STUDY OF STRUCTURE AND THERMAL CHARACTERISTICS OF STYRENE ACRYLIC POLYMER FILMS LACRYTEX 430 FILLED OF TITANIUM DIOXIDE

Ihor Horokhov, Irina Kulish, Tatyana Asaulyuk, Yulia Saribyekova, Sergey Myasnykov, Olga Semeshko and Natalia Skalozubova

Kherson National Technical University, Berislav highway 24, 73008 Kherson, Ukraine
kulish.in.411@gmail.com

Abstract: *The research is devoted to study the influence of nanosized titanium dioxide on the structure of polymer films formed from styrene acrylic polymer for the development of fire retardant finishing compositions for textile materials. An aqueous dispersion of styrene acrylic polymer Lacrytex 430 and nanosized titanium dioxide were used as the objects of study. Standardized methods have been applied to study the stability of suspensions of aqueous systems and the structure formation, surface morphology, degree of thermal destruction of filled and unfilled with titanium dioxide styrene acrylic polymer films. The degree of dispersion of the nanofiller in the styrene acrylic polymer matrix is determined. The morphology of the formed films is considered and the optimal concentration of titanium dioxide in the polymer film is determined. The degree of interaction between the components of the mixture was estimated and it is shown that titanium dioxide does not change the structural parameters of the filled and unfilled polymer at a concentration of 1-2 wt.%. Increased concentration of titanium dioxide negatively affects both on the density of crosslinking of the polymer units and on the molecular weight of the polymer chain segment due to the agglomeration of titanium dioxide nanoparticles in the polymer matrix, which can create stress concentration zones and suppress the effect of interfacial interaction of the components. Considering that the introduction of fillers into polymers can change the temperature characteristics of polymer composite materials, the process of thermooxidative decomposition of formed polymer films and the formation of coke residue have been studied. It is determined that the introduction of nanosized titanium dioxide promotes coke formation and increases the thermal stability of the filled polymer film.*

Keywords: *styrene acrylic polymer, polymer film, nanoparticles, titanium dioxide, thermal degradation, coke forming ability, fire retardant finishing compositions.*

1 INTRODUCTION

The problems of the environment and human health that arise when using flame retardants motivate scientists to search for new environmentally friendly substances. Traditional flame retardants for treatment of textile materials, such as halogen-containing substances or additives containing heavy metals, have a number of negative properties. It is forbidden to use formaldehyde-containing preparations for fabrics that are introduced into the fire retardant composition in order to increase its resistance to washing.

Among the directions for slowing down combustion processes, the introduction of nanoparticles into flame retardant finishing compositions as thermophysical additives can be noted [1].

For impregnation of nanoparticles, polymers or polymer blends are most often used. Due to the combination of various functional features, the formed nanocomposites are capable of providing excellent, often synergistic, material properties.

One of the main effects of the introduction of inorganic additives into the polymer is the dilution of the organic structure and its distribution to isolated domains, filling the pores and amorphous regions of the polymer. Therefore, during ignition, the destruction of such a structure becomes a more complex process due to the need to increase the amount of heat to achieve the pyrolysis temperature. This effect of "heat dissipation" is enhanced by higher heat capacity and lower thermal conductivity of the fillers or their endothermic decomposition. Aluminium oxide, mica, feldspar, clay, titanium dioxide, etc. can be used for this purpose.

It was shown in [2] that the addition of nanoparticles reduces the flammability of polymers due to a decrease in the rate of heat release, an increase in the time of ignition, and an ability to self-extinguish. The mechanisms of such protection include physical barrier effects and catalytic processes that can modify the degradation of polymers and form charred protective layers reinforced by nanoparticles. The inherent properties of nanoparticles are dependent on dispersion and chemical modifications to improve compatibility with polymers.

Nanoparticles of metal compounds showed good results in reducing flammability, since these substances are resistant to temperatures up to 1000°C (hydroxides, carbon nanotubes, etc.). Substances that decompose at temperatures below 400-500°C (hydroxides, salts) also give high flame retardant properties [3]. Metal oxides are also able to catalyze coke formation processes and form a protective layer on the surface of a burning polymer.

