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STRUCTURE AND PROPERTIES OF POLYAMIDE COATINGS FORMED USING INDUCTION HEATING

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Abstract

The article studies the physical and mechanical characteristics of coatings formed from powders of polyamides PA 11, PA 6 obtained by cryogenic grinding of semi-finished products cooled to liquid nitrogen temperature. Polyamide coatings were created by two different technological methods from a fluidized state. The morphology of polyamide particles was studied using optical and scanning microscopy. The structure of polymer composite materials has been studied by IR spectroscopy, optical and atomic force microscopy, and X-ray diffraction analysis. The conducted studies have shown that induction heating of steel substrates makes it possible to provide higher adhesive characteristics of polyamide coatings. Structural changes in coatings have a significant impact on the tribotechnical characteristics of coatings. It has been established that an increase in the degree of crystallinity and molecular order in the amorphous phases of the polymer leads to an increase in the hardness and wear resistance of polyamide coatings.

Keywords: polyamide, coating, morphology, wear, spectrum, powder, adhesion, heating.

СТРУКТУРА И СВОЙСТВА ПОЛИАМИДНЫХ ПОКРЫТИЙ, ПОЛУЧЕННЫХ МЕТОДОМ ИНДУКЦИОННОГО НАГРЕВА

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Реферат

В статье проведено исследование физико-механических характеристик покрытий, сформированных из порошков полиамидов ПА 11, ПА 6, полученных криогенным измельчением полуфабрикатов, охлажденных до температуры жидкого азота. Полиамидные покрытия создавались двумя различными технологическими способами из псевдооживленного состояния. С помощью оптической и сканирующей микроскопии изучена морфология частиц полиамида. Методами ИК-спектроскопии, оптической и атомно-силовой микроскопии, рентгеноструктурного анализа исследована структура полимерных композиционных материалов. Проведенные исследования показали, что индукционный нагрев стальных подложек позволяет обеспечить более высокие адгезионные характеристики полиамидных покрытий. Структурные изменения в покрытиях оказывают значительное влияние на триботехнические характеристики покрытий. Установлено, что повышение степени кристалличности и молекулярной упорядоченности в аморфных фазах полимера приводит к повышению твердости и износостойкости полиамидных покрытий.

Ключевые слова: полиамид, покрытие, морфология, износ, спектр, порошок, адгезия, нагрев.

Introduction

In mechanical engineering, over the past decade, there has been a trend to reduce weight in various designs used for the manufacture of components and assemblies, including the manufacture of components for automotive and tractor equipment [1]. In particular, in passenger cars, steel products are being replaced by products made of aluminum and magnesium alloys. This achieves the cost-effectiveness of the operation of manufactured structures for mechanisms and apparatus. However, in recent years, areas of application of so-called hybrid composite materials have been developing, which combine the high strength of the metal and the antifriction characteristics of polymers [2]. At the same time, hybrid components and composite materials are becoming increasingly important. Hybrid components and composite materials provide a performance advantage by highlighting the favorable properties of materials used in various designs and reducing their disadvantages. In this way, materials can be combined, which has not previously been given sufficient attention.

Polymers are an example of this fact. Light weight and ease of forming products from them are only two aspects that make polymers interesting for large-scale production. The disadvantages of polymers are low resistance to abrasive wear and UV radiation, which is unacceptable for most technical applications. To improve the physical and mechanical characteristics, polymers are combined with various solid materials in order to improve the performance properties of polymers [2, 3]. At present, polymer coatings are widely used in various technical fields. The most common are partially crystalline thermoplastics with high wear resistance values. In particular, polyamides belong to this class of materials. The use of PA11 as a protective, anti-friction coating has been known for a long time. However, the disadvantage of this material is that this substance is an imported product, has a high wear compared to polyamides 6 and 66, as well as its cost. The possibility of solving problems associated with the use of polyamide 11 is determined by four directions. The first direction is the replacement of polyamide 11 with domestic analogues. In this regard, studies were

carried out on the creation of composite coatings [4–6] based on polyamide 6 and 66 to replace PA11. In a number of cases, high tribological and operational characteristics of these coatings were achieved [4–6], but a lower adhesion strength to metal substrates was observed compared to PA11. In a number of cases, additional technological processing of polyamide coatings was necessary, associated with obtaining coatings exactly in size and removing the surface layers of the polymer. Polyamide 11 also showed its best deformation and strength characteristics compared to PA6 and PA66 during the process, for example, of pulling splined bushings of cardan gears with a polymer coating. There was less rejection associated with the peeling of the polymer coating when using PA11. The second direction is the creation of own production for the production of polyamide 11. Currently, there are small specialized production facilities that allow the production of small batches of domestic production of polyamide 11. However, at the moment, these capacities are not enough to provide all consumers with this polymer. The third direction is the modification of polyamide 11 with domestic modifiers, in particular, nanometer dimensions to give the required performance characteristics, as well as the development of new technological approaches in the formation of polyamide coatings [7–9].

