**ANNOTATION**

**dissertations for the degree of Doctor of Philosophy (PhD) in the specialty 8D07113 – «Nanomaterials and nanotechnology in chemistry» by Zhanat Kudaibergenovna Myshyrova**

**on the topic «Development of high-strength sealing materials modified with nanofillers»**

The fields of application of sealing materials and adhesives are expanding annually, and the demand for these products is growing accordingly. In the successfully developing Kazakhstan automotive industry, anaerobic silicone sealing materials, which are completely imported from other countries, have become the most widespread. Electrically conductive or vice versa dielectric coatings used in the manufacture of electrical engineering and instrumentation are composite materials containing a polymer matrix and various fillers. This work is aimed at synthesizing polysulfide oligomers doped with carbon fillers to produce sealing materials with improved physico-mechanical, rheological, heat-resistant, strength, and waterproof properties, which is of scientific and technical interest and is undoubtedly of practical importance, since the areas of use of adhesives and sealants are increasing every year.

**Relevance of the research topic**

The requirements for sealing materials imposed by the modern level of technology and engineering development in the construction industry are quite high: it is necessary to meet the requirements of competition, guarantee a strong connection, and at the same time have high performance characteristics. The high physical and mechanical characteristics of sealing materials depend on the improvement of the production technology and on the degree of use of the latest technologies and materials. The inclusion of nanometer-sized particles as additives in various polymer matrices has opened up a new class of materials - nanocomposites, which makes it possible to create a new type of adhesives with enhanced physical and mechanical properties. Having a large surface area and a nanometer size, nanoparticles are a completely different type of fillers that provide enhanced physical and mechanical properties, and a set of other physical properties not observed in composites with conventional fillers.

**The purpose of the work**

The purpose of this dissertation is to develop formulations and technologies for the production of new sealing materials based on polysulfide oligomers with enhanced performance characteristics, using nanomaterials as fillers and additives.

**Work objectives**

• Development of technology for the production of new sealing compositions modified with carbon nanoparticles synthesized by plasmochemical pyrolysis, chemical deposition from the gas phase and carbonation.

• Investigation of the effect of the concentration and chemical nature of carbon nanomaterials on structure formation, agglomerate formation in oligomers, and the effect of curing processes on the size of nanoparticle agglomerates during the transition from a liquid oligomer to a solid polymer;

• Investigation of the effect of compositions, concentrations, and sizes of nanostructured filler agglomerates on the improvement or deterioration of the physico-mechanical properties of sealing materials;

• Development of new sealing compositions with minimal residual stresses and shrinkage during curing and improved mechanical and strength properties. Investigation of the effect of nanoparticle agglomerate sizes and filler concentrations on the rheological characteristics of composites.

Research methods

The research methodology included the implementation of a complex of physico-mechanical tests of synthesized adhesive polysulfide materials in accordance with the state standards for adhesive materials in force in the Republic of Kazakhstan, with the determination of tensile strength, Shore hardness, elongation at break, etc. The results were compared with commercial analogues.

Physicochemical research methods (IR spectroscopy, Raman spectroscopy, TGA, SEM) were jointly used to study the effects of carbon nanostructures of sealing compositions on the processes of structure formation and agglomeration.

**Scientific novelty of the research**

1. The technology for producing polysulfide oligomers has been modified, using $Na_2S$, $NaHSO_4$, $Na_2SO_3$ compounds instead of NaSH, $Na_2SO_3$ at the cleavage stage, and the exclusion from the cycle of washing thiocol dispersion from tetrasulfide.

2. It was first established that by changing the ratio of $Na_2S$ components:$NaHSO_4$:$Na_2SO_3$ in combination with carbon fillers (MCNT, CRS, CNPP), the rheological characteristics of sealants can be changed, in particular, synthesized thiocols increase the tensile strength of sealants by 16% and reduce the elongation at break to 15%.

3. For the first time, it was found that when testing for resistance to aggressive media, synthesized modified PSOs with the addition of CB, CB + MCNT, MCNT increase the resistance of sealing compositions to gasoline by up to 18%.

4. For the first time it was revealed that at a concentration of CB 30 wt.For silicone-based sealants, the electrical conductivity value is $1.11\times10^{2}$ $(Ohms\times m)^{-1}$, for PSO-based sealing compositions, the electrical resistance was $2.34\times10$ Ohms $\times$m.

The novelty of the work lies in the use of nanomaterials of various morphologies obtained by plasma chemical spraying, chemical gasification and carbonation.

The use of carbon components of sealing materials as fillers allows for improved viscosity, gives thixotropic properties, ensures minimal shrinkage during curing of sealants, these properties determine the possibility of their use in construction, aviation and mechanical engineering, medicine, electronics. The use of carbon nanostructures makes it possible to obtain sealants with increased thermal resistance and water resistance.

Ultimately, a technology for the synthesis of sealing compositions using non-traditional industrial fillers with sufficient mechanical strength and improved performance properties is proposed.

**The main provisions submitted for protection**

1.Improved technology for the production of polysulfide oligomers through the synthesis of 2,2-dichlorodiethylformal and tetrasulfide at a ratio of $NaHSO_4$ components:$Na_2SO_3$ 1:3, using $Na_2S$, $NaHSO_4$, $Na_2SO_3$ at the cleavage stage and excluding from the cycle the washing of thiocol dispersion from sodium tetrasulfide.

2. By varying the ratio of $NaHSO_4$ components:$Na_2SO_3$, 1:3 thiocols were obtained in which, with the addition of carbon fillers (MCNT, CRS, CNPP), the physico-mechanical characteristics of sealants were changed, with an increase in tensile strength to 16% and a decrease in elongation at break to 15%, with a content of mercaptan groups -SH in the composition up to 2.1%.

3. Semiconductor materials based on silicone sealants with a content of CB 30 wt.parts with a value of specific electrical conductivity $\sigma = 1.11\times 10^2$ (Ohms $\times$ m)$^{-1}$, and sealing compositions based on PSO with a specific electrical resistance p = 2.34 $\times$ 10 Ohms $\times$m.

4.Adhesives PMS-10, RMX-200 used as additives to sealing compositions based on PSO can reduce the operating temperature of sealants to T = -60 0 C and improve adhesion characteristics up to 0.8 N/mm$^2$

**Theoretical significance**

The theoretical significance of the thesis lies in simplifying the technology for the production of polysulfide oligomers, developing formulations and technologies for the production of sealing materials containing carbon fillers, including MNT, low molecular weight siloxane compounds, with enhanced performance characteristics.

The use of nanomaterials as fillers makes it possible to improve the rheological properties of sealing materials, help eliminate existing defects inherent in traditional sealing materials (insufficient adhesion to plastics, wet surfaces, insufficient joint strength with uneven separation, difficulty repairing joints) and open up new areas of possible application of sealing materials.

**Practical significance**

Foreign companies, mainly European ones, remain the main suppliers of sealants in the Kazakhstan market. In general, although there are slow trends in the growth of chemical products in Kazakhstan, the displacement of the share of imported materials and their replacement with domestic products may indicate the potential of the sealant market. The production of silicone sealants is the most attractive, due to the fact that Kazakhstan has large resources of sulfur-containing raw materials, and the use of domestic components, the development of chemical infrastructure and developments in this area may be economically significant and of commercial value.

**Connection with scientific research and government programs**

The work is proactive, the materials and reagents were purchased at the expense of the author's personal funds.

**Approbation of the work**

The materials of the dissertation were presented and discussed at the following international symposia and conferences:

Collection of articles based on materials from the International Student Scientific and Practical Conference. Novosibirsk, 2021, Russia, 04/18/2021-04/25/2021

Symposium"XIII International Symposium "Chemical Physics, Materials Science, Nanomaterials", International level, Al-Farabi Kazakh National University, chem. Faculty, 12/20/2022-12/21/2022

The Symposium "XIV International Symposium "Gorenje i plasmochemistry. Physics and Chemistry of carbon and nanoenergetic materials", International level, Al-Farabi Kazakh National University, chem. Faculty, 07.11.2023-08.11.2023

Republican conference "Science and Business", Almaty. – April 19, 2024

Proceedings of the International Conference of Students and Young Scientists "Фараби әлемі", the city of Almaty. – April 10, 2023.

**The author's personal contribution** consists in conducting experiments, determining methods of analysis and solutions to theoretical and practical problems, interpreting and summarizing the results obtained, writing articles and reports.

**Publications**

As a result of research on the topic of the dissertation, 8 scientific papers were published, including: 2 articles included in the Scopus database (Electrically Conductive Sealing Silicone Compositions Filled with Carbon Materials", Iranian Journal of Chemistry and Chemical Engineering, 2023, 12, #42, 4167-4175. DOI: 10.30492; Myshyrova, Z., Tulepov, M., Sassykova, L., & Busquets, R. (2024). Sealing Compositions Based on Polysulfide Oligomers Obtained by a Modified Method. Eurasian Chemico-Technological Journal, 26(4), 253–263. https://doi.org/10.18321/ectj1649 ), 2 articles – in publications recommended by the Committee for Control in the Field of Education and Science of the Republic of Kazakhstan, 4 articles – in collections of international symposiums and foreign conferences.

**Scope and structure of work**

The thesis is presented in 101 pages and includes 56 figures and 12 tables. The work consists of an introduction, the main part, a conclusion and a list of used sources from 104 bibliographic references to domestic and foreign authors.