SOI: 1.1/TAS DOI: 10.15863/TAS

International Scientific Journal

Theoretical & Applied Science

p-ISSN: 2308-4944 (print) **e-ISSN:** 2409-0085 (online)

Year: 2022 **Issue:** 10 **Volume:** 114

Published: 16.10.2022 **http://T-Science.org**

Issue **Article**

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NANOCOMPOSITE MATERIALS BASED ON THERMOPLASTICS AND LAYERED ORGANOSILICATES FOR MEDICAL DEVICES

Abstract: *Composite materials based on linear low-density polyethylene (LDPE) containing up to 3 wt. % of aluminosilicates that have high performance properties and a pronounced bactericidal effect, and composites based on fire-resistant aliphatic polyamides, diffusion-modified with nanosized copper particles, characterized by high resistance to thermal oxidative aging, have been developed. The developed composite materials based on polyolefins and polyamides can be used in the production of medical product's elements, such as disposable removable nozzles for hydro vacuum aspiration of palatine tonsils and multiple-action injectors for injection of the special preparations (antidotes, drugs, stimulants, etc.) under extreme conditions (in the zone of military training exercises and maneuvers, fighting and special operations, disaster relief, etc.), which used in specialized units and structural subdivision of the Ministry of Health and the Ministry of Defense of the Republic of Belarus.*

Key words: *nanocomposite materials, polyolefins, polyamides, organosilicates, clay, diffusion treatment, exfoliation, intercalation, medical devices.*

Language: *English*

Citation: Klochko, P., et al. (2022). Nanocomposite materials based on thermoplastics and layered organosilicates for medical devices. *ISJ Theoretical & Applied Science, 10 (114),* 138-144.

Soi: http://s-o-i.org/1.1/TAS-10-114-25 ***Doi***: crossref https://dx.doi.org/10.15863/TAS.2022.10.114.25

Scopus ASCC: *2507.*

Introduction

Polymer composite materials are the main type of raw material used in the industrial production of special-purpose products used in medical practice, providing for special units of the ministries of defense, emergencies and other departments, at food and processing industries [1, 2]. In particular, in the medical practice of domestic medical institutions, endoprostheses made from polymer materials and composites based on its are widely used for the treatment of otorhinolaryngological diseases, disorders of the musculoskeletal system, as well as special tools and containers for delivering drugs to the affected areas (nozzles for hydro vacuum aspiration of palatine tonsil lacunae) and collection of biological products from patients in order to monitor the general physical condition and treat diseases (containers for collecting plasma, blood and other biological substances).

To ensure the effectiveness of the actions of military and specialized units of the Ministry of Defense, the Ministry of Emergency Situations, etc., special devices (injectors) are used to injection special preparations (antidotes) that reduce the effect of damaging factors on the body of soldier. To reduce the chance of unfavorable environments entering the body in the extreme situations, it is necessary to ensure a pronounced bactericidal activity of the structural elements of injectors made from polymer composites.

Currently, the domestic industrial production of composite materials with a pronounced bactericidal effect does not function due to not have enough of systematic research in the field of functional nanocomposites based on thermoplastic matrices [2–5]. At the same time, a lot of studies carried out by domestic and foreign specialists unequivocally indicate the prospects for using the phenomenon of the nanostate of condensed matter in the processes of controlling the kinetics of adverse biochemical processes that cause damage to organic substances and the development of diseases of various types.

At present, polymeric nanocomposite materials based on an organosilicate modifier and a thermoplastic matrix (polymersilicate nanocomposites) are one of the most promising materials with an optimal combination of high performance, environmental safety, and relatively low-cost characteristics when they are processed into products on an industrial scale [6].

An important step before using the clay filler is its modification, in which the covalent bond between the clay layers is destroyed due to the introduction of surfactants or hydrophobic functional fragments, which leads to an increase in the degree of clay dispersion and expansion of the interplanar space (base distance), that is, to intercalation of the polymer chain.

At the same time, numerous studies are being carried out to develop polymer nanocomposites containing in their composition dispersed particles of layered silicates that could exfoliate (separate) into single layers of nanometer thickness in a thermoplastic matrix. As a thermoplastic matrix, polyolefins, which are characterized by increased parameters of technological and service characteristics, and high chemical resistance, are most widely used.

