

EFFECT OF STYRENE ACRYLIC AND URETHANE POLYMER COATINGS FILLED WITH TITANIUM DIOXIDE ON THERMOPHYSICAL PROPERTIES OF FABRIC SURFACE

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

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

Abstract: The goal of the work is to study the effect of styrene acrylic and urethane polymer films filled with titanium dioxide nanoparticles on the change in the thermophysical properties of the cotton fabric surface. Aqueous dispersions of styrene acrylic polymer Lacrytex 640 and polyurethane Aquapol 14 were selected as film-forming substances. Nanosized titanium dioxide was investigated as a thermophysical additive. The effect of the filler on the structural properties of polymer composites was investigated using the equilibrium swelling method. The mechanical properties of the obtained nanocomposites were evaluated in terms of breaking load and elongation at break. The surface morphology of the nanocomposite coated fabric before and after ignition was investigated using scanning electron microscopy. Based on the results of the study of the dependence of the structural and mechanical properties of polymer films on the nanofiller content, it was found that a high degree of polymer - filler interaction efficiency is observed at titanium dioxide concentrations up to 5 wt.%. It has been proven that the interfacial interaction of titanium dioxide with polyurethane Aquapol 14 is higher than that with styrene acrylic polymer Lacrytex 640. It was found that the introduction of nanosized titanium dioxide increases the tensile strength, but decreases the plasticity of nanocomposites in comparison with unfilled polymer matrices. It is shown that the studied styrene acrylic and polyurethane coatings filled with nano-sized titanium dioxide lead to the formation of coke residue on the fiber surface under the action of a flame, which makes it possible to preserve the fabric structure upon ignition. The obtained research results are of practical importance in the development of fire retardants for finishing textile materials.

Keywords: styrene acrylic polymer, polyurethane, nanocomposite, titanium dioxide, structural characteristics, mechanical properties, coke forming ability, fire retardant coating.

1 INTRODUCTION

Concerns about the toxicity of fire retardants commonly used in the processing of textile materials have directed researchers towards creating more environmentally friendly compositions and finding effective solutions for fire protection technologies of fabrics [1, 2]. In this regard, nanostructured compositions are of interest, which can provide barrier properties to textile materials by reducing the penetration of oxygen from the fire zone to the surface of the fabric, and prevent droplet formation of the synthetic textile component during combustion. In addition, nanocomposites ensure the formation of a self-expanding thermophysical barrier on the surface, which can reduce heat and mass transfer from the atmosphere to the substrate. These advantages appear to be the most promising for the development of fire retardant compositions. Among modern coating technologies for textile materials, technologies have been developed based on the adsorption of nanoparticles (NP) and layer-by-layer assembly of components (LbL), the essence of which is one- or multi-stage surface adsorption

of nanoparticles or polyelectrolytes from dilute (≤ 1 wt.%) aqueous suspensions or solutions. In [3, 4], a highly efficient starch-based LbL coating was considered, which demonstrated the self-extinguishing behavior of cotton after 4-8 stages of deposition. The creation of ultrathin nanostructured coatings is based on the stepwise layer-by-layer deposition of various polymers and nanoparticles, which can be nanoclays, glass fabrics, silsesquioxanes (POSS), and layered double hydroxides [5-10]. The technology for obtaining such coatings is also based on multiple and alternate immersion of a textile substrate in a polymer and nanoparticles to create multilayer organic-inorganic phases.

Despite the good fire retardant properties, the significant disadvantages of the listed technologies include the multistage deposition required to achieve the desired properties (about 20-40 processing stages), which is practically unrealizable in real production conditions. However, taking into account the undoubted advantages of precisely surface methods of protecting textile materials, an urgent task is to develop simple, quickly

scalable technologies for the formation of coatings with an individual nanostructure based on readily available components with fire-fighting properties.

2 THE GOAL OF THE STUDY

The goal of the work is to study the properties of acrylic and urethane polymer films filled with nanosized titanium dioxide and the effect of the obtained polymer nanocomposites on the change in the thermophysical properties of the textile materials surface.