The fourth direction for reducing the cost and improving the performance of polyamide coatings is the optimization of existing technologies for the formation of these macromolecular compounds on metal substrates.

The purpose of this work is to study the physical and mechanical characteristics of polyamide coatings formed by different technological approaches from a fluidized state.

Experimental technique

To prepare powder materials, we used powders of polyamides PA 11, PA 6 obtained by cryogenic grinding of semi-finished products cooled to liquid nitrogen temperature. Fractionation of powders was carried out using a set of sieves. For the manufacture of composite materials for coatings, fractions with a cross-sectional size of $100 \leq d \leq 200 \mu\text{m}$ were used. The morphology of the polyamide particles was studied using optical (MMV 2200) and scanning microscopy (Mira Tescan). The sizes of polymer particles were estimated using an NT-206 atomic force microscope. The structure of polymer composite materials (PCM) was studied by IR spectroscopy (Tensor-27), optical (MMV 2200) and atomic force (NT 206) microscopy, X-ray diffraction analysis (DRON-3.0). The physical and mechanical characteristics of the coatings were evaluated according to generally accepted methods. Adhesion strength was evaluated by peeling at an angle of 180° . The coatings were applied according to two technological approaches. The first one is a standard coating formation technology currently used at OAO Belcard for the formation of polyamide coatings on splined bushings of cardan gears of various nomenclature. The essence of the technology (technology 1) is the formation of an adhesive sublayer of the Rilprim primer on the surface of the sleeve and heating a batch of sleeves with a primer in a chamber furnace to $400\text{--}420^\circ\text{C}$, followed by exposure to air until the polyamide components are completely melted. In some cases, to create an adhesive-active layer, phosphating a metal surface is used. The surface of the metal sample was cleaned from oxides and contaminants by treatment with abrasive powder and degreased with gasoline. Another technological approach for the formation of polyamide coatings is heating the splined bushing or sample to $400\text{--}420^\circ\text{C}$ by using induction heating using the original inductor design (technology 2).

Research results

Figure 1 shows pictures of PA11 (Rilsan), PA6 powders obtained by solution and cryogenic technology for the formation of dispersed polyamide particles. The morphology of polyamide particles (PA 11) obtained by solution technology has a smoothed appearance close to a sphere. PA6 particles have a developed comminuted body appearance and hence higher specific surface area. The calculation of the shape factor, which is a generalizing parameter for assessing the shape of an object, showed values for polyamide 11 – 0.8, for PA6 – 0.4. This parameter is a dimensionless coefficient independent of orientational effects in the object structure. The maximum value of this coefficient is equal to one in the case of a circle and is determined based on the ratio of the area of the object to the square of its perimeter, multiplied by 4π .

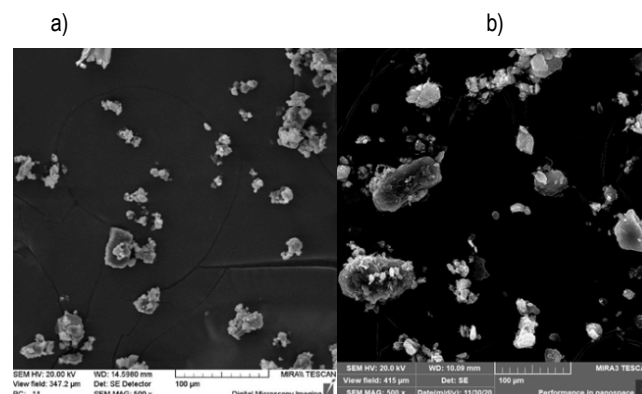
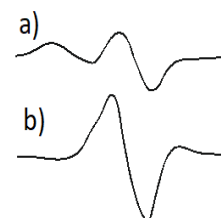