The development of new nanocomposite materials based on polyolefins will significantly expand the areas of their practical application as structural materials with increased parameters of stress-strain, barrier characteristics and resistance to combustion. The structure of such nanocomposites is a system consisting of many thin silicate plates with a thickness of about 1 nm and a transverse size from 30 nm to several microns, located in a polyolefin matrix. Dispersed particles of the modifier can form individual crystallites from several (about tens) parallel plates or be randomly distributed over the volume of the material. In the first case, nanocomposites are called intercalated; in the second, they are called exfoliated. However, due to the limited compatibility of non-polar polymers (in particular, polyolefins) with aluminosilicates and the poor delamination of the particles of the layered filler into single nanolayers in the polymer matrix, it has not yet been possible to achieve the same significant effects of changing the entire complex of mechanical and functional properties, as in the case of use in as polymer matrices of polar polymers (polyamides, polyesters, etc.). Therefore, an urgent task of modern polymer nanomaterials science is a systematic search for highly efficient ways to increase polymer intercalation and exfoliation of layered silicate particles in nonpolar polymer matrices and to study the effect of the layered silicate organomodifier composition on the properties of the target nanocomposite [6].

The purpose of this work was development of functional nanocomposite materials based on polyolefins and polyamides with high barrier, performance properties and increased resistance to thermal-oxidative aging for the production of medical products.

Research methods

As polymer matrices for composite materials, thermoplastic polymers of the class of polyolefins (linear low-density polyethylene F-0320 produced by the Shurtan Gas Chemical Complex, Uzbekistan) and polyamides (PA6 FR, PA6-GF20 FR produced by the Branch "Khimvolokno Plant" JSC "Grodno Azot", Belarus).

To modify thermoplastic materials, we used dispersed particles of modified montmorillonite brand "Cloisite 20A" manufactured by Southern Clay Production Inc., USA and organically modified natural sodium bentonite clay (Na^+-montmorillonite) with quaternary alkylammonium chloride produced by Scientific and Production Closed Joint-Stock Company "Sinta", Belarus. Low molecular weight maleinized polyethylene (PEMA) with a residual content of maleic anhydride of 0.5 wt. % was used as a compatibilizer.

Mixing of components of composites based on polyolefins was carried out in a mixing chamber (volume 30 cm^3) of a Brabender plasticorder (Plasticorder Brabender OHG Duisburg, Germany) at a temperature of 180±2°C. The speed of rotation of the plasticorder cams was 50 rpm.

To modify polyamide matrices, we used dispersed particles of metals (copper) obtained by thermolysis of metal-containing compounds (formate salts) in a melt medium. The evaluation of the effectiveness of the action of nanosized metal-containing particles was determined on model composites based on aliphatic polyamides containing nanosized copper particles in an amount of 0.075–0.6 wt. %. A nanosized metal-containing modifier was obtained by heat treatment of granular or powdered semi-finished products, diffusion-modified in aqueous solutions of a metal-containing precursor (copper formate) for 1–10 hours.

Molding of standard samples was carried out on a laboratory injection molding machine (Zamak Merkator, Poland) under the following technological conditions: injection pressure – 60 MPa for polyolefins and 90 MPa for polyamides, melt temperature – 180±0.5°C for polyolefins and 260±0.5°C for polyamides.

X-ray diffraction analysis of samples of the studied materials was carried out on a Rigaku D/max 2400 X-ray unit (CuK_α-radiation (λ = 1.54056 Å), current voltage 40 kV, current strength 200 mA). The counter rotation rate was 2 deg/min. The shooting range was 2–30 deg on the 2θ scale.

Comparative evaluation of the effectiveness of the action of nanosized metal-containing modifiers in composite materials based on aliphatic polyamides was carried out according to the stress-strain properties of standard samples subjected to thermal-oxidative aging at a temperature of 150±5°C in air for up to 200 hours. As a criterion, the parameter of tensile strength σt (MPa) was chosen.