3 MATERIALS AND METHODS

A finely dispersed aqueous suspension of titanium dioxide was obtained by stirring on a magnetic stirrer at 600 rpm for 20 min, followed by ultrasonic treatment with an acoustic frequency of 20 kHz and exposure duration of 10 min.

An aqueous dispersions of styrene acrylic polymer Lacrytex 640 (OOO Polymer-Lak, Ukraine) and polyurethane Aquapol 14 (OOO NPP Makromer, Russia) were studied as film formers. Characteristics of the dispersions are given in Table 1.

Nanocomposites were prepared by introducing a suspension of titanium dioxide into polymer dispersions Lacrytex 640 and Aquapol 14 with stirring. Then, from the mixtures obtained, films were formed on a glass substrate and dried at 80°C. The thickness of the formed films was 0.7±0.05 mm.

The degree of interaction of the filler with the polymer matrix and the structural characteristics of the nanocomposites were studied using the equilibrium swelling method.

The polymer – filler interaction was evaluated by the change in the degree of equilibrium swelling of the obtained hybrid organic-inorganic films. For this purpose, film samples were immersed in isopropanol solvent for 24 hours. Then, after drying, the sample was weighed, placed in an oven for 24 hours at 60°C to remove residual solvent, and weighed again. The efficiency of polymer - filler interaction was calculated using the Lorentz and Parks equation [11]:

$$\frac{Q_f}{Q_g} = ae^{-z} + b \quad (1)$$

Subscripts *f* and *g* characterize filled and unfilled polymers, respectively; *z* is the weight ratio of filler to polymer; *a* and *b* are constants.

Q is determined in grams of solvent per gram of polymer and is calculated by the formula:

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

where *M_s* is the mass of the swollen sample; *M_d* is the mass of the dry sample.

The mechanical properties of nanocomposites were investigated by determining the tensile strength and elongation at break of polymer films.

The formation of a nanocomposite coating on a textile material was carried out by impregnating a cotton fabric in a solution containing 10, 20 and 30 wt.% preliminarily dispersed nano-TiO₂ and 15 wt.% polymer dispersion, followed by squeezing to 80% and drying at 80°C for 10 min.

Fabrics with a nanocomposite coating containing TiO₂ were examined by scanning electron microscopy (SEM) to study the surface morphology and structure of the textile material before and after the flammability test.

4 RESULTS AND DISCUSSION

One of the most valuable flame retardant strategies used in volumetric addition relies on the production or accumulation of a heat resistant surface layer capable of acting as a barrier to mass and heat transfer [12]. This layer, often composed of inorganic nanoparticles, forms after the substrate is ignited due to decomposition of the surface layer of the polymer.

The combustion process of a textile material can be briefly described in two stages. In the first stage, reaching the surface of the fabric, heat from a flame or other heat source is transferred into its volume. In the second stage, volatile thermal decomposition products diffuse from the fabric volume over its entire surface to the gas phase, thereby feeding the flame.

Thus, it is the surface that is the region that controls the mass and heat transfer at the interface between the gas and condensed phases [13]. The thermophysical properties of the fabric surface play a dominant role at the stages of preliminary ignition and combustion of the textile material. Therefore, a change in these surface properties can provide an increase in the fire retardant properties of the fabric.

Mineral substances are often used as fire retardants due to the physical nature of their fire retardant effects at high temperatures. With an increase in temperature, endothermic decomposition of mineral fillers occurs with energy absorption, the release of non-combustible substances (water, carbon dioxide), which dilute flammable gases, and a protective ceramic or glassy layer is formed.

Table 1 Characteristics of polymer dispersions

Trade name	Chemical composition	Dry residue [%]	pH	Particle size [μm]	Viscosity [mPa.s]
Lacrytex 640	aqueous dispersion of acrylic copolymer, modified by the addition of an adhesion promoter	55-57	2-3	≈ 0.2	<5000
Aquapol 14	aqueous dispersion of aliphatic polyurethane	35	7.4	≈ 0.1	20.1