The most studied metal oxides include titanium dioxide, which in addition to thermal properties has a number of defining characteristics: non-toxicity, good electrical, chemical, thermal and photocatalytic properties.

The effect of the introduction of nanosized particles of titanium oxide (TiO_2) and iron oxide (Fe_2O_3) on thermal stability and reaction to the action of fire of polymethylmethacrylate (PMMA) was studied in [4]. It was shown that introduction of a small amount (5 wt.%) of nanosized Fe_2O_3 and TiO_2 increased the thermal stability of PMMA nanocomposites. The improvement in fire resistance of PMMA/TiO_2 and PMMA/Fe_2O_3 nanocomposites is explained by the limited mobility of polymer chains as a result of the reinforcing effect between the polymer and the surface of nanoparticles.

The inclusion of TiO_2 nanoparticles in PMMA leads to an improvement in fire resistance with a decrease in the peak heat release rate by ~40% [5].

Several works have focused on such approaches, as combining the flame retardant action of nanosized metal oxides (TiO_2, Al_2O_3) with coke formation induced by phosphorus flame retardant systems (ammonium polyphosphates, phosphinates) in PMMA [6]. Using the method of cone calorimetry with irradiation of 30 kW/m^2, it was established that in the presence of 20% nano-TiO_2 the heat release rate of the PMMA-based nanocomposite decreases by 50%. And when ignited, this index increases significantly (by more than 20 s). This phenomenon is explained by heat transfer between metal oxide nanoparticles and polymer chains due to an increase in the nanofiller/polymer contact surface. In addition, it was found that the introduction of TiO_2 into the PVC melt significantly inhibits the release of hydrogen chloride, flammable and toxic gases during the combustion process. Transition metal oxides such as MnO_2 and Fe_2O_3 do not have this advantage. Moreover, they contribute to the process of release and combustion of hydrogen chloride.

Given the above, it can be concluded that the development trends of the finishing industry are aimed at creating and expanding the introduction of organo-inorganic composite materials that can improve the quality of textile materials. The combination of the properties of inorganic nanoparticles, in particular heat resistance and reinforcing ability, with the technological characteristics of the polymer will contribute to the production of nanocomposite materials with desired properties for finishing industry.

2 THE GOAL OF THE STUDY

The goal of the work is to study the efficiency of filling a polymer film with nanosized titanium dioxide, and to establish the effect of this additive on the structure formation and thermophysical characteristics of the Lacrytex 430 styrene acrylic polymer.

3 MATERIALS AND METHODS

The zeta potential of the aqueous suspension of titanium dioxide with concentration of 0.02 wt.% depending on pH was measured by introducing a small amount of the suspension into the cells of Malvern Instruments Technical Note MRK 654-01 (Malvern, England) at room temperature and in the pH range from 2 to 10. Previously the suspension was stirred for 20 minutes on a magnetic stirrer. To improve the result, the suspension of titanium dioxide was subjected to 15 minutes of ultrasonic treatment.

An aqueous dispersion of styrene acrylic polymer Lacrytex 430 manufactured by OOO Polymer-Lak (Ukraine) was studied as a film former. Characteristics of the dispersion are given in Table 1.

Table 1 Characteristics of Lacrytex 430

Chemical composition	Dry residue [%]	pH	Particle size [µm]	Viscosity [MPa·s]
aqueous dispersion of copolymers of ester of acrylic acid and styrene	50	7.5-8.5	≈ 0.1	5000-15000

A polymer nanocomposite was created by introducing previously prepared suspensions of titanium dioxide in various concentrations into an aqueous dispersion of a styrene acrylic polymer.

The surface morphology of composite polymer films was studied using scanning electron microscopy.

Structural parameters of polymer films filled with titanium dioxide were determined by sol-gel analysis.

The chemical structure of polymer films filled with nanosized titanium dioxide was studied using IR spectroscopy. The spectra were obtained on a Nicolet-iS10 IR Fourier spectrometer (Thermo Fisher Scientific, USA) using a DTGS detector, a Smart Performer attachment equipped with a ZnSe crystal. The measurements were carried out with an expansion of 4 cm^{-1}, spectral region 4000-650 cm^{-1}. The spectra were processed using the OMNIC-7.0 program.