Tests of samples from polymers and polymer composites for the stress-strain properties were carried out on an INSTRON 3365 tensile testing machine in the uniaxial tension mode with a set strain rate at a sample strain rate of 50 mm/min.

Results and discussion

In order to improve the performance properties of polyolefins and add the barrier (bactericidal) characteristics to its, compositions based on linear low-density high-pressure polyethylene PE (F-0320) with the introduction of silicate-containing particles and a compatibilizer - low molecular weight maleinized polyethylene (PEMA) with a residual content of maleic anhydride 0,5 wt.% – PEMA (MA-0.5%):

1) PE/MMT – polyethylene (97 wt.%) + montmorillonite (original clay) (3 wt.%);

2) PE/PEMA/Cloisite 20A – polyethylene (85 wt.%) + PEMA (12 wt.%) + organoclay Cloisite 10A (3 wt.%);

3) PE/PEMA/OMMT (Belarus) – polyethylene (85 wt.%) + PEMA (12 wt.%) + organoclay OC (Belarus) (3 wt.%).

Confirmation of the introduction of modifier molecules into the interlayer gallery of the layered aluminosilicate is the experimental data obtained by X-ray diffractometry, presented in Fig. 1 and Fig. 2.

The obtained results of X-ray patterns, reflecting the interlayer distances of the studied types of montmorillonite (Fig. 1) and the developed composites based on polyolefins (Fig. 2), corresponding to a certain diffraction reflection, indicate that the intercalation of modifier molecules into the interlayer gallery of the layered aluminosilicate leads to an increase in the width of the interplanar distance.

Table 1 presents the parameters of the stress-strain characteristics of linear low-density polyethylene and composites based on it.

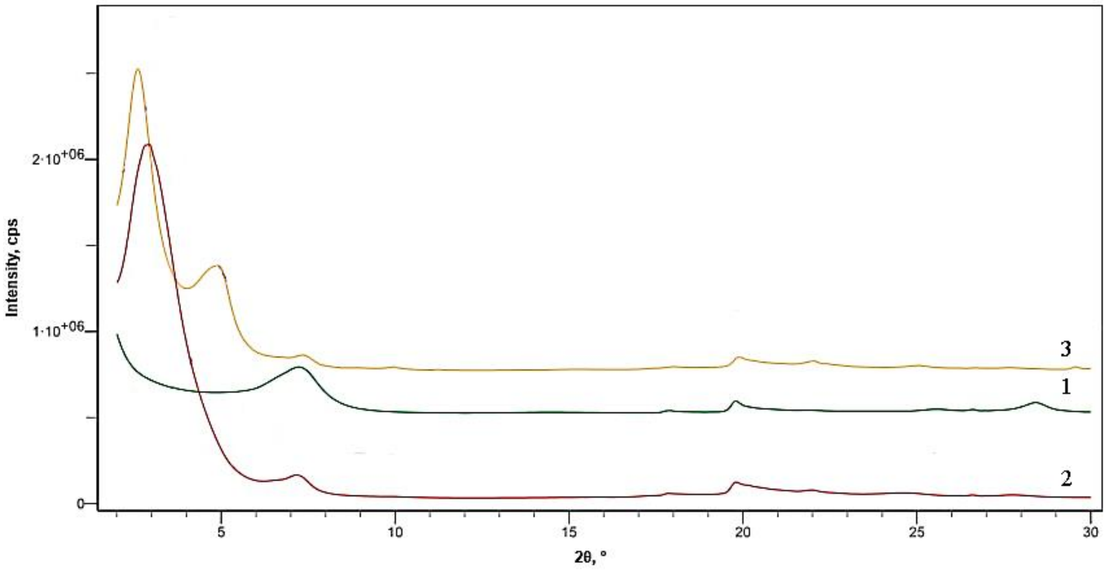

Fig. 1. X-ray scattering patterns of various types of montmorillonite: montmorillonite (1), Cloisite 20A (2), OMMT(Belarus) (3)

