

Potassium Layered Poly titanates Influence on Low-pressure Polyethylene Properties in Wide Concentrations Range

Igor Burmistrov^{1,2,a)}, Lidiya Panova^{1,b)}, Alexey Shevelev^{1,c)},
Anna Ermolenko^{1,d)}, Igor Ilinykh^{2,e)} and Anna Godymchuk^{2,3,4,f)}

¹*Yuri Gagarin State Technical University of Saratov, 77 Polytehnicheskaya Street, Saratov 410054 Russian Federation*

²*National University of Science and Technology "MISiS", 4 Leninsky Prospekt, Moscow 119049 Russian Federation*

³*Tomsk Polytechnic University, 30 Lenina Avenue, Tomsk 634050 Russian Federation*

⁴*Derzhavina Tambov State University, 33 Internatsionalnaya Street, Tambov 392000 Russian Federation*

^{a)}corresponding author: glass100@yandex.ru

^{b)}xt.techn@tsstu.ru

^{c)}titans5@rambler.ru

^{d)}molish01@rambler.ru

^{e)}ilinyh.igor@gmail.com

^{f)}godymchuk@mail.ru

Abstract. Thermoplastic composites based on low-pressure polyethylene and layered potassium titanates have been made in the work. We have shown the possibility to processing the composites into the products by injection molding at polytitanates content up to 50%wt. Technological properties of composites at low concentrations of filler are established. Layered potassium polytitanates influence on the mechanical and thermophysical properties of low-pressure polyethylene in a wide range of concentrations is investigated: from 1 to 50 %wt. Essential increase of complex of mechanical properties of polyethylene at introduction of small amounts of layered potassium polytitanates is shown. Due to the layered structure of the potassium polytitanates with particle size of about 500 nm in diameter and a thickness of less than 10 nm durability to shock loads increase comparable to the results of the introduction of fibrous potassium hexatitanates is reached.

INTRODUCTION

Filling is the most widespread physical method of polymers modification which changes intermolecular bonds energy at the interphase level. Among the dispersed fillers for polyethylene, talc, calcium carbonate, oxide fillers, and wood flour are the most widely used in order to reduce polymers' cost but preserve a comprehensible complex of material mechanical properties [1-3]. Functional fillers seem to be environmentally friendly, highly perspective and effective additives in order to strengthen polymers and confer them new operational characteristics. Several years ago, the authors showed that the most perspective and effective approach to structure polymeric materials was the transition to the regulation of materials properties on submicron and nanoscale level [4, 5]; where relatively new class of ceramic oxide fillers – potassium polytitanates – seemed to be of high interest in terms of research and practical use. The most effective and the least expensive method for polytitanates production is crystallization from melted salts [6,7]. Depending on synthesis conditions and chemical composition, they are either amorphous compounds with layered structure (potassium polytitanates) or crystalline submicro- and nanofibers (potassium tetra-, hexa-, or octatitanates) [8-10]. Layered structures are characterized by low energy of interlayer shift and high values of reflection and absorption in visible and infra-red spectrum areas. Fibrous materials possess high mechanical durability, low thermal conductivity and good reflectivity over a wide spectral range [11, 12]. The authors [13-17] show the big

prospects in application of fibrous tetra- and hexatitanates at thermoplasts reinforcing (polypropylene, polyamide, acrylic-styrene-stirolla, etc.).

There is still lack of attention of researchers to the creation of composite materials based on layered polytitanates. The purpose of the present work was to compare the mechanical properties of polyethylene (PE) modified by layered potassium polytitanates with the properties of well-known composites based on polyethylene and calcium carbonate.

EXPERIMENTAL PART

Potassium polytitanat (PPT) was produced by crystallization technology from a mixture of melted potassium hydroxide (KOH, chemically pure, Russia) and nitrate (KNO_3 , chemically pure, Russia) and titanium dioxide (TiO_2 , chemically pure, Russia) [6,7] on the industrial production line on the basis of LLC "Nanocomposite" Saratov, Russia. Low density polyethylene (HDPE) grade 273 (LLC "Stavrolen", Russia) was used as polymer matrix for preparation of composites. Samples of HDPE were combined with PPT in single-screw extruder EPK25x30, Russia. The received composite material was processed by injection molding in injection molding machine D3023, Russia into test specimens by injection molding at 220 °C and 80 MPa.

The morphology of samples surface was observed with a scanning electron microscope Hitachi TM-1000. Structure of the polytitanates particles was studied through transmission electron microscope JEOL JEM 1400 at an accelerating voltage of 120 kV; the samples for the study were prepared by ultrasonic (22 kHz, 100 W) dispersion in ethanol (0.1 wt.%), followed by sedimentation of particles from the top of the stable suspensions onto a substrate. Particles size distribution was determined by laser diffraction method at analyzer Fritsch Analysette-22 Nanotech in the range 0.01-1000 microns, the dispersion medium was distilled water.

Specific surface area of PPT was measured by the BET method by analyzer specific surface area and porosity Quantachrome Nova 2200 (US), at degassing temperature – 150 °C and degassing time – 3 h.

Investigation of tough characteristics of polymer composite materials (density, melt index and mechanical properties) were made with the help of test machines IR 5046-5 and PT250-2, pendular poppet KM05 and durometer TB5004. The density was found by gravimetric weighing, melt index tests were conducted at a temperature of 190 °C and a pressure of 100 kPa, and mechanical properties were investigated in accordance to standards GOST 4647-80, GOST 4670-91 of the Russian Federation.

RESULTS AND DISCUSSION

Fractional structure of PPT studied in aqueous dispersion at ultrasonic treatment was characterized by a multimodal particle size distribution, which was, most likely, caused by formation of aggregates from primary particles with sizes of 0.1-0.5 μm (Fig. 1).

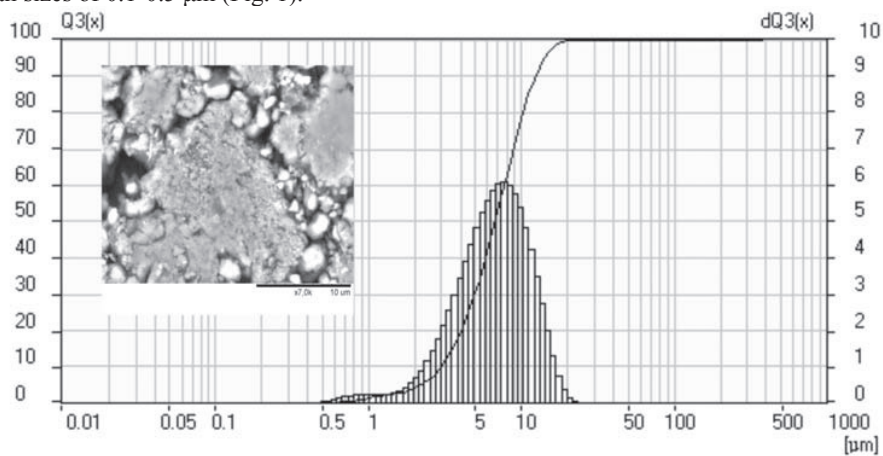


FIGURE 1. SEM image and size distribution of PPT particles.

The average particle size in powder PPT was 2-20 μm at the specific surface area 8.29 m^2/g . Investigation of PPT particles by scanning and transmission electron microscopy allowed to define the morphology and particles size of PPT (Fig. 2).

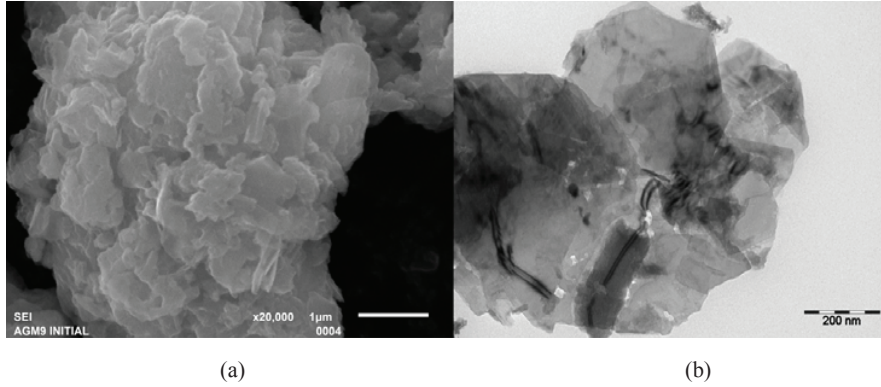


FIGURE 2. The morphology of the PPT particles by scanning (a) and transmission (b) electron microscopy.

