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The study the possibility of development of environment safety technology of creating polymer composites in the conditions of small innovative enterprises

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ABSTRACT

The creation of competitive products with a high degree of science intensity is impossible without the use of innovations. However, in their creation process does not always comply with the environmental safety requirements, which leads to negative consequences for the natural environment and human health. This article presents the results of research work group of authors to create wear-resistant polymer composites and their rational use in the processes of parts manufacturing machines running under the impact of the abrasive particles in the absence or limited admission Lube. A method of applying a metal coatings on fibers and powders, in which a metal coating layer with a thickness from 50 nm is applied to the surface by thermal decomposition organometallic compounds vapour using CVD-method, and device for molding polymer composites pressure. Developed innovative polymer composites based on polyamide-6.6 reinforced with metallic fibers and powders used for the manufacture of parts of construction, emergency rescue and other types of equipment. As a result of conducting a comprehensive study reported an increase resources manufactured parts relative serial assembly units. The ecological nature of the creating polymer composites in the conditions of small innovative enterprises was ensured by conducting the process in a closed cycle with the possibility of re-use of the reagents. This eliminated the flow of pollutants into the environment and allowed the implementation of the principles of resource and energy conservation.

Keywords: CVD-method, organometallic compounds, polymer composites, resource saving, environment safety, innovations.

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Introduction

The functioning of innovative enterprises is one of the conditions for the progressive development of the economy of a modern state. The possibility of obtaining an innovative commercial product in medium and small-scale production provides undeniable advantages in the development of the sales market and the search for optimal product characteristics for the consumer. At the same time, in the conditions of small innovative enterprises, there are objective prerequisites for the implementation of technological processes, taking into account the requirements of technosphere safety, energy and resource saving through the development and implementation of low-waste technologies, as well as the involvement of regional natural resources in production processes [[1], [2], [3], [4]].

When creating a new composite at an enterprise operating on the basis of a scientific center (university, scientific institute, etc.), the possibility of approbation of the current results of scientific research (technologies and equipment) at the stages of development and experimental design is of particular importance. At the same time, the most difficult and interesting task is the choice of the optimal composition and technological regimes that ensure the production of materials with desired physical, mechanical and operational properties. It is necessary to take into account the whole range of operating factors of machine parts and equipment for which it is intended, testing various options for the composition and ratio of the material components. Such tasks are of an explicit research nature and require deep study at the theoretical and empirical levels of research using the methods of thermodynamics, electron microscopy, energy dispersive X-ray spectroscopy, as well as bench and operational tests of samples of materials and parts of machines and equipment.

The purpose of this study is to analyze the possibilities and prospects for developing an environmentally friendly method for producing composites based on thermoplastics, the use of which in small-scale production will ensure the creation of an innovative product.

Experimental Part

Composites based on thermoplastics are widely used in various industries, including mechanical engineering and repair production in the manufacture and restoration of machine parts operating under the influence of wear factors and a corrosive environment. The required properties (wear resistance, hardness, heat resistance, shrinkage, etc.) are obtained by combining the characteristics of the matrix and filler [1].

To achieve optimal compatibility of the filler elements with the matrix, they were metallized by the CVD method of organometallic compounds in the technological modes presented in the works [[1], [5]].

The study of the quality of metal coatings was carried out using a two-beam system (small dual beam, FIB / SEM) in a scanning electron microscope Quanta 3D FEG.

Obtaining images and parts from polymer composites based on polyamide - 6.6 was carried out using a device for injection molding of thermoplastics and composites based on them under pressure [6].

Bench and operational tests of images and parts made of polymer composites were carried out on the basis of state and interstate standards:

- state standard 18616-88 “Plastics. Method for determining shrinkage”,
- state standard 11629-2017 “Plastics. Friction Coefficient Determination Method”,
- state Standard 21341-2014 “Plastics and ebonite. Method for determining heat resistance according to Martens".

Research discussion

As part of the research activities of the authors, the development of methods for obtaining wearresistant polymer composites for the manufacture and restoration of mating parts of road construction, emergency rescue, tillage and mining machines using the Chemical Vapor Deposition method (CVD), that is, "chemical vapor deposition”) of organometallic compounds (OMC). Using this method, it is possible to improve the characteristics of the filler elements of the composite through their metallization, achieving optimal adhesive compatibility with the matrix [[5], [6]].

The essence of the CVD method is to convert the initial OMC into a vapor state by evaporation or sublimation and deposition of the metal on the surface of the substrate heated to the decomposition temperature of the OMC.