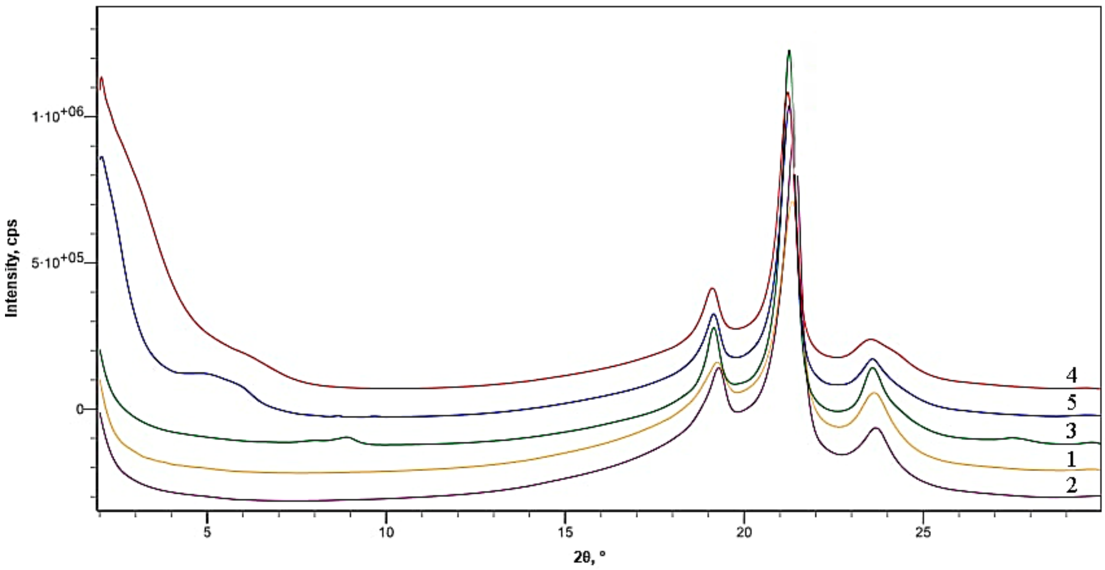

Fig. 2. X-ray scattering patterns of composite materials based on polyolefins: PE (F-0320) (1), PEMA (MA-0,5%) (2), PE/MMT (3), PE/PEMA/Cloisite 20A (4), PE/PEMA/OMMT(Belarus) (5)

Table 1. Parameters of the mechanical characteristics of the developed compositions of composites based on polyolefins

Material	Modulus of elasticity, MPa	Strain-to-failure, %	Yield point, MPa
PE (F-0320)	129,9±3,3	655±0,5	20,3±0,5
PEMA (MA-0,5%)	155,9±14,2	421,0±95,2	32,11±1,3
PE/MMT	198,6±6	91,7±5,5	32,48±1,9
PE/PEMA/Cloisite20A	193,4±22,0	163,2±12,2	26,21±0,5
PE/PEMA/OMMT (Belarus)	181,6±16,4	116,0±4,7	24,22±0,5

A technically significant effect of increasing the resistance to thermal oxidative aging was achieved for samples made from composite materials based on polyamide PA6 modified with flame retardants (PA6 FR) and a combination of flame retardants and 20 wt. % glass fiber (PA6-GF20 FR). The

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introduction of nanosized copper particles into polymer matrices in the amount of 0.085–0.6 wt. % by diffusion treatment in an aqueous solution of copper formate significantly increases not only the initial parameters of the stress-strain characteristics, but also their values after 100 hours and 200 hours of thermal oxidation at a temperature of 150±5°C (Fig. 3 and Fig. 4).

