significantly lower than required for thermal degradation of polyester. Thus, cotton acts as the initial source of ignition in the mixed cotton/PES fabric. Therefore, in the second temperature range, mass loss occurs mainly due to the complete decomposition of cotton and the partial decomposition of polyester [77–79].

Table 15

Change in mass of cotton/PES fabric samples depending on temperature

Sample composition	The main stage of destruction		Mass fraction of residue with increasing temperature, %							
	$T_d^{0,1}$, °C	$T_d^{0,5}$ °C	100	200	300	400	500	600	700	800
Initial cotton/PES fabric	321	347	96.85	96.35	95.44	32.66	3.84	2.70	1.05	0.91
Cotton/PES fabric with basic treatment	193	378	98.16	89.26	65.98	40.96	26.34	15.33	9.88	4.84
Cotton fabric with basic treatment + Na^+-MMT + melamine	192	384	97.98	90.87	69.93	44.14	29.80	19.80	12.23	5.39

The main stage of destruction of the cotton/PES fabric treated with the base composition and the composition containing APP, Na^+-MMT and melamine, as in the case of finishing the cotton sample, occurs with the formation of a protective barrier at $T_d^{0,1}$ equal to 193 and 192°C, the result of which is an increase in $T_d^{0,5}$ to 378 and 384°C.

In the third temperature range at 600°C, the coke residue of the initial cotton/PES fabric is 2.7%. Treatment with flame retardants increases the mass fraction of the residue at 600°C and corresponds to 15.3% for the base composition, and 19.8% for the composition containing APP, Na^+-MMT and melamine.

After analyzing the data on the coke-forming ability of cotton and cotton/PES fabrics, we can conclude that when flame retardant with a composite containing APP, Na^+-MMT and melamine, the initial temperature of fiber degradation is significantly reduced due to the formation of a fire-retardant barrier, while the mass fraction of carbonized cotton fabric residue at 600°C increases from 1.9 to 19.7%, and cotton/PES fabric – from 2.7 to 19.8%.

Thus, the rationale behind the purposeful selection of environmentally friendly fire retardant components is laid in the work, taking into account their synergistic action and the ability to provide a stable finish. Effective fire retardant compositions based on the Na^+-form of montmorillonite, phosphorus–nitrogen–containing flame retardant, intumescent agent and an aqueous dispersion of styrene-acrylic polymer have been developed.

Taking into account the chemical structure of the components of the flame retardant composition, a probable mechanism for the formation of a thermal barrier in the process of thermal degradation of the composition due to the accumulation on the surface of the textile material of a silicon–aluminum–phosphate structure obtained as a result of the interaction of the acid catalytic centers of the Na^+-form of montmorillonite and phosphoric acid generated by ammonium polyphosphate is proposed.

The effectiveness of adding a styrene-acrylic binder to the fire retardant, which is able to form a dense spatial network on the fiber surface, has been proved, which contributes to the immobilization of flame retardants in the polymer matrix, increasing the resistance of the finish to physico-chemical influences and increasing the strength of the treated textile materials.

Due to the fact that Na^+ interlayer ions have low electric charges, leading to deflocculation and dispersion of mineral particles in water, a suspension of montmorillonite Na^+-form is obtained, which is stable over a wide pH range.

To predict the formation of a transparent film, X-ray diffraction analysis of compositions containing layered silicate was performed. It was found that when a suspension of the Na^+-form of montmorillonite is introduced into the styrene-acrylic polymer up to 2%, an exfoliated (stratified) silicate structure is formed with a uniform distribution of the plates in the polymer matrix. An increase in the content of flake filler to 3% leads to aggregation of the plates into packs with an increase in the interlayer space, which is accompanied by a decrease in the optical characteristics of the composites.

The introduction of a 4% layered silicate into the polymer matrix leads to an increase in the cross-linking strength on the polymer/clay interface, which occurs due to the formation of a physical network of polymer macromolecules with silicate filler nanoparticles, and also helps to reduce the diffusion of solvent, gas molecules or flame into the polymer matrix, by increasing the barrier properties of polymer composites.

The use of montmorillonite alone is not sufficient to impart flame retardant properties to textile materials. However, the structure of the shielding layer on the surface of elementary fibers was established, formed as a result of sintering of laminated plates of the Na^+-form of montmorillonite and protecting the fiber from flame.

The work shows the effectiveness of using layered silicate in a composition with ammonium polyphosphate and melamine, due to the synergistic effect of flame retardants, which increases the refractory characteristics of cotton and cotton/PES fabrics. By the method of mathematical modeling, it was determined that the maximum flame retardant effect is achieved by introducing the Na^+-form of montmorillonite into the fire retardant composition in an amount of 2% for cotton fabrics and of 2.3% for cotton/PES fabrics.

The micrographs of the charred fabric sections demonstrate the formation of a dense carbonized layer with silicate particles on the fiber, which slows down the pyrolysis of the film-forming styrene-acrylic polymer and, as a consequence, the textile substrate, which is confirmed by the increase in the mass fraction of the coke residue and the increase in the oxygen index.

In addition, the migration of silicate plates onto the surface of the carbonized layer is enhanced by the formation of gas bubbles initiated by the decomposition of both ammonium polyphosphate and melamine and polymer chains, thus forming a foamed fire-retardant screening barrier against a flame on the fabric surface, under which the fibers remain relatively intact.

CONCLUSIONS

In the course of the study, the composition was developed for the fire retardant finish of cotton and cotton/polyester fabrics, containing ammonium polyphosphate, an intumescent additive melamine, montmorillonite nanofiller, that are introduced into the polymer film. The synergistic effect of composition components increases the yield of coke residue and the oxygen index during thermolysis of the treated materials.

Aggregate-resistant aqueous suspensions of montmorillonite were obtained by converting the natural mineral to the anionic Na^+-form, which ensures the formation of a layered structure of the mineral in the composite on the fiber surface.

It is proved that the plate form of montmorillonite provides the formation of a dense shielding layer, which serves as a barrier to the penetration of oxygen, heat and flame into the internal structure of the fiber. It has been established that an increase in the cross-linking strength at the polymer / layered silicate interface occurs due to the formation of a physical network of styrene-acrylic polymer macromolecules with filler nanoparticles, which helps to reduce the diffusion of solvent and oxygen molecules or flame into the polymer matrix by increasing the barrier properties of polymer composites.

A probable mechanism of the formation of a silicon-aluminium-phosphate structure as a result of the reaction between phosphoric acid generated by ammonium polyphosphate and the acid catalytic centers of montmorillonite is proposed, which leads to an acceleration of the oxidative dehydrogenation of the composition and the formation of cross-linked coke on the surface of textile fibers. The effectiveness of melamine as an intumescent agent that promotes the migration of plates of the Na^+-form of montmorillonite during thermal decomposition with the formation of an insulating foam coke layer on the surface of a textile material is shown.

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