Figure 1 shows the general scheme of the process.

$$\begin{matrix}[OMC]\xrightarrow[liquid]{Evaporation}\\ [OMC]\xrightarrow[powder]{Sublimation}\end{matrix}[OMC]\xrightarrow[gas]{Decomposition}[Metal]+\begin{bmatrix}Related\\ products\end{bmatrix}$$

Figure 1 - General scheme for implementing the OMC CVD method

When implementing the OMC CVD method, an active atomic background is formed, which is accompanied by a spontaneous thermodynamically favorable arrangement of the substance on the metallized surface and contributes to obtaining a uniform metal coating with a thickness of 50 nm to 200 mm on substrates, incl. complex configuration (powder particles, fibers, etc.) [[5], [7]].

As initial metallization reagents, carbonyl, cyclopentadienyl and bisarene OMCs can be used, which have the volatility required for the CVD method, the absence of aggressiveness with respect to the substrate and the equipment used, as well as a relatively low decomposition temperature (up to 600°C), which is important for implementing the principle of energy saving of technological process [[8], [9], [10]].

When carbonyl organometallic compounds of nickel, iron, molybdenum, and other metals are

Table 1 – Nomenclature and Characteristics of Initial OMCs, Substrates, and CVD Metal Coatings

Substrate		Original OMC			Coating	
View	***Size, microns***	***View***	***Temperature, ℃***		***Basis***	***Thickness, microns***
			Evaporation / sublimation	***Expansions***		
Glass fibers	5 – 10 (diameter)	$Ni(CO)_4$	30	60 - 200	Ni	0.01 - 0.05
Carbon fibers		$Ni(C_5H_5)_2$	100	400 - 450	Ni	0.50 - 1.00
Particles of quartz sand	140 - 280	$Fe(CO)_5$	100	60 - 250	Fe	0.50 - 1.00
Metal powders PG-US25	125 - 200	$Mo(CO)_6$	40	130 - 400	Mo	0.08 - 0.10

used as initial reagents, the main reaction of the process is the thermal dissociation of OMC:

$$M_x(CO)_y \xrightarrow{t} xM + yCO,$$

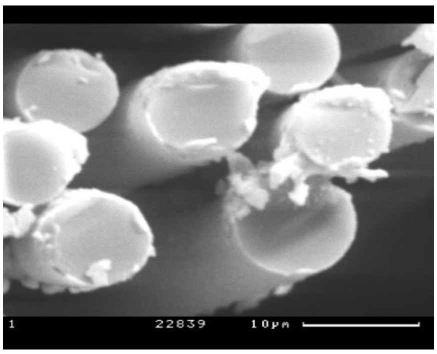
where M is a transition metal of groups V ... VIII of the Periodic system of chemical elements of D.I. Mendeleev;

t – decomposition temperature OMC, ℃.

The implementation of the process is based on changing its temperature regime at the stages of transferring the initial OMC to a vapor state and the interaction of the OMC with a substrate heated to the temperature of its decomposition. The ongoing chemical reactions are reversible, which makes it possible to ensure the cyclicity of metallization and to use the initial reagents that have not come into contact with the substrate in the repeated stages of the process. This ensures low waste and resource saving for technological processes of metallization using the CVD method.

Table 1 lists the filler (substrate) elements of composites obtained using the OMC CVD method [1].

Figure 2 shows the appearance of metallized powders and fibers obtained by the CVD OMC method.



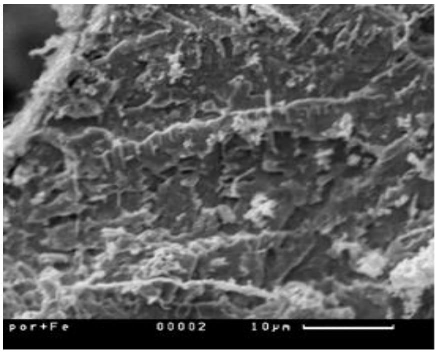


Figure 2 – Cross-section of glass fibers and quartz sand powder particles metallized by the CVD OMC method

To obtain composites based on thermoplastics using modified fillers by injection molding, to study and optimize their properties in order to achieve the characteristics required under specific operating conditions, a device has been developed, the scheme of which is shown in Figure 3.

With this device, which is compact and simple in design, it is possible to obtain a wide range of samples of materials and parts. The principle of its operation is based on filling the melt accumulator with 9 thermoplastic granules (formaldehyde-dioxolane copolymer, polyamide-6, polyamide-6.6, acrylobutadiene styrene plastic, low-pressure and high-pressure polyethylene, polypropylene, etc.) and a filler of the appropriate type (metallized powders, granules, fibers 5 - 7 mm long) in the required amount (from 1 to 50% (wt.) and their uniform heating to the melting temperature of the thermoplastic (180 - 250˚C)).