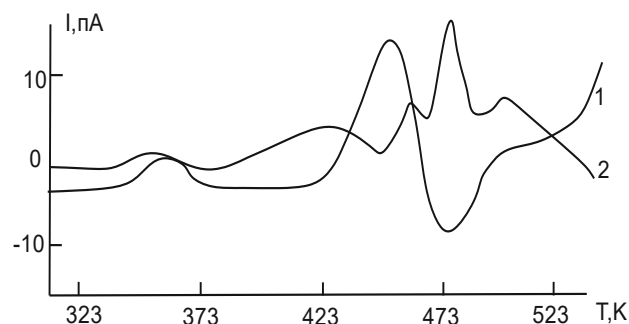
Figure 1 – Morphology of PA11 (a), PA6 (b) particles
Dispersion of particles from 60 to 100 microns

The developed habit of the particles of polyamide powders and high values of the specific surface indicate the activity of these particles, which may be due to the presence of an uncompensated charge formed during mechanical dispersion at low temperatures. This assumption is confirmed by the results of studies carried out by the methods of EPR and thermally stimulated currents (Figures 2, 3).



a – characteristic view of the EPR spectra of dispersed particles of polyamide 11, obtained by polymerization; b – characteristic view of the EPR spectra of dispersed particles of polyamide 6 obtained by cryogenic technology

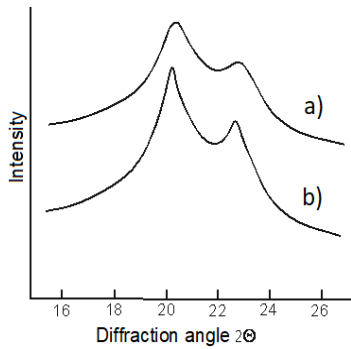
Figure 2 – EPR spectra of powders of polymeric materials



1 – characteristic view of the TCT spectrum of dispersed particles of polyamide 11 obtained by polymerization; 2 – characteristic view of the TCT spectrum of dispersed particles of polyamide 6 obtained by cryogenic technology

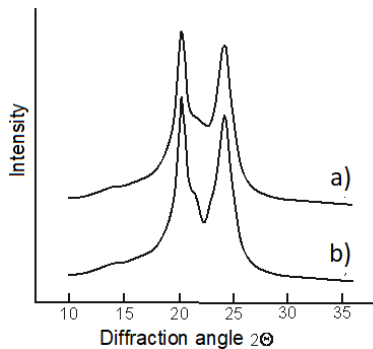
Figure 3 – TCT spectra of powders of polymeric materials

The X-ray diffraction studies of coatings formed according to two technological approaches showed that the use of induction heating makes it possible to obtain protective coatings with higher values of the degree of crystallinity, both for coatings based on polyamide 11 and polyamide 6 (Figures 4, 5).



a – heating was carried out in a chamber furnace; b – induction heating

Figure 4 – X-ray patterns of polyamide 11 coatings obtained on steel 40X using various technological approaches for heating the steel substrate



a – heating was carried out in a chamber furnace; b – induction heating

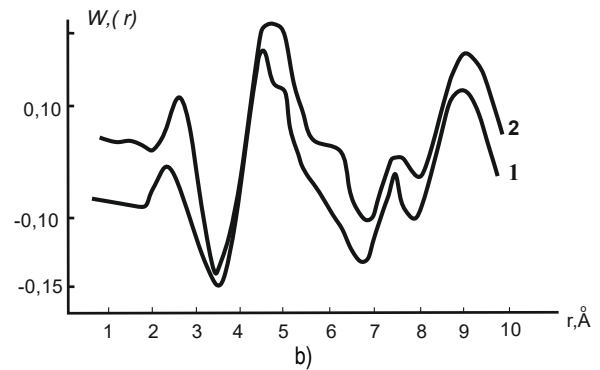
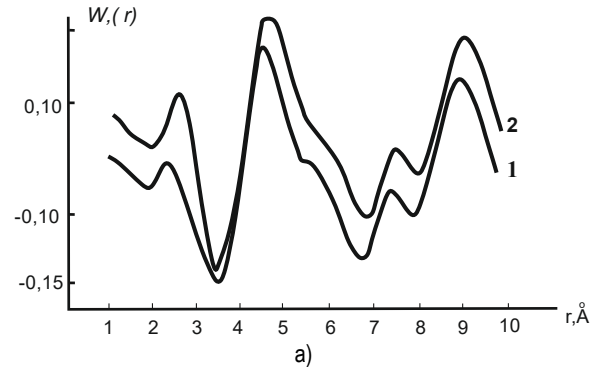
Figure 5 – X-ray patterns of polyamide 6 coatings obtained on steel 40X using various technological approaches for heating the steel substrate

The deposition of polyamide coatings from polyamide 11 on splined bushings made of steel 40X leads to the formation of α -crystals in the polymer structure, as evidenced by the appearance of diffraction maxima in the region $2\theta \sim 20^{\circ}25'$ and $22^{\circ}45'$. This process occurs as a result of natural cooling of the samples to normal temperature. The technology of forming tribological coatings from polyamide 11 has a significant impact on the degree of crystallinity of the obtained protective coatings (table 1). The method proposed in [10] was used to calculate the degree of crystallinity. This approach does not give absolute values of the degree of crystallinity, but allows one to estimate with high reliability the changes in molecular order (degree of crystallinity) in polyamide matrices when external or internal factors change during the formation of coatings or products from a given polymer material.

