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COMPOSITE HEAT-RESISTANT MATERIALS BASED ON THERMOPLASTIC MATRICES

[1]Elvira T. Krut'ko, [2]Alexander S. Antonov, [2]Alexander N.Lesun, [2]Vasiliy A. Struk

[1]Belarusian State Technological University, 13a Sverdlova Str., 220006 Minsk, Belarus
[2]Yanka Kupala State University of Grodno, 22 Ozheshko str., 230023 Grodno, Belarus
e-mail: ela_krutko@mail.ru

Abstract

Literature data on methods of modification of industrially produced polymeric materials have been analyzed. It is established that among the priority directions of development of material science for tribological systems is the development of the method of modification of thermoplastic matrices of industrial production with functional components that contribute to the inhibition of unfavorable processes leading to the destruction of the surface layer of products. The features of the structure and parameters of the characteristics of composite materials based on thermoplastic matrices of industrial production, modified by oligomers of cross-linking resins of various composition and synthesis technology are considered. It has been shown that the introduction of a methyl derivative of dimethylvinylethynylphenol VD grade, phenol-formaldehyde resin oligomer, FA monomer (a mixture of furfurylideneacetone and difurfurylideneacetone in a ratio of 4:1), oligoimides of unsaturated dicarboxylic acids into the composition of polyamide 6 and polytetrafluoroethylene, makes it possible to achieve a synergistic effect of increasing the parameters of stress-strain and tribological characteristics in the implementation of the thermomechanical modification technology, as well as resistance of composites to thermal oxidation. The effect is due to the interaction of the atomic groups of oligomers with the active groups of the macromolecule and the process of cross-linking of oligomeric components, which leads to the formation of a cross-linked structure with increased resistance to the effects of operational factors. Composites based on aliphatic polyamides and polytetrafluoroethylene, modified with imide-containing compounds, with increased performance parameters, have been developed and recommended as functional materials for the manufacture of products for automotive units, sealing and shut-off valves of technological equipment for the production of compressed and liquefied media

Keywords: *polyamide, polytetrafluoroethylene, oligomer, oligoimides, imide-containing compounds, diffusion stabilization*

Introduction

Specific operating conditions of products made of thermoplastic materials in the structures of machines, mechanisms and technological equipment necessitate targeted modification of polymer binders, which reduces the disadvantages of thermoplastics and enhances their advantages. Significant disadvantages of industrial structural thermoplastics are a comparatively high coefficient of friction, which reaches 0.6-0.8 under friction without lubrication, low thermal and heat resistance, and insufficiently high parameters of deformation and strength characteristics. These features of polymer binders do not allow them to be used in an unmodified form for the creation of composites, the products of which are operated at ambient temperatures above 373 K. No less important is the insufficiently high resistance of thermoplastics to the effects of external operating conditions (ultraviolet, ozone, oxygen in the air, thermal-oxidizing environments). Macromolecules of structural thermoplastics contain active sites due to the structure of the chain or the peculiarities of synthesis. These centers can interact with various reagents, such as oxygen in the air. As a result, there is a significant decrease in the service characteristics of thermoplastic products. This fact is of particular importance in the case of mechanical impact of polymeric materials on products, in which the number of active sites in the macromolecules of the surface layers increases sharply and mechanochemical reactions are initiated [1-4].

In this regard, one of the directions of modern composite materials science is the development of methods for modifying structural thermoplastics, produced by the domestic industry on a large scale, with targeted additives that would eliminate or reduce the initial prerequisites for the destruction of their macromolecules under the influence of operational wear factors, primarily tribochemical.

One of the simplest and most affordable methods for obtaining polymer-polymer bonds is the mixing of components in a viscous-flowing state in various technological installations. This method makes it possible to significantly expand the range of structural materials by combining polymers and oligomers with different properties [5-9].

The analysis of the literature data allows us to outline some ways of modifying high-tonnage polymeric materials in order to improve the performance characteristics of antifriction materials based on them (Fig. 1).

The purpose of this work was to study some directions of control of the parameters of the structure and performance characteristics of industrial thermoplastics.

Experimental Part

As matrices for the development of composite materials, industrially produced thermoplastics were used: polyamide 6 (branch "Plant Khimvolokno" of JSC "Grodno Azot") and polytetrafluoroethylene (F-4M produced by JSC "Halogen", Russia).

To create materials with increased performance parameters, oligomers of phenol-formaldehyde resins (PFR, VDU, phenoloalcohol) and bifunctional imids of unsaturated dicarboxylic acids were used.