The formed melt, using a cylindrical pusher, fills the cavity of the mold 11, in which it is kept under pressure at the pressing temperature for a given time. Then the pressure is released, the mold 10 is cooled, the finished material sample (part) is removed [6].

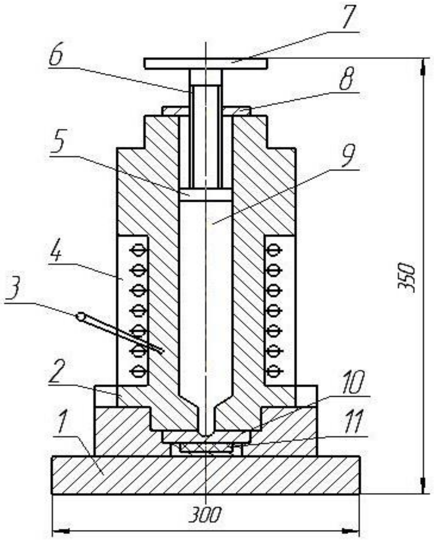


Figure 3 - Scheme of the device for molding composites under pressure: 1 - base; 2 - body; 3 – thermocouple; 4 - heater; 5 - cylindrical pusher with plasticator; 6 - stock; 7 - flywheel; 8 - threaded cover; 9 - melt accumulator; 10 - mold; 11 - mold cavity

Figure 4 shows a composite based on polyamide-6.6 (PA 66) with a filler in the form of short glass fibers metallized by the CVD method (the initial reagent is nickel tetracarbonyl), a sample of which was obtained by injection molding using the developed device [1].

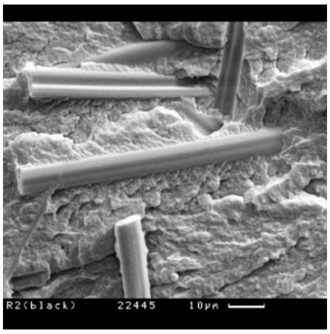


Figure 4 - Polyamide-6.6 armed with glass fibers in a nickel film

Comparative characteristics of composites based on polyamide-6.6 filled with metallized powders and fibers are presented in Table 2.

The developed composites were studied for the possibility of using for the production and restoration of machine parts (sliding bearings, seals for hydraulic system parts, etc.) operating in corrosive and abrasive environments with a limited supply of lubricants.

In particular, based on the analysis of a set of material properties, load-speed modes and operating conditions for the manufacture of guide bearings for the outreach mechanism of an MTA-160 crane installation with a maximum load of 10 kN, the optimal composite is polyamide-6.6 filled with metallized carbon fibers; filling - 20% (wt.).

Figure 5 shows a general view of the manufactured parts.

Figure 5 – Guide supports of the MTA-160 crane installation, made of polymer composite

In the course of operational tests of four crane installations in construction organizations of the Tver region of the Russian Federation, it was found that the wear of guide supports made from the developed polymer composite is 60 - 70% less than that of similar serial parts made from the VMT "Sipas"composite.

Table 2 - Comparative characteristics of composites based on polyamide-6.6 obtained by the developed technology

Properties	**Type and content of the filler**							
	Metal powders PG-US25		***Carbon fibers***		***Glass fibers***		***Particles of quartz sand***	
	OMC	***% (масс.)***	***OMC***	***% (wt.)***	***OMC***	***% (wt.)***	***OMC***	***% (wt.)***
	$Mo(CO)_6$	***10-50***	***$Ni(C_5H_5)_2$***	***10-20***	***$Ni(CO)_4$***	***10-20***	***$Fe(CO)_5$***	***10-50***
Hardness, MPa	111 - 140		110 - 138		110 - 150		115 - 151	
Shrinkage, %	0.60 - 1.30		0.85 - 1.50		0.90 - 1.60		0.62 - 1.40	
Heat resistance according to Martens, ℃	140 - 230		144 - 210		115 - 190		150 - 205	
Friction coefficient without lubricant	0.11 – 0.19		0.07 - 0.08		0.09 - 0.10		0.25 - 0.38	

Conclusions

Firstly, a fundamental approach to the development of an environmentally friendly technology for the production of polymer composites is proposed, which is based on the principles of low waste and resource saving, implemented through innovative solutions to optimize the properties of the filler through metallization by the CVD method of organometallic compounds.

Secondly, a device for molding composites based on thermoplastics under pressure has been developed, characterized by compactness, reliability, structural simplicity, controlled consumption of raw materials and a wide range of obtained samples of materials and parts, using which composites based on thermoplastics filled from 10 to 50% (wt.) powders and fibers metallized by the CVD method OMC, having shrinkage during injection molding 0.6 - 1.6%, friction coefficient when working without lubricants 0.07 - 0.38, heat resistance 115 – 230 °C.