Table 1 – Dependence of the degree of crystallinity of polyamide coatings on the type of deposition technology

Formation technology, polymer-grade	PA 6, option 1	PA 6, option 2	PA 11, option 1	PA 11, option 2
Degree of crystallinity (ϵ), %	1.51	1.63	2.1	2.14

According to the data obtained for polyamide 6, two intense reflections are observed in the 2θ region from 15° to 30° . The calculation performed showed that this corresponds to interplanar distances $d_1=3.76 \text{ \AA}$ and $d_2 = 4.38 \text{ \AA}$. Similarly, as for polyamide 11, option 2 of the technology for forming polyamide coatings increases the degree of crystallinity of polyamide coatings for the crystalline phase of the polymer material. It is possible to assume that molecular ordering will also be observed in the amorphous phase of polyamide coatings. The construction of the atomic density radial distribution function (RDDF) for the studied polymers [2] made it possible to establish that molecular ordering increases in the amorphous phase of the polymer matrix when using the second variant of the formation of polyamide coatings (Figure 6).



a,1 – coating based on PA6, formed according to technology 1; a,2 – coating formed according to technology 2; b, 1 – coating based on PA11, formed according to technology 1; b, 2 – coating formed according to technology 2

Figure 6 – FRRAP of polyamide coatings

Based on the data obtained by X-ray diffraction analysis, it is possible to assume that as a result of the use of automated induction heating of splined bushings, the physical and mechanical characteristics of polyamide coatings will change. One of the main parameters determining the adhesive characteristics of polyamide coatings is adhesive strength. Conducted studies to determine the adhesive characteristics of polyamide coatings formed according to different technological approaches showed that induction heating of steel substrates makes it possible to provide higher adhesive characteristics compared to heating slotted bushings in chamber furnaces (Figure 7).

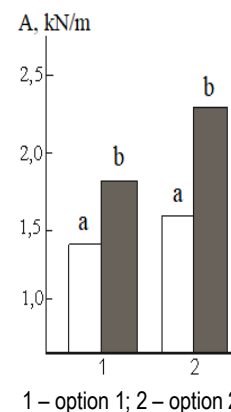
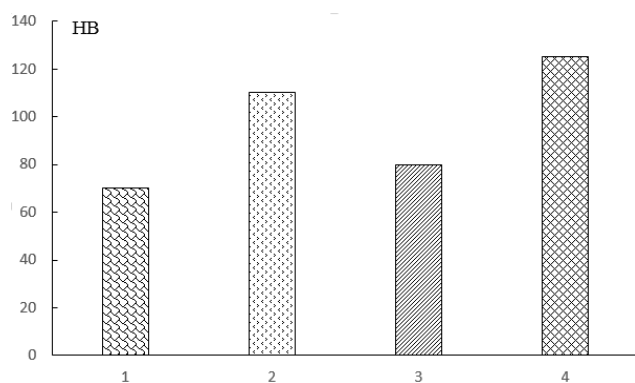


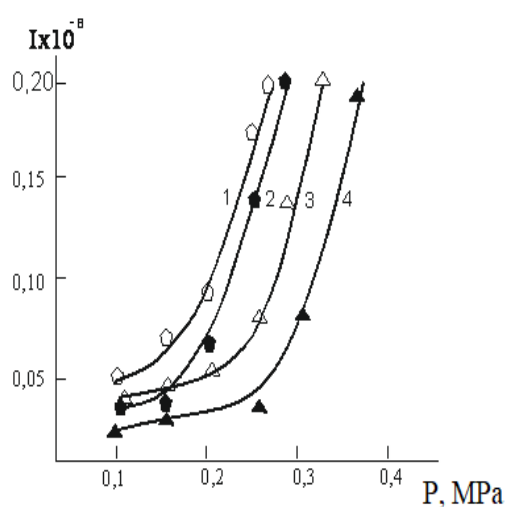
Figure 7 – Adhesion strength of a coating based on PA6 (a) and P11 (b) with different coating formation technologies

Structural changes observed in coatings have a significant impact on the tribotechnical characteristics of polyamide coatings formed using various technological approaches. An increase in the degree of crystallinity and molecular ordering in the amorphous phases of the polymer leads to an increase in the hardness of the coatings (Figure 8) and, as a consequence, an increase in wear resistance (Figure 9).