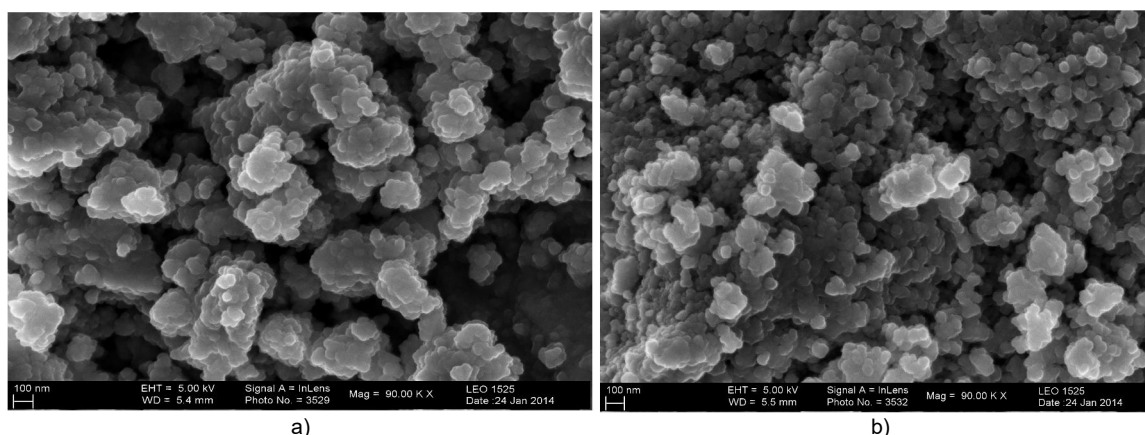


Figure 1 Micrographs of the nanosized titanium dioxide suspension: a) before ultrasonic treatment; b) after ultrasonic treatment

The introduction of nanoparticles proved to be effective to improve the shielding ability of char. In addition, an increase in fire resistance is often accompanied by an improvement in related properties, such as mechanical strength, self-healing ability, thermal conductivity, etc.

One of the basic rules for obtaining compact insulating char on the surface of textile materials is a good dispersion of nanoparticles in the polymer matrix.

In this work, nanosized titanium dioxide was investigated as a thermophysical additive. Micrographs of the aqueous suspension of nanosized titanium dioxide obtained before and after ultrasonic treatment are presented in Figure 1.

Particles of titanium dioxide before ultrasonic treatment (Figure 1a) as a result of high surface energy are significantly aggregated and form large agglomerates in suspension, which can negatively affect the uniform distribution of the filler in the polymer matrix, increase the stress in the polymer system and worsen the operational properties. As a result of sonication (Figure 1b), titanium dioxide agglomerates are significantly reduced, which makes it possible to obtain a more finely dispersed aqueous system.

Methods for achieving fire retardant properties of textile materials should be based on predicting the direction of decomposition of a nanostructured surface coating. One of these methods is the formation of a bulk carbonaceous residue, which slows down heat transfer and thereby reduces the diffusion of flammable volatile gases, which makes it possible to achieve an increase in the fire retardant properties of the fabric. In this case, the use of polymers makes it possible not only to fix nanoparticles on the fiber surface, but also to promote the formation of a protective carbonaceous layer due to the organic nature of the film former.

In this work, we investigated aqueous dispersions of styrene acrylic polymers and polyurethanes capable of forming a carbonaceous residue in order to impregnate titanium dioxide nanoparticles on the surface of a textile material. Since the properties of composites are determined by the nature of the mixed components and their structure, it is necessary to study the degree of interaction between the components of the mixture.

The Q_f/Q_g ratio characterizes the degree of interaction between the filler and the matrix. Moreover, the higher the value of this ratio, the lower the efficiency of the interaction between the filler and the matrix. The calculation data are shown in Figure 2.

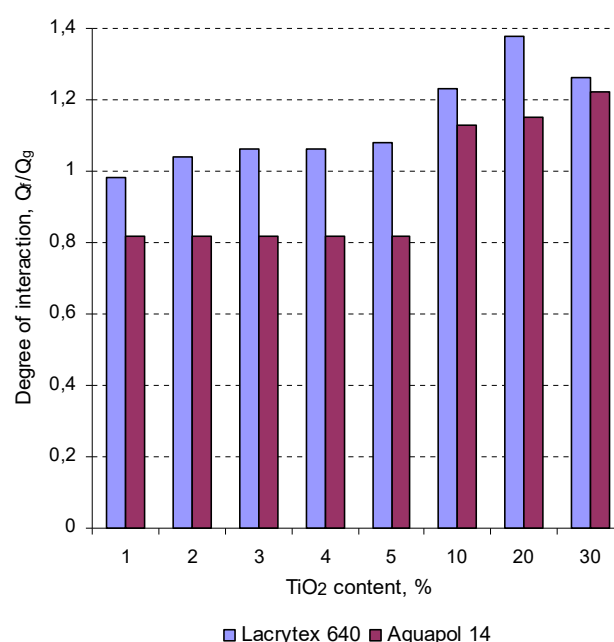


Figure 2 Degree of interaction between nanosized titanium dioxide and polymer matrix

Table 2 Structural parameters of polymers filled with TiO₂

TiO ₂ content [%]	Lacrytex 640			Aquapol 14		
	Q_f/Q_g	M_c [g/mol]	$\nu \times 10^{-3}$ [mol/cm ³]	Q_f/Q_g	M_c [g/mol]	$\nu \times 10^{-3}$ [mol/cm ³]
–	–	50	10	–	1240	0.40
1	0.98	50	10	0.82	1032	0.48
2	1.04	52	9.6	0.82	967	0.52
3	1.06	67	7.5	0.82	922	0.54
4	1.06	81	6.2	0.82	913	0.55
5	1.08	95	5.3	0.82	944	0.53
10	1.23	103	4.8	1.13	1240	0.08
20	1.38	112	4.5	1.15	1432	0.08
30	1.26	128	3.9	1.22	1527	0.07

Q_f/Q_g - the degree of interaction between TiO₂ and polymer; M_c - the average molecular weight of the chain segment; $\nu \times 10^{-3}$ - the crosslinking density of the polymer.

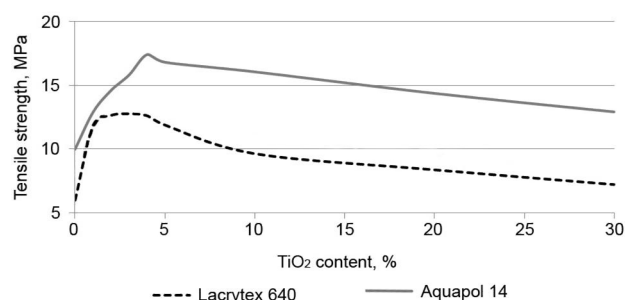
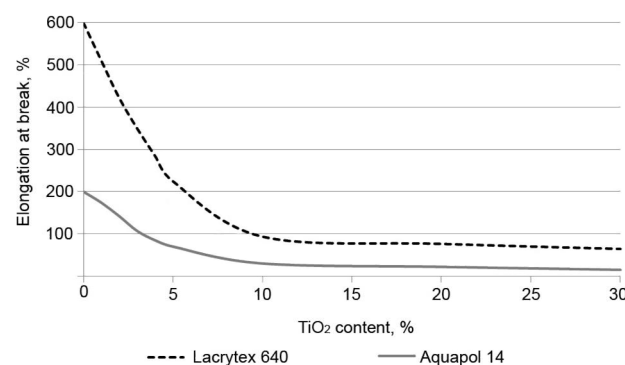
Analysis of the data presented in Figure 2 shows that the introduction of nanosized titanium dioxide in an amount of up to 5 wt.% leads to low values of the Q_f/Q_g ratio, which explains the appearance of a rather high degree of polymer–filler effective interaction. It should be noted that the efficiency of the interaction of titanium dioxide with the urethane polymer of Aquapol 14 is in all cases higher than with the styrene acrylic polymer Lacrytex 640.

Based on the experimental results obtained using the equilibrium swelling method, the crosslinking density of the polymer and the average molecular weight of the chain segment enclosed between two crosslinks were calculated. The data are shown in Table 2. The results obtained (Table 2) indicate that the introduction of titanium dioxide nanoparticles into the styrene-acrylic polymer matrix does not improve the structural parameters of the nanocomposites. At a concentration of nanosized TiO₂ up to 1 wt.%, the average molecular weight of the chain segment and the crosslinking density remain unchanged. An increase in the nanofiller content leads to a decrease in the studied parameters.