The method of thermogravimetric analysis was used to determine the efficiency of titanium dioxide as a thermophysical additive in a styrene acrylic polymer. The change in mass when exposed to elevated temperatures on the polymer was studied using TGA 7 (Perkin Elmer, USA). The samples of polymer films weighing 15 mg were heated at a temperature of 40 to 800°C at a constant heating rate of 10°C/min.

4 RESULTS AND DISCUSSION

In the textile industry, the studied nanomaterials are most often dispersed in multicomponent water systems. This can potentially lead to physicochemical changes in properties. For example, the state of agglomeration and surface charge are important characteristics of dispersions. During dispersion of nanoparticles in aqueous solutions, surface ionization and adsorption of cations or anions leads to the formation of a surface charge and the formation of an electric potential between the surface of particles and a volume of the dispersion medium.

To effectively control the properties of suspensions of amphoteric oxides, in particular titanium dioxide, the pH of the medium is changed, and additives of low molecular weight surfactants are introduced [7]. The aggregate stability of aqueous suspensions of titanium dioxide without surfactant additives is determined by the ion-electrostatic factor in accordance with the theory of Deryagin – Landau – Fairway – Overbek. The main factor affecting aggregative stability is the electrostatic barrier of interaction between particles.

Depending on the measurement technique, the surface charge can be represented by the surface charge density (potentiometric titration) or the zeta potential (electrokinetic method).

In the work, the stability of an aqueous suspension of titanium dioxide was evaluated based on measurements of the zeta potential using electrophoretic mobility. As a rule, in order to achieve a stable dispersion, the necessary value of the zeta potential should be below -30 mV or above 30 mV, i.e. in the range of -30 mV > ζ > 30 mV.

Agglomeration of nanoparticles in an aqueous system can be controlled by the hydrodynamic diameter of the dispersion. In the classical theory of stability of dispersed systems of Deryagin – Landau – Fairway – Overbek, the agglomeration of nanoparticles is determined by the sum of the electrostatic repulsive forces (the interaction of the double electric layer surrounding each particle) and the attractive force. An increase in the surface charge of particles (zeta potential) can increase the electrostatic repulsive force, prevent agglomeration and, therefore, reduce the hydrodynamic size of the dispersion.

A graph describing the effect of the pH of solution on the zeta potential of titanium dioxide nanoparticles is in Figure 1.

According to the results of measuring the electrokinetic properties, it was found that at the pH of 7 to 10, the suspension of titanium dioxide is stable because it has a significant negative zeta potential (from -30 mV to -45 mV). These results are consistent with published data [7-10].

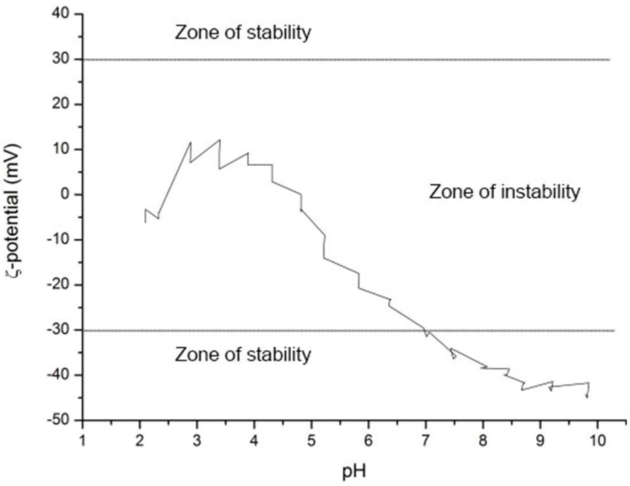


Figure 1 Dependence of the zeta potential of titanium dioxide nanoparticles on the pH of a medium

At the pH values from 2 to 7, the zeta potential is in the instability zone (from 10 mV to -30 mV). As a result, the attractive forces can prevail over the repulsive forces, that leading to the aggregation of titanium dioxide nanoparticles. The pH of the aqueous dispersion of styrene acrylic polymer Lacrytex 430 is in the range from 7.5 to 8.5, which is a favorable medium for nano-TiO_2 dispersion.