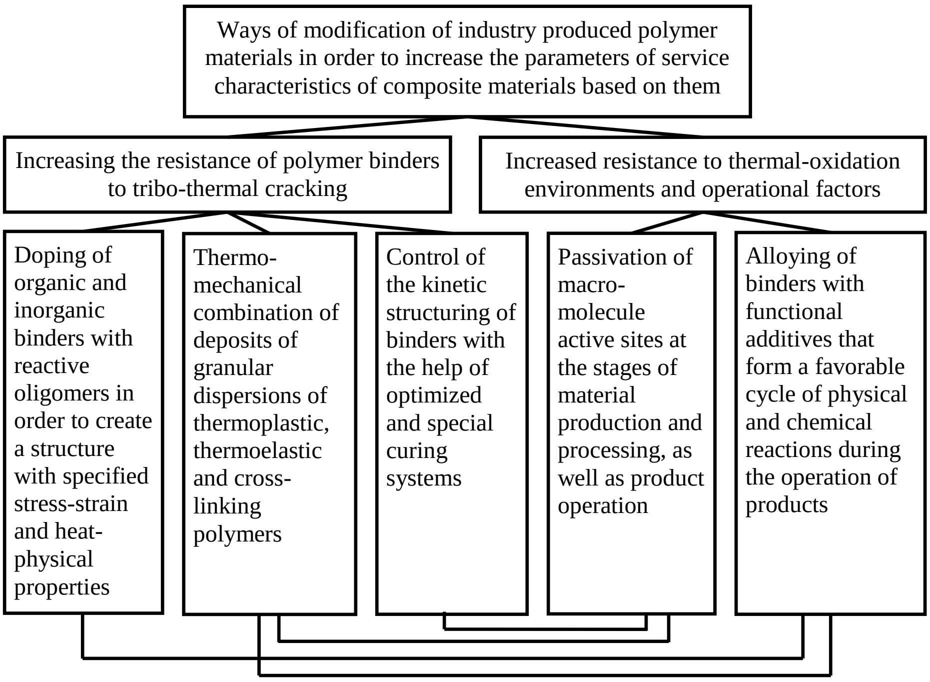

Fig. 1. Some areas of inoculation of high-tonnage polymer materials

The study of physical and chemical processes in the static and dynamic (frictional) interaction of polymers and metals was carried out using IR spectroscopy methods (UR-20), mass spectroscopy (MX-7301), electron paramagnetic resonance (РЭ 1301), X-ray diffraction (Dron-2), thermal (Q-1500D) and dilatometric (“Thermoflex”) analyses. The structure of the materials was assessed using optical (Neophot) and electron (JSM-50A) microscopes. The study of the kinetics of cross-linked structure formation in the process of material formation was carried out using specially developed methods: dilatometric and spectrometric. The temperature deformation of the sample and the relative signal intensity of the binder's own paramagnetic centers were used as structurally sensitive parameters characterizing the degree of curing of the binder.

Tribochemical processes were studied using friction machines МИ-1М, МИ-2, СМЦ, UMT-1 and special attachments to the mass spectrometer МСХ-4 by schemes «shaft – partial liner», «pin – pad», «roller – roller» in air, vacuum and liquid media of various compositions. Metal counterbodies were made of iron-based alloys (steel 3, steel 45, cast iron СЧ, stainless steel X18H10T).

The parameters of the physical and mechanical characteristics of the developed composite materials were determined according to the relevant standards.

Experimental studies and processing of the results were carried out with the involvement of methods of factor design of experiments, using standard and developed methods.

Results and Discussion

The initial prerequisites for the destruction of products made of thermoplastic polymer binders are low thermal and heat resistance, phase and structural inhomogeneities due to the structure of the macromolecule, the technology of synthesis and processing. To eliminate the initial prerequisites for wear of products based on thermoplastic binders, various methods of their modification are used. An effective method of improving the performance characteristics of thermoplastics is the introduction of reactive oligomers of cross-linking resins – phenol-formaldehyde, polyester, epoxy, organosilicon and others – into their composition at the stage of processing. [10, 11]. This method is based on the possibility of interaction of thermoplastic macromolecules and a structuring oligomer in place of active functional groups to form a composite that usually combines the advantages of both components.

Oligomers of thermosetting resins, which form a cross-linked structure by the mechanism of polycondensation, contain reactive groups of the type — CH_2OH, — OH, — NH_2 etc. and can be used to modify thermoplastic binders. Of particular interest are the oligomers of multi-tonnage produced thermosetting resins: phenol-formaldehyde (PFR), methylene derivative of dimethylvinylethynylphenol VD grade. The properties of polyamide 6 modified by small additives (0.5-5.0 wt. %) of oligomers of phenolaldehyde resins LBS-3 grade and VD and thermomechanical action in the process of the composition processing on injection molding machines and after heat treatment of the PA6 block, diffusion-stabilized with oligomer solutions were studied. It has been found that the introduction of 0.5–5.0 wt. % into PA6 of oligomers of the LBS and VD grades, or their treatment with oligomer solutions with subsequent heat fixation, changes the strength characteristics (Fig. 2) and causes an increase in the resistance of the modified binder to the effects of high temperatures in air. Obviously, in the process of processing, it is possible for amide groups of polyamide 6 to interact with methylol groups of oligomers to form a partially cross-linked structure [10, 12].

Given that residual formaldehyde is present in industrial oligomers, the cross-linked structure can also be formed as a result of polycondensation of the formed methylomen groups of polyamide and methylol groups of oligomers. The validity of the proposed mechanism is confirmed by the results of DTA and IR spectroscopy. In the IR spