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Research Article

Charge activity of silicon-containing nanophase particles intended for modification of polymer matrices

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Abstract

The article considers the influence of various technological methods for obtaining nanosized silicate-containing particles. Each of the methods has its advantages and disadvantages, none of them is universal. It is shown that, depending on the methods of formation of particles, their activity changes. Silicon carbide particles obtained as a result of the thermolysis process with preliminary chemical treatment from natural raw materials of organic origin are of interest for further research. These particles have an increased charge activity in relation to other studied classes of charged particles.

Introduction

One of the effective ways to significantly change the performance characteristics of multi-tonnage polymer materials is the introduction of various types of substances in doping concentrations. The presence of a modifier in the polymer matrix significantly affects the physical and mechanical characteristics of polymers and ultimately determines the quality of the products obtained. Based on the available research, it is believed that modified thermoplastics can be processed by all known methods. Usually, when modifying polymer materials, shrinkage decreases or stabilizes, more stable viscosity characteristics are observed, and the course of relaxation processes changes [1-10].

The use of nanoparticles that can be attributed to superhard materials (nanodiamonds, diamond-containing charge, nanoparticles based on tungsten carbide, etc.) in most cases leads to an intensification of the wear process, a faster change in the geometric dimensions of the counterbody in the friction node, due to changes in tribochemical test conditions [11-12]. The use of various types of nanorods can also lead to a change in the performance characteristics of polymers in the direction of deterioration of properties, due to the heterogeneity of the distribution of this type of modifiers in the polymer matrix, as well as by creating local regions with different orientation of the modifier in the volume of a high-molecular compound.

The authors [13] studied the effect of the number of SiO_2 nanoparticles on the physico-mechanical properties, heat resistance, and tribological characteristics of flame-retardant polyamide coatings. The absence of oxidative degradation of polyamide with an optimal content of SiO_2 nanoparticles is shown.

It was found in [14] that the introduction of hydrosilicate nanoparticles into the polymer matrix leads to a noticeable increase in the modulus of elasticity of the material.

The authors [15] describe the characteristics of nanoparticles and the effect of nanoparticle sizes on the mechanical

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properties of composite nanomaterials (strength, elongation, Young's modulus). Mechanisms of modification and evaluation of properties of polymer materials modified by nanoparticles are discussed.

In [16], experimental results show the electrothermopolarization of polymer-nanoparticle-based compositions changes its charge state, the supramolecular structure of the polymer changes, the interfacial interactions between the components of the composition and the thickness of the interfacial layer, as a result of which the strength properties change.

Thus, the use of modifiers and fillers of various dispersities can allow solving various problems of materials science, in the field of creating new structural materials, by optimal selection of a modifying agent. Currently, various types of silicate particles are widely used as modifiers of polymer materials. Depending on the chemical composition, structure, and morphology, these particles have different activity, which determines their degree of modifying effect on the high-molecular matrix [17].

Currently, the main methods for producing nanoparticles are: compaction of isolated nanoclusters obtained by evaporation and condensation, precipitation from solutions or decomposition of precursors; crystallization of amorphous alloys; intense plastic deformation; ordering of highly nonstoichiometric compounds and solid solutions. Each of the methods has its advantages and disadvantages, none of them is universal [18].

For the modification of thermoplastic polymer matrices, the most promising is the use of nanodispersed particles of silicon carbide obtained by thermolysis technology of natural raw materials containing this chemical compound. Currently, the industry needs for this superhard compound (SiC) are provided by particles obtained by the Acheson method using solid-phase chemical reactions at high temperatures. However, these particles are obtained with a high content of metal compounds used as catalysts in the production of the product. The presence of these additional chemical inclusions degrades the characteristics of low-dimensional SiC particles and complicates their application, in particular, in the radio-electronic industry. The use of the thermolysis process with preliminary chemical treatment of natural raw materials makes it possible to obtain high-purity silicon carbide particles [19-24].

The purpose of this work is to study the activity of silicate particles of various types by the method of thermo-stimulated current spectroscopy.

Materials and methods of research

Ultradisperse silicate-containing particles of various production technologies, compositions, and structures were studied using the method of thermally stimulated depolarization (TST spectroscopy, thermally stimulated current spectroscopy) [17]. The essence of the method is to study the relaxation of the charge that causes the electret state, that is, a state in which surface charges arise on the surface of the dielectric under the influence of external factors such as an electric field, irradiation with electrons, ions, etc. To ensure rapid relaxation, thermal stimulation of the dielectric discharge is used at a constant heating rate. The analysis is based on the property of charges accumulated by dielectrics to be released when heated and on fixing the parameters of the current flowing at the same time. The current graph in the temperature function is a spectrum of TST, by the nature of which the mechanisms responsible for the manifestation of the effect are judged. The TST analysis was carried out in the range of 20 °C - 270 °C using a device for measuring thermally stimulated currents ST-1 (ODO "Microtestmashiny", Belarus, Gomel) (Figure 1) according to the developer's methodology.

Results and discussions

The TST spectrum of flint (Figure 2a) is characterized by a weakly expressed peak, the maximum of which is in the region of ~ 27 °C - 29 °C, and the maximum intensity is 3.2 pA. Flint is most likely characterized by a heterocharge, which decreases over time to a certain constant value determined both by the structure of the material and by the external conditions under which the sample is located. Carrying out mechanical activation of flint (Figure 2b) leads to a shift of the maximum peak of the thermally stimulated currents to the region of 33 °C - 37 °C and an increase in the intensity of the TST peak by about 3 times (Imax ~10 pA). In the case of mechanical activation, the flint most likely acquires a homocharge, which passes through the maximum and then changes little.

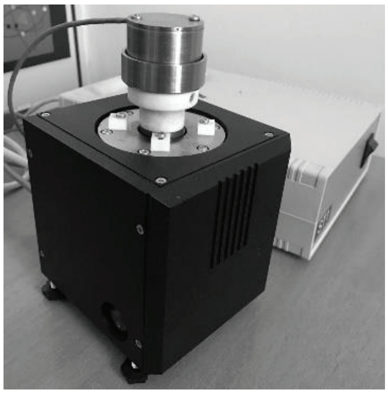

Figure 1: Device for measuring thermally stimulated currents ST-1.

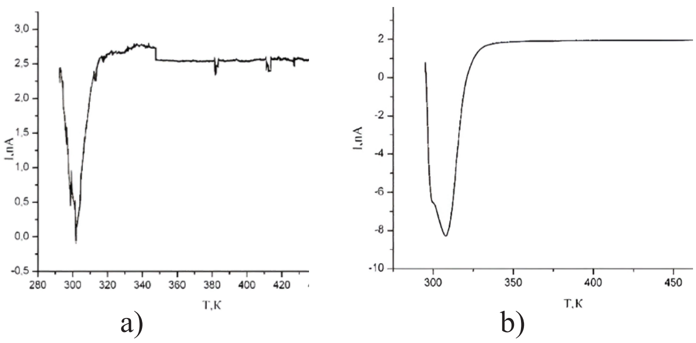

Figure 2: TST spectrum of silicate–containing particles based on flint: a) Flint, b) Mechanically activated flint.

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Studies by the method of thermally stimulated depolarization have shown the presence of a maximum in the spectrum of the TST aerosol (Figure 3c), located in the temperature range T~39 °C - 41 °C, with an Imax peak intensity of ~ 0.32 pA. An aerosol is characterized by a homocharge [17].

Based on the conducted studies, it can be seen that aerosil is the least active in terms of charging activity; mechanically activated flint has the maximum charging activity. Carrying out mechanical activation enhances the charging effects in the starting materials. The joint mechanical activation of aerosil with silicon (Figure 3d) reduces the charge activity in comparison with mechanically activated silicon, but in comparison with the starting materials, there is a sharp increase in the activity of the resulting composite system [17].

Shungite is characterized by a wide temperature range of charge activity from 20 °C - 80 °C (Figure 4e) and is most likely effective for use in cold-cured composite materials, such as epoxy, polyester, urea-formaldehyde resins, etc.

Studies conducted to study the charge activity of silicon carbide particles obtained using this technology have shown the presence of an intense peak in the TST spectrum in the region of 150 °C - 190 °C (Figure 4f), which indicates a high charge activity of silicon-containing material. The temperature range of the SiC charge activity is in the processing area of most thermoplastic polymers. It is possible to assume a significant influence of silicon carbide particles obtained from natural raw materials on the structure and physico-mechanical characteristics of thermoplastic polymer composites with the doping content of the modifier. The mechanism explaining the modifying effect of these particles is the formation of a labile network of physical bonds in the polymer matrix between modifier particles and polymer molecules.

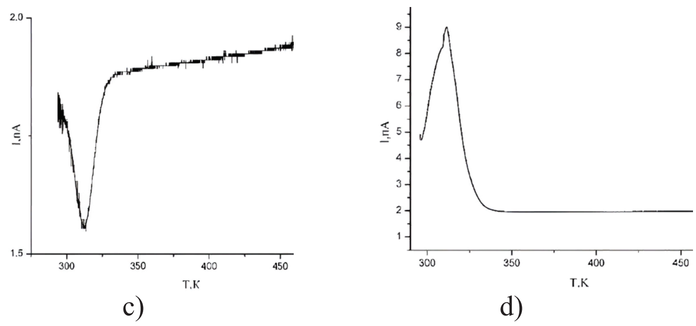

Figure 3: TST spectrum of silicate-containing particles based on aerosil: c) Aerosil, d) Flint – 65%, SiO2 – 35%. The composition was mechanically activated for 30 sec at an acceleration of 20 g.

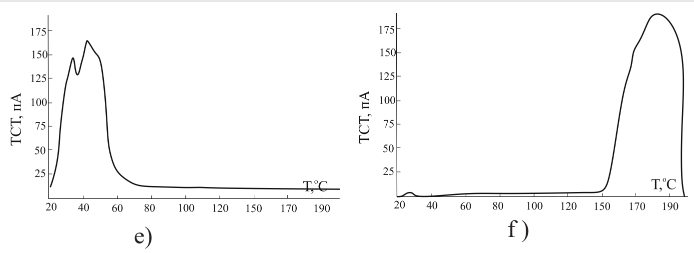

Figure 4: TST spectrum of silicate-containing particles obtained from natural raw materials. e) Shungite, f) Silicon carbide.

The presence of peaks of thermally stimulated currents in silicate-containing particles indicates the activity of the material during heating. These TST peaks are located in the temperature range of processing of high-tonnage polymer materials (polyolefins, polyamides, polyethylene terephthalate). In this regard, these nanophase silicate-containing particles obtained from organic raw materials can be used as modifiers of polymer materials to create composites with increased resistance to radiation and electromagnetic radiation in the microwave range.

Conclusion

Thus, an analysis of the activity of existing low-dimensional silicate-containing particles used to modify polymer matrices has been carried out. The prospects of using ultrafine SiC particles obtained from natural raw materials by thermolysis for modifying thermoplastic polymer materials are shown.

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