The dispersion of nanofiller in a polymer matrix affects the properties and purpose of nanocomposites. Considering that the use of nanoparticles with high uncompensated surface energy in a composition with a polymer can lead to the formation of aggregates, we studied the morphology of polymer films by the distribution of TiO_2 nanoparticles in the Lacrytex 430 polymer matrix. The research results are presented on micrographs of the surface of composite polymer films (Figure 2) obtained by scanning electron microscopy (SEM).

As can be seen from microphotographs in Figures 2a, 2b, the distribution of TiO_2 nanoparticles in styrene acrylic polymer with a filling of 1-3 wt.% is homogeneous with an insignificant amount of small agglomerates. With an increase in the TiO_2 content in the polymer matrix to 5 wt.%, the formation of large agglomerates (more than 1 mm) is observed (Figure 2c). Thus, the tendency to agglomeration of nanoparticles increases with a higher filling of the polymer with titanium dioxide (above 5 wt.%), which can negatively affect the initial properties of nanocomposites.

It is known that the introduction of fillers in polymers significantly changes the properties of polymer composite materials. In this regard, the study of the influence of fillers on the structural characteristics of the polymer films of styrene acrylic polymer Lacrytex 430 is of particular importance.

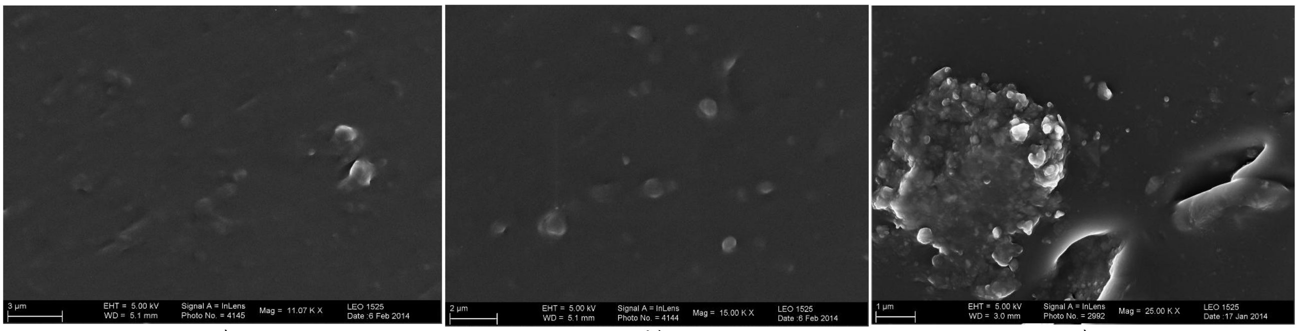
The degree of interaction between components of the mixture was estimated by sol-gel analysis through the equilibrium swelling of nanocomposites in solvents (Table 2).

According to the results of the study (Table 2), it was found that the introduction of titanium dioxide nanoparticles into the styrene acrylic polymer Lacrytex 430 does not lead to an improvement in the structural parameters of nanocomposites. At a concentration of nano-TiO_2 up to 2 wt.%, the average molecular chain length and the degree of crosslinking remain unchanged. Increasing the concentration of titanium dioxide reduces the studied parameters. As can be seen from the data of Table 2, the TiO_2 content above 3 wt.% increases the average molecular length, reduces the crosslinking density, which may be a consequence of the agglomeration of particles of titanium dioxide in the polymer.

The results of studying the chemical structure of polymer films using IR spectroscopy are presented in Figure 3.

The IR spectra of nano-TiO_2 are recorded in the frequency range 600-4000 cm^{-1}. Peaks at 1800-1630 cm^{-1} and wide peaks arising at 3100-3600 cm^{-1} correspond to stretching and deformation vibrations of hydroxyl groups on the surface of TiO_2 particles. A peak of about 2300 cm^{-1} is associated with CO_2 adsorbed on the surface of titanium dioxide. Strong absorption bands between 700 and 600 cm^{-1} relate to vibrations of Ti-O and Ti-O-Ti.