In order to select the injection molding mode melt flow rate was investigated and the viscosity of the material was calculated (Table 1). Test load was varied from 0.6 to 104 N, the temperature from 150 to 200 °C. Melt flow rate corresponding to possibility of processing by injection molding is reached for filled PE at 190 °C and a pressure - 100 MPa.

TABLE 1. Rheological properties of HDPE and composites.

Content of the components, wt. parts.	The content of fillers, volume %	Density, kg/m ³	Melt flow rate, g/min	Viscosity, Pa*s
100 HDPE	—	985	6.0	182.5
100 HDPE +1PPT	0.4	990	5.9	179.5

At introduction of PPT in amount from 1 to 50% possibility of processing the material by injection molding is remained. The mechanical properties of composites received are shown in table 2.

TABLE 2. The properties of composites based on polyethylene and polytitanates of potassium.

Content of the components, wt. parts per 100 wt. parts of the PE	Impact strength, kJ/m ²	Flexural Strength, MPa	Brinell hardness, MPa	Tensile strength, MPa	Elongation, %	Vicat, °C
HDPE	67.6	22	40.9	14.8	15.3	112
HDPE +1PPT	89	30.1	41.8	20.5	39.7	102
HDPE +5 PPT	17.6	32.8	77.1	30.1	6.3	120
HDPE +20 PPT	23	25.6	69	22	1	124
HDPE +50 PPT	15.9	30.5	48.8	20.1	5.4	-

At increase of the filler content a regular decrease of impact strength and tensile strength is observed. It should be noted that at the introduction of 1% of PPT a considerable increase of composite properties is observed compared to the original HDPE. Strength to bending stress and hardness on Brinell have a maximum values at a PPT content equal to 5%.

Analysis of the data received shows regular for dispersion filled polymer composite materials impact strength reduction at degree of filling increase (table 2). However at introduction of 1% of PPT its increase is observed in comparison with the original polymer. Comparing the obtained data with the results of polyethylene filling with nanodispersed calcium carbonate with an average particle diameter of 20 nm and the degree of filling of 5-30 % [18] it could be noted that polytitanates even at high degrees of filling provide better properties of the composite. Despite the fact that the original polyethylene chosen for the study had a lower set of mechanical properties [18], it is possible to notice that best results received with nanodispersed carbonate calcium introduction surpass the original material on 20 % and at the introduction of PPT on 32 %.

Increasing properties in case of polytitanates concentration about 1 wt.% can be explained as effect of small additions. In these cause nanoparticles plays a role of centres of crystallization and increase the crystallinity degree and decrease of crystallites size. At concentration about 20 wt.% of polyethylene playing the role of a conventional filler, receiving load from the composite matrix.

Obviously, the significant increase of impact strength can be expected at introduction of fibrous fillers. In [19-22] fibrous titanates introduction influence on the mechanical properties of thermoplastics investigated, it is

thus shown that impact strength of initial materials can increase on 100 % at filling by hexatitanates fibers treated with dressing additions (for undressed PTP fibers the impact strength decreases).

CONCLUSION

In this paper the influence of layered potassium polytitanates on the low-pressure polyethylene properties was investigated. The increasing of tensile and bending stresses (up to 33 %) was achieved with the filling of the polyethylene matrix with potassium polytitanates.

In the investigation of the effect of polytitanates concentrations on the polyethylene strength two maximums of mechanical properties was found: Increasing tensile strength in case of small polytitanates additions (1 wt.%) and at 20 wt.% of polyethylene, when they playing the role as a conventional filler, receiving load from the composite matrix.

Improvement of polyethylene properties with the incorporation of small additions of polytitanates can be explained with the increase of the crystallinity degree and decrease of crystallites size in case of appearance additional centres of crystallization onto polytitanates nanoparticles.

ACKNOWLEDGMENTS

This research was financially supported by the Ministry of Education and Science of the Russian Federation (State assignment No 1242).

REFERENCES

1. N. Chen, L. Ma, and T. Zhang, *Rare Met.* **25**, 422–425 (2006).
2. J. González, C. Albano, M. Ichazo, and B. Díaz, *Eur. Polym. J.* **38**, 2465–2475 (2002).
3. C. S. Sylvia, M. M. Moreira, A. P. Lima, S. L. Santos, B. M. Rocha, E. S. Lima, R. A. A. F. Costa, A. L. N. Silva, M.C.G. Rocha, and F.M.B. Coutinho, *Polymer Testing.* **24**, 983–987 (2005).
4. A.P. Kumara, D. Depana, N.S. Tomer, R.P. Singha, *Progr. in Polym. Sci.* **34**, 479–515 (2009).
5. D.V. Kuznetsov, V.V. Cherdyn'tsev, D.S. Muratov, A.G. Yudin, D.V. Lysov, and S.D. Kaloshkin, *Sci. Mater.* **7**, 35–40 (2010).
6. T. Sanchez-Monjaras, A.V. Gorokhovskiy, and J.I. Escalante-Garcia, *J. Am. Ceram. Soc.* **91**, 3058–3065 (2008).
7. S. Takaya, Y. Lu, S. Guan, K. Miyazawa, H. Yoshida, H. Asanuma, *Surf. Coat. Technol.* **275**, 260–263 (2015).
8. I. N. Burmistrov, D. V. Kuznetsov and A. G. Yudin, *Refractories and Ind. Ceram.* **52**, 393–397 (2012)
9. A. V. Gorokhovskiy, J. I. Escalante-Garcia, E. Sanchez-Valdes, I. N. Burmistrov and D. V. Kuznetsov, *Ceramics Intern.* **41**, 13294–13303 (2015).
10. A. S. Mostovoi, E. A. Yakovlev, I. N. Burmistrov and L. G. Panova, *Russ. J. Appl. Chem.* **88** 129–137 (2015).
11. A. V. Gorokhovskiy, A. I. Palagin, L. G. Panova, T. P. Ustinova, I. N. Burmistrov and D.V. Aristov, *Nanotechnology [Nanotechnika - in Russian]*, **20**, 90-94 (2009).
12. B. Ningzhong, F. Xin, L. Xiaohua, S. Liming and Y. Kazumichi, *AIChE J.* **50**, 1568–1577 (2004).
13. L. Jiazhen and L. Xiaohua, *J. Appl. Polym. Sci.* **82**, 368–374 (2001).
14. S. C. Tjong and Y. Z. Meng, *J. Appl. Polym. Sci.* **70**, 431–439 (1998).
15. S. C. Tjong and W. Jiang, *Polym. Composites*, **20**, 748–757 (1999).
16. M. I. Biryukova, I. N. Burmistrov, G. Yu. Yurkov, I. N. Mazov, A. A. Ashmarin, A.V. Gorokhovskii, V.I. Gryaznov and V. M. Buznik, *Theoretical Foundations of Chem. Eng.* **49**, 485–489 (2015).
17. I. N. Burmistrov, N. V. Shatrova, A. S. Mostovoy, I. N. Mazov, D. V. Kuznetsov, L. G. Panova, A. V. Gorokhovskiy and A. G. Yudin, *Polymer Engineering and Science.* **54**, 2866–2871 (2014).
18. M. Zhang, P.F. Fang, S.P. Zhang, B. Wang and S.J. Wang, *Radiat. Phys. Chem.* **68**, 565–567 (2003).
19. A. Lazzera, S.M. Zabarjadb, M. Pracellac and K.R. Cavalierd, *Polymer*, **46**, 827–844 (2005).
20. O. Yuchun, Y. Feng, and C. Jin, *J. Appl. Polym. Sci.* **64**, 2317–2322 (1997).
21. S. Chen, Q. Wang, T. Wang and X. Pei, *Materials & Design.* **32**, 803–807 (2011).
22. Y. Li, Y. Shi, F. Cai, J. Xue, F. Chen and Q. Fu, *Composites Part A: Appl. Sci. Manufacturing*, **78**, 318–326 (2015).