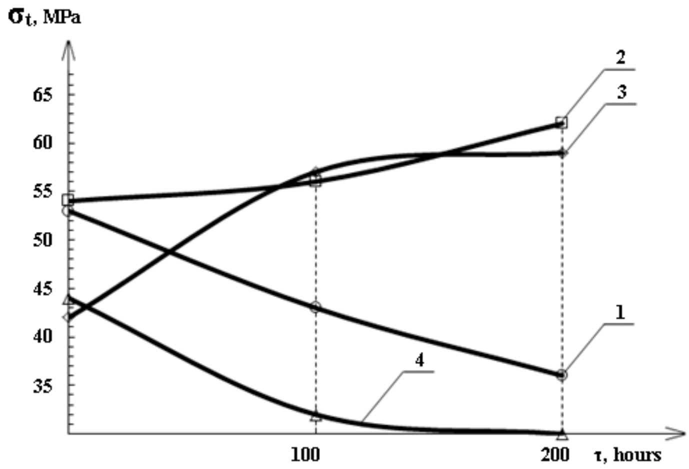

Fig. 3. Effect of copper nanosized particles on the resistance of nanocomposites to thermal oxidative destruction:
PA6 FR (1), PA6 FR + copper formate after treatment for 1 h (2),
PA6 FR + copper formate after treatment for 10 h (3), PA6 (4)

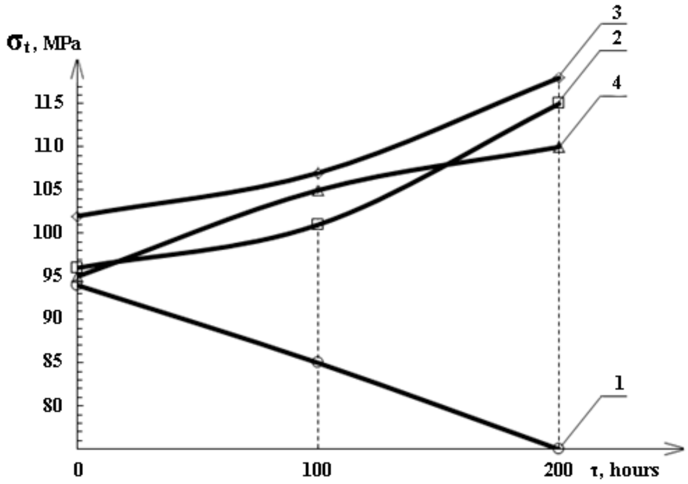

Fig. 4. Effect of copper nanosized particles on the resistance of nanocomposites to thermal oxidative destruction:
PA6-GF20 FR (1), PA6-GF20 FR + copper formate after treatment for 1 h (2),
PA6-GF20 FR + copper formate after treatment for 5 h (3),
PA6-GF20 FR + copper formate after treatment for 10 h (3) (4)

The developed composite materials based on polyolefins and polyamides containing dispersed particles of silicates and copper are recommended to be used for the production of elements of medical and special purpose products.

One of the most effective directions for the practical implementation of the invention is the use of the developed nanocomposite materials that have a pronounced bactericidal effect in the original design of the domestic injector for the introduction of special preparations into the affected areas of military personnel in extreme situations. The appearance of the developed design of the injector is shown in Fig. 5.

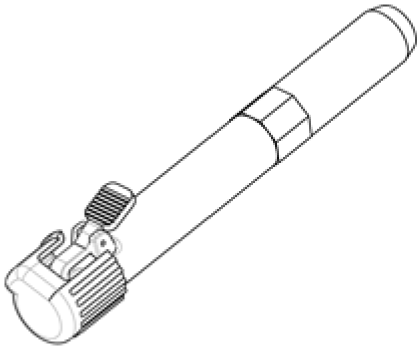

Fig. 5. The developed design of the special-purpose injector

As already noted, the developed design of domestic injector is made from nanocomposite materials based on polymer matrices with a pronounced bactericidal effect. It allows the injector to be used in the field conditions without special sterilization treatment while minimizing the chance of introducing pathogenic substances into the affected area.

The developed design of the injector has no domestic analogues and can be a full-fledged alternative to imported developments of a similar purpose. The developed design of the injector is focused on domestic materials and technological equipment available at the disposal of specialized enterprises for the production of polymer products. It allows to reduce the cost of the injector by at least 1.5-2 times compared to imported analogues.

The second direction of the practical implementation of the developed nanocomposite materials based on thermoplastics was their use in the design of functional nozzles for the treatment and prevention of otorhinolaryngological diseases.

A design of a nozzle for the apparatus for hydro vacuum aspiration of the lacunae of the palatine tonsils (Fig. 6) has been developed. This nozzle was designed for localized and dosed delivery of drugs to the affected area and controlled removal of products of inflammatory processes in a non-contact way.