The IR spectra of the TiO_2/polymer nanocomposite are a combination of typical absorption spectra of the styrene acrylic polymer Lacrytex 430 and TiO_2. The characteristic absorption bands of the corresponding monomeric units of acrylate [11] are present at 1728 cm^{-1}, which is the result of asymmetric and symmetric stretching vibrations of the C=O carboxyl group. The S-O-C sites are observed at 1158 cm^{-1}, and deformation vibrations of $C\text{-}CH_3$ are observed at 1452 cm^{-1}. While the C-H out-of-plane peak is observed at 758 cm^{-1}, other prominent absorption peaks at 2955, 2923 and 2853 cm^{-1} are due to aliphatic (C-H) regions such as – CH_2 and -CH_3. The peak of average absorption at 698 cm^{-1} is associated with the externally in-plane bending of the phenolic ring. The spectrum of the TiO_2/polymer nanocomposite shows significant absorption at 668 cm^{-1}, which represents the Ti-O band.



a) b) c)

Figure 2 SEM image of the surface of Lacrytex 430/TiO_2 nanocomposites: a) Lacrytex 430/TiO_2 1 wt.%; b) Lacrytex 430/TiO_2 3 wt.%; c) Lacrytex 430/TiO_2 5 wt.%

Table 2 Structural parameters of Lacrytex 430 polymer films filled with TiO_2

TiO_2 content in polymer film [wt.%]	Structural indicators		
	Interaction index polymer/filler	Molecular weight of the chain segment Mc [g/mol]	Crosslinking density $v \times 10^{-3}$ [mol/cm^3]
without additives	–	52	9.6
1	0.94	52	9.6
2	0.97	52	9.6
3	1.01	62	8.1
4	1.02	67	7.5
5	1.03	67	7.5
10	1.06	70	7.1
20	1.10	78	6.4
30	1.14	83	6.0

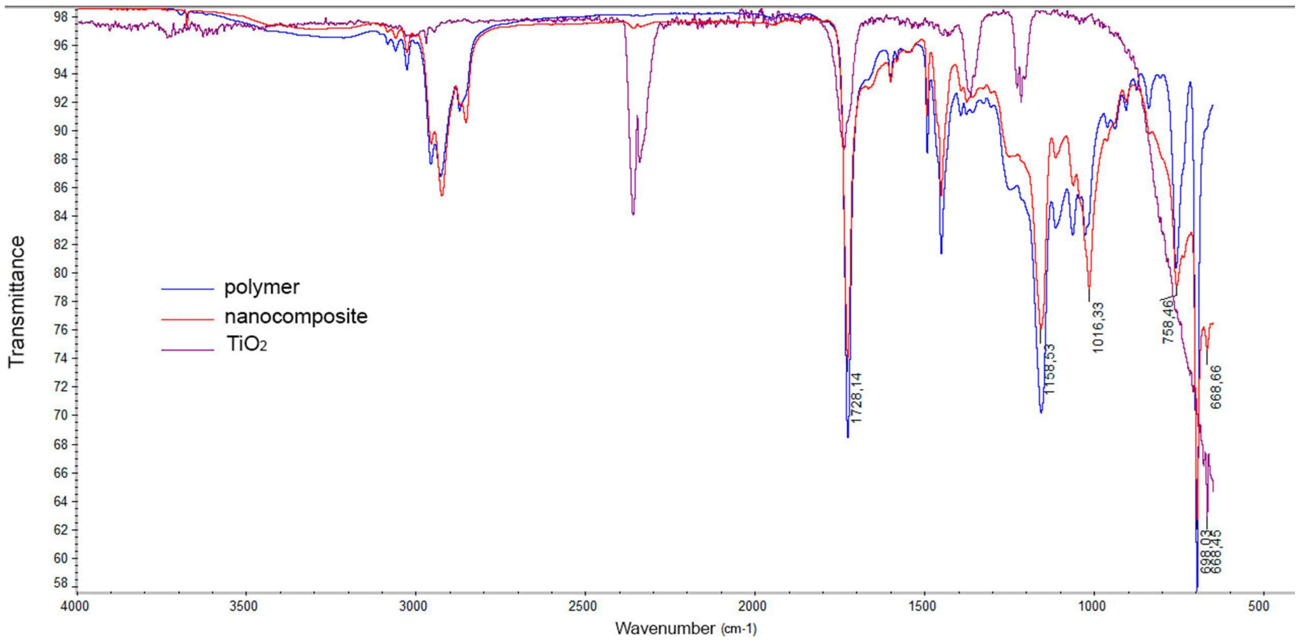


Figure 3 IR spectra of styrene acrylic polymer films

The effect of filling a polymer film with titanium dioxide on the process of thermooxidative decomposition of materials and the formation of a coke-like residue was evaluated by the method of thermogravimetric analysis. The thermograms of polymer composites are shown in Figure 4.

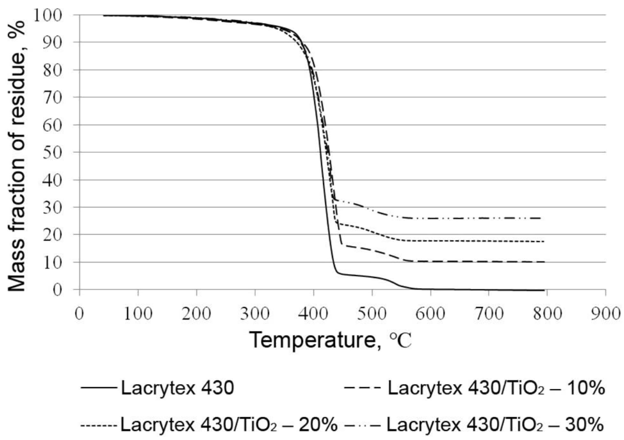


Figure 4 Thermogravimetric analysis of styrene acrylic film filled with titanium dioxide

The main stages of thermal destruction of the polymer composites are presented in Table 3.

According to the Table 3, styrene acrylic polymer has an initial decomposition temperature of 379°C. The initial temperature of destruction of $T_d^{0.1}$ for nanocomposites with TiO_2 of 30 wt.% corresponds to 372°C, and the half stage of destruction of $T_d^{0.5}$ rises to 425°C.

As can be seen from the obtained data (Table 3), an unfilled styrene acrylic polymer at a temperature of 600°C almost completely degrades, while the coke residue of nanocomposite films with different filling ranges from 10.39 to 25.95% and increases with increasing titanium dioxide content.

It can be concluded that the thermal degradation of nanocomposites is significantly affected by the interfacial interaction between the polymer and the nanoparticle, which allows nanoparticles to act as restriction zones (limitations). In turn, restricting the movement of the polymer chain makes its destruction more difficult at low temperatures and moves the temperature of the destruction of the polymer film filled with titanium dioxide to higher temperatures.

Table 3 Effect of temperature on the mass change of the styrene acrylic polymer Lacrytex 430 filled with titanium dioxide

Nanocomposite films [wt.%]	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
Lacrytex 430	379	411	99.87	98.97	97.08	70.67	4.55	0.11	0	0
Lacrytex 430/TiO_2 10	377	421	99.68	98.62	96.71	82.11	14.38	10.39	10.29	10.14
Lacrytex 430/TiO_2 20	373	423	99.61	98.91	96.81	77.12	21.12	17.85	17.76	17.56
Lacrytex 430/TiO_2 30	372	425	99.71	99.12	97.26	78.02	28.89	26.95	26.05	25.95

5 CONCLUSIONS

As a result of the experiment, the effect of the addition of nanosized titanium dioxide on the structural characteristics and thermal properties of styrene acrylic polymer Lacrytex 430 was studied. The degree of interaction between the components of the mixture was estimated and it was shown that titanium dioxide does not change the structural parameters of the polymer at a concentration of 1-2 wt.%. The efficiency of titanium dioxide as a thermophysical additive in a styrene acrylic polymer was established due to a shift in the thermal degradation of the resulting composite to a region of higher temperatures.