Thirdly, the results of comparative bench and operational tests of samples of materials and parts substantiate the feasibility of using the developed technology in the conditions of small innovative enterprises in the restoration and manufacture of machine parts.

Compliance with Ethical Statement

On behalf of all authors, the correspondent author declares that there are no potential conflicts of interest in this research.

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Шағын инновациялық кәсіпорындар жағдайында полимерлі композиттерді өндірудің экологиялық таза технологиясын жасау мүмкіндігін зерттеу

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ТҮЙІНДЕМЕ

Ғылымды аса қажет ететін бәсекеге қабілетті өнімді инновацияларсыз жасау мүмкін емес. Бірақ оларды игеру барысында экологиялық қауіпсіздік талаптары сақтала бермейді, бұл табиғи орта мен адам денсаулығына жағымсыз жағдайларға әкеледі. Мақалада тозуға төзімді полимерлі композиттерді жасау және оларды майлау материалдарының жоқтығы немесе жеткізілімі шектеулі жағдайда абразивтік бөлшектердің әсерінен жұмыс істейтін машина бөлшектерін өндіруде ұтымды пайдалану бойынша авторлар тобының ғылыми-зерттеу жұмыстарының нәтижелері берілген. CVD әдісімен талшықтар мен ұнтақ бөлшектеріне металл жабындарын жағу әдісі әзірленді, онда металлорганикалық қосылыстардың буларының термиялық ыдырауы арқылы субстрат бетінде қалыңдығы 50 нм-ден көп металл жабын қабаты пайда болады және олардың негізіндегі термопластиктерді және композиттерді қысыммен қалыптауға арналған құрылғы жасалды. Металдандырылған талшықтармен және ұнтақтармен нығайтылған полиамид-6.6 негізіндегі инновациялық полимерлі композиттер жол құрылысына, авариялық құтқару және басқа да техника түрлеріне арналған бөлшектерді жасау үшін пайдаланылды. Кешенді зерттеуді жүзеге асыру нәтижесінде сериялық құрастыру қондырғыларына қатысты өндірілген бөлшектердің ресурсы ұлғайды. Шағын инновациялық кәсіпорындар жағдайында полимерлі композиттерді алу технологиясының экологиялық тазалығы реагенттерді қайта пайдалана отырып процесті тұйық циклде жүргізу арқылы қамтамасыз етіледі. Бұл қоршаған ортаға ластаушы заттардың түсуін болдырмайды және ресурс пен энергияны үнемдеу қағидаттарын іске асыруға мүмкіндік береді.

Түйін сөздер: CVD әдісі, металлорганикалық қосылыстар, полимерлі композиттер, ресурстарды үнемдеу, экологиялық қауіпсіздік, инновация.

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Исследование возможности разработки экологически безопасной технологии получения полимерных композитов в условиях малых инновационных предприятий

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АННОТАЦИЯ

Создание конкурентоспособной продукции с высокой степенью наукоемкости невозможно без применения инноваций. Однако в процессе их разработки не всегда соблюдаются требования экологической безопасности, что приводит к негативным последствиям для природной среды и здоровья человека. В статье приводятся результаты научно-исследовательской работы коллектива авторов по созданию износостойких полимерных композитов и их рациональному применению в процессах изготовления деталей машин, работающих в условиях воздействия абразивных частиц при отсутствии или ограниченном поступлении смазочных материалов. Разработан способ нанесения металлических покрытий на волокна и порошковые частицы CVD-методом, в котором на поверхности подложки формируется слой металлического покрытия толщиной от 50 нм посредством термического разложения паров металлоорганических соединений, и устройство для литья термопластов и композитов на их основе под давлением. Инновационные полимерные композиты на основе полиамида-6.6, армированного металлизированными волокнами и порошками, применялись для изготовления деталей дорожно-строительной, аварийно-спасательной и других видов техники. В результате реализации комплексного исследования зафиксировано увеличение ресурса изготовленных деталей относительно серийных сборочных единиц. Экологичность технологии получения полимерных композитов в условиях малых инновационных предприятий обеспечивается проведением процесса в замкнутом цикле с возможностью повторного использования реагентов. Это исключит поступление загрязняющих веществ в окружающую среду и позволит реализовать принципы ресурсо- и энергосбережения.

Ключевые слова: CVD-метод, металлоорганические соединения, полимерные композиты, ресурсосбережение, экологическая безопасность, инновации.

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