1.3 - option 1 of coating formation, 2.4 - option 2 of coating formation

Figure 8 – Dependence of the hardness of coatings from PA 11 (1.3) and PA 6 (2.4) on steel 60 PP



1.3 – option 1 of coating formation, 2.4 – option 2 of coating formation

Figure 9 – Dependence of wear intensity on load during friction of coatings made of PA 11 (1.3) and PA 6 (2.4) on steel 60 PP; sliding speed 0.6 m/s

Based on the data presented in Figure 9, the wear intensity is reduced by 30–70 % for coating option № 2 compared to option № 1. This effect is typical for all grades of the studied polyamides and in a given range of loads.

Conclusions

The use of induction heating of splined bushings made of 40X steel leads to uniform heating of the samples under study, which makes it possible to more accurately determine the temperature ranges for the formation of polyamide coatings. The developed technological approach makes it possible to increase the values of the degree of crystallinity and molecular ordering in the amorphous phase of the polymer, which leads to an increase in the hardness and wear resistance of polyamide coatings formed from polyamide powder materials of various chemical structures and formation technologies. This article will be useful to specialists in the field of condensed matter physics, design engineers and technologists specializing in the development of automotive and tractor equipment, as well as graduate students and undergraduates.

References

1. Kravchenko, V. I. Kardannye peredachi: konstrukcii, materialy, primeneniye / V. I. Kravchenko, G. A. Kostyukovich, V. A. Struk ; pod red. V. A. Struka. – Minsk, 2006. – 523 s.
2. Noveye materialy i tekhnologii, primenyaemye pri proizvodstve kardannykh peredach / V. I. Kravchenko [i dr.] // Vestnik Belorussko-Rossiiskogo universiteta. – 2006. – № 4 (13). – S. 91–99.
3. Tribotekhnicheskie materialy v konstrukciyakh kardannykh valov / V. I. Kravchenko [i dr.] // Sb. «Mashinostroeniye i tekhnosfera na rubezhe XXI veka». – Doneck, 2001. – S. 170–171.
4. Dovgalyo, V. A. Kompozitsionnye materialy i pokrytiya na osnove dispersnykh polimerov / V. A. Dovgalyo, O. R. YUrkevich. – Minsk, 1992. – 256 s.
5. Nanokompozitsionnye mashinostroitel'nye materialy: opyt razrabotki i perspektivy primeneniya / V. I. Kravchenko [i dr.] // Tonkie plenki i nanostrukturnyye materialy mezhdunarodnoy nauchnoy konferentsii, Moskva, 22–26 noyabrya 2005 g. / Moskovskiy gosud. institut radiotekhniki, elektroniki i avtomatiki. – Moskva, 2005. – CH. 2. – S. 129–135.
6. CHvalun, C. N. Polimernyye nanokompozity / S. N. CHvalun // Priroda. – 2001. – № 1. – S. 1–12.
7. Struk, V. A. Tribotekhnicheskie materialy bespasebnoy termoplasticheskoy modifikatsiyi ultradispersnykh klustrov uglerodnykh / V. A. Struk, A. A. Skaskevich, V. I. Kravchenko // VII-th International symposium: Tribological problems in exposed friction systems – The High Tatras, 1999. – P. 149–154.
8. Metallopolimernyye nanokompozity: osobennosti struktury, tekhnologiya, primeneniye / A. A. Ryskulov [i dr.] ; pod nauchn. red. V. A. Struka, V. A. Liopo. – Grodno, 2010. – 335 s.
9. Nanokompozitsionnye materialy i tekhnologii, primenyaemye pri proizvodstve kardannykh peredach / V. I. Kravchenko [i dr.] // Vestnik GrDU. Seriya 6. – 2012. – № 1 (123). – S. 83–93.
10. Rentgenodifraktsionnyye issledovaniya struktury osobennostey polimernykh materialov, modifitsirovannykh ul'tradispersnyimi uglerodnymi napolnitelyami / V. A. Liopo [i dr.] // Vestnik GrGU. Seriya 2. – 1999. – № 2. – S. 47–53.

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