6 REFERENCES

1. Weil E.D., Levchik S.V.: Flame Retardants I Commercial Use or Development for Textiles, chapter 11 in Flame Retardants for Plastics and Textiles: Practical Applications, Hanser Publisher, Munich, 2009, pp. 197-226, ISBN: 978-3-446-41652-9
2. Lopez-Cuesta J.M.: Flame-retardant polymer nanocomposites, chapter 16 in Advances in Polymer Nanocomposites: Types and Applications, Woodhead Publishing: Series in Composites Science and Engineering, 2012, pp. 540-566, https://doi.org/10.1533/9780857096241.3.540
3. Yurtov E.V., Sertsova A.A., Marakulin S.I.: Ispol'zovaniye nanochastichek soyedineniy metallov dlya sozdaniya trudnogoryuchikh polimernykh tekstil'nykh materialov [The use of nanoparticles of metal compounds to create flame-retardant polymer textile materials], Proceedings of XIX Intern. Science-practical Forum SMARTEX-2016, Ivanovo, IVGPU, May 2016, Part 1, pp. 36-39 (in Russian)
4. Laachachi A., Cochez M., Ferriol M., Lopez-Cuesta J.M., Leroy E.: Influence of TiO_2 and Fe_2O_3 fillers on the thermal properties of PMMA, Materials Letters 59(1), 2005, pp. 36-39, https://doi.org/10.1016/j.matlet.2004.09.014
5. Pasini S.M, Batistella M.A., Guelli Ulson de Souza S.M.A., Wang J., Hotza D., Ulson de Souza A.A.: Thermal degradation and flammability of TiO_2-polyetherimide nanocomposite fibers, Polymer Bulletin 9/2020, 2019, https://doi.org/10.1007/s00289-019-02970-1
6. Laachachi A., Cochez M., Leroy E., Gaudon P., Ferriol M., Lopez Cuesta J.M.: Effect of Al_2O_3 and TiO_2 nanoparticles and APP on thermal stability and flame retardance of PMMA, Polymers for Advanced Technologies 17(4), 2006, pp. 327-334, https://doi.org/10.1002/pat.690
7. Petrishin R.S., Yaremko Z.M., Soltis M.N. Vliyaniye pH sredy i poverkhnostno-aktivnykh veshchestv na dzeta-potentsial i agregativnuyu ustoychivost' suspenziy dioksida titana [The effect of pH of the medium and surfactants on the zeta potential and aggregative stability of titanium dioxide suspensions], Kolloidnyy zhurnal [Colloid journal] 72(4), 2010, pp. 512-517 (in Russian)
8. Tutigin A.S., Aizenshtadt A.M., Aizenshtadt M.A., Makhova T.A.: Vliyaniye prirody elektrolita na protsess koagulyatsii saponit-soderzhashchey suspenzii [The influence of the nature of the electrolyte on the coagulation process of a saponite-containing suspension], Geoekologiya, inzhenernaya geologiya, gidrogeologiya, geokriologiya [Geoecology. Engineering geology. Hydrogeology. Geocryology] 5, 2012, pp. 470-474 (in Russian)
9. Uphill S.J., Gosgrove T., Briscoe W.N.: Flow of nanofluids through porous media: Preserving timber with colloid science, Colloids Surfaces A: Physicochemical and Engineering Aspects 460, 2014, pp. 38-50, https://doi.org/10.1016/j.colsurfa.2014.05.008
10. Kuznetsova Yu.V., Kazantseva A.A., Rempel A.A.: Dzeta-potentsial, razmer i poluprovodnikovyye svoystva nanochastits sul'fida tsinka v stabil'nom vodnom kolloidnom rastvore [Zeta potential, size and semiconductor properties of zinc sulfide nanoparticles in a stable aqueous colloidal solution], Zhurnal fizicheskoy khimii [Russian Journal of Physical Chemistry A] 90(4), 2016, pp.625-630 (in Russian), DOI: 10.7868/S0044453716040154
11. Wang S.T., Poehlein G.V.: Characterization of water-soluble oligomer in acrylic acid-styrene emulsion copolymerization, Journal of Applied polymer Science 50(12), 1993, pp. 2173-2183, https://doi.org/10.1002/app.1993.070501217