However, in the case of using polyurethane as a polymer matrix, the polymer - filler interaction is 0.82 with a nanosized TiO₂ content of up to 5 wt.%. A decrease in the average molecular weight of the chain segment by 17 - 24% is also observed. This phenomenon is caused by an increase in the polymer - filler interphase interaction, which made it possible to reduce the rate of solvent transfer by lengthening the average diffusion path. TiO₂ content above 5 wt.% negatively affects the average molecular weight of the chain segment and lowers the crosslinking density.

The interface between nanoparticles and the polymer matrix plays a decisive role in the structure - property relationship and is one of the most important factors affecting the mechanical properties of nanocomposites. The results of studying the effect of the concentration of nanofiller on the tensile strength and elongation at break of polymer composites are shown in Figures 3 and 4, respectively.

On the basis of the obtained experimental data (Figures 3, 4), it was found that nanocomposites have higher tensile strength, but lower plasticity compared to unfilled polymer matrices. With the content of nanosized TiO₂ up to 3 wt.% nanocomposites exhibit excellent mechanical properties. The tensile strength for Lacrytex 640 / TiO₂ is 12.74 MPa, which is 2 times higher than for unfilled styrene acrylic polymer. For Aquapol 14 / TiO₂, this indicator is 14.5 MPa, which exceeds the strength of unfilled urethane polymer by 1.5 times. It should be noted that with the introduction of TiO₂ nanofiller above 3 wt.% there is a decrease in tensile strength for all nanocomposites. This fact can be explained by the presence of aggregates of TiO₂ nanoparticles.

**Figure 3** Effect of TiO₂ content on tensile strength of polymer composites**Figure 4** Effect of TiO₂ content on elongation at break of polymer composites

The aggregation of nano-TiO₂ in the polymer matrix can create zones of stress concentration and suppress the effect of interfacial interaction; therefore, the mechanical properties of nanocomposites decrease. Elongation at break of the studied nanocomposites (Figure 4) with nanoparticle content of 3 wt.% is reduced by almost 25% for the styrene acrylic polymer matrix Lacrytex 640 and by 50% for the Aquapol 14 polyurethane.

Analysis of the results of studying the mechanical properties of filled polymer films shows that the presence of nanosized TiO₂ in the polymer matrix limits the mobility of polymer chains, as a result of which the plasticity of nanocomposites decreases. If ignition occurs, the limited mobility of the polymer macromolecules will provide a reinforcing effect on the composite surface, which will help to reduce the drop formation of the synthetic component of the textile material.

At the next stage of the work, a study of the fire resistance of textile materials treated with the investigated polymer nanocomposites was carried out.

There is a significant difference in the size of the flame between the untreated samples and fabrics with polymer coating containing 10, 20 and 30 wt.% nano-TiO₂. The height of the flame for vertical combustion 6 s after ignition is lower on fabrics with a nanocomposite coating than

on the untreated sample. In addition, after removal of the flame, a more intense residual glow was observed on the untreated samples. The residual smoldering time for untreated samples is 15 s, and for fabrics with nanocomposite coating it is 10 - 12 s.

Micrographs of untreated fabric sample and samples with nanocomposite coatings before and after thermal exposure are shown in Figure 5.

The flammability test shows that the untreated textile is completely destroyed by flame, so there is no micrograph of the surface of this sample after ignition. The results of SEM analysis of the fabric microstructure indicates that all samples with nanocomposite coating (Figures 5b, 5c) showed the presence of significant coke residue, which made it possible to prevent further thermal degradation of the fiber-forming polymer (Figures 5d, 5e).

A decrease in the flammability of a polymer under the action of nanoparticles occurs through several mechanisms, which consist in limiting the transition of combustible substances into a flame, the formation of a charred protective layer, etc. Analysis of the fabric samples surface with a nanocomposite coating (Figure 5) showed that the presence of 20 wt.% nanosized TiO₂ in the polymer matrix preserve fabric structure after ignition. However, a high concentration of nanofillers leads to uneven distribution and aggregation of nanoparticles on the fiber surface.