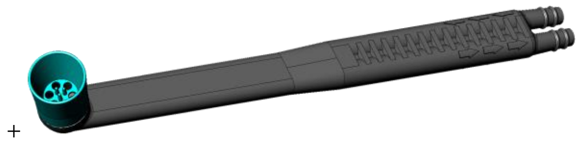

Fig. 6. The developed design of the removable nozzle for the hydro vacuum aspiration of the palatine tonsils lacunae

The use of nozzles for the treatment of otorhinolaryngological diseases can reduce the treatment time by 2-3 times, provide a prolonged protective effect, and prevent possible relapses. The nozzle is made from a special composite material with a bactericidal effect, which allows its repeated use without additional sterilization, provided that the removable disposable applicator is changed.

Conclusion

Thus, functional nanocomposite materials based on the thermoplastics with high performance properties and pronounced bactericidal activity have been developed for use in innovative designs of medical devices. These materials make it possible to inhibit or suppress the development of unfavorable biochemical processes on the medical devices' elements.

The prospect of development is expressed by the possibility of equipping special units of the Ministry of Defense and institutions of the Ministry of Health of the Republic of Belarus with domestic products that are not inferior in terms of functional action at a significantly lower price range.

In addition, the developed nanocomposite materials can be used in the manufacture of multilayer films with a prolonged bactericidal effect for the production of packaging elements for long-term storage of food and special products in warehouse and field conditions.

Acknowledgments

The given research was carried out within the framework of integrated assignment 8.4.1.4 "Mechanisms of directed structure formation of functional thermoplastic composites under energy and mechanical influences" of R&D "Investigation of the multilevel structuring mechanisms of functional nanocomposites based on thermoplastics under conditions of the realization of physicochemical synergistic effects" and R&D "Investigate the structure formation mechanisms of regenerated thermoplastics and develop methods for increasing the parameters of stress-strain and rheological characteristics of functional composites based on its" included in the subprogram "Multifunctional and composite materials" of the State programs for scientific research "Materials science, new materials and technologies" in 2021-2025. Also the given research was carried out within the framework of integrated assignment 5.6 "Research of the processes of creation and use of polymer packaging materials to ensure the quality and safety of food products" of R&D "Investigation of the processes of structure formation of thermoplastic nanocomposites for obtaining film semi-finished products with increased parameters of characteristics" included in the subprogram "Food security" of the State programs for scientific research "Agricultural technologies and Food security" in 2021-2025.

References:

1. Struk, V.A. (1988). *Tribochemical concept for the creation of antifriction materials based on multitonnage polymer binders*. Dr. tech. sci. diss (325 p.). Minsk (in Russian).
2. Avdeychik, S.V., Kostyukovich, G.A., Kravchenko, V.I., Lovshenko, F.G., Lovshenko, G.F., Panteleenko, F.I., Rogachev, A.V., Struk, V.A., & Tochitskiy, E.I. (2006). *Nanocomposite construction materials: development and application experience* (403 p.). Grodno: Yanka Kupala State University of Grodno (in Russian).
3. Avdeychik, S.V., Liopo, V.A., Ryskulov, A.A., & Struk, V.A. (2009). *Introduction to the physics of nanocomposite construction materials* (439 p.). Grodno: Grodno State Agricultural University (in Russian).
4. Avdeychik, S.V., Struk, V.A., Antonov, A.S. (2017). *Nanostate Factor in Materials Science of Polymer Nanocomposites* (468 p.). Saarbrücken: LAP Lambert Academic Publishing (in Russian).
5. Avdeichik, S.V., Gol'dade, V.A., Struk, V.A., Antonov, A.S., & Ikromov, A.G. (2022). Implementation of the nanostate phenomenon in materials science of functional nanocomposites based on industrial polymers. *Surface Engineering and Applied Electrochemistry*, Vol.58, No.3, pp. 211–220.
6. Struk, V.A., Prushak, V.Ya., Avdeychik, S.V., Liopo, V.A., Dmitrochenko, V.V., Protasenya, A.V. (2007). *Polymer-silicate construction materials: physical chemistry, technology, application* (431 p.). Minsk: Tekhnalogiya (in Russian).