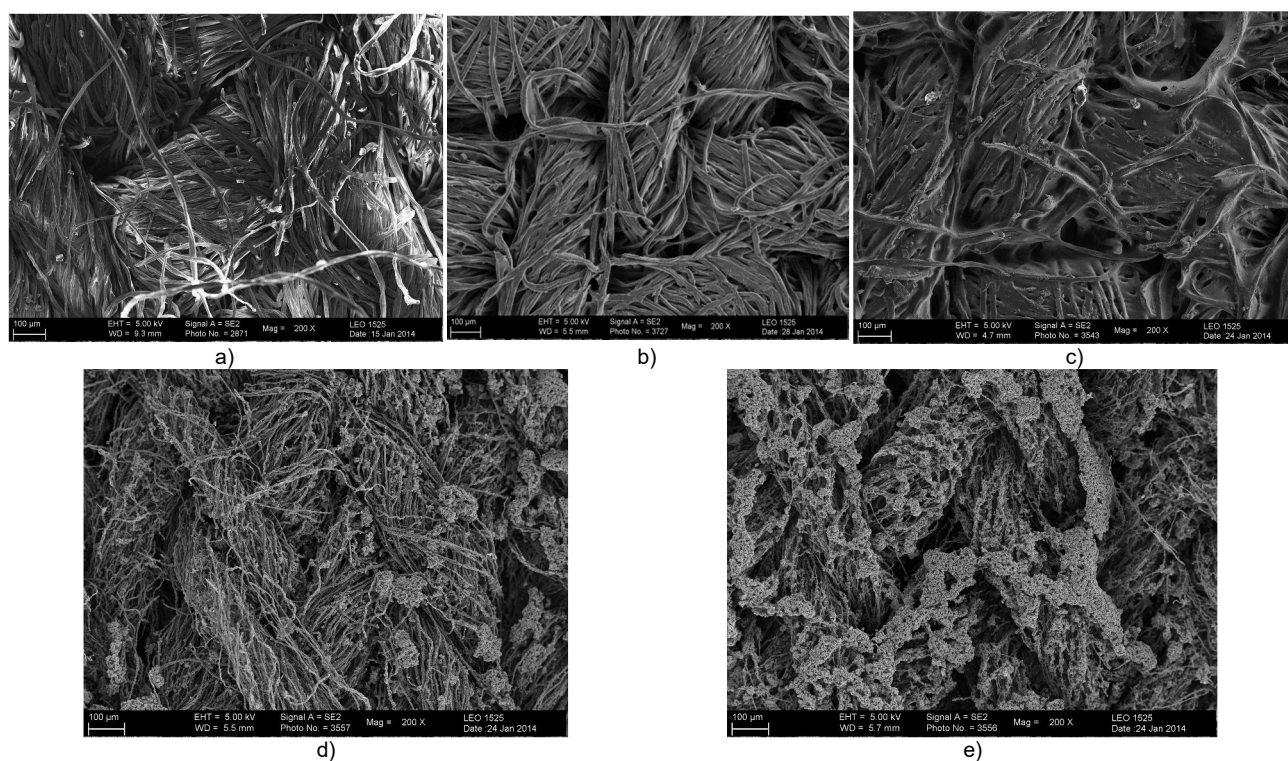


Figure 5 Micrographs of the fabric surface at 200x magnification: a) untreated sample before ignition; b) Lacrytex 640 / TiO₂ (20%) coated sample before ignition; c) Aquapol 14 / TiO₂ (20%) coated sample before ignition; d) Lacrytex 640 / TiO₂ (20%) coated sample after ignition; e) Aquapol 14 / TiO₂ (20%) coated sample after ignition

5 CONCLUSIONS

The results of studying the effect of polymer nanocomposite coatings on the change in the thermophysical properties of the fabric surface show that the introduction of titanium dioxide nanoparticles into the polymer matrix provides a reinforcing effect to the textile material. The presence of titanium dioxide nanoparticles in the polymer coating leads to the formation of coke residue on the fiber under the influence of the flame, which allows the fabric surface structure to be preserved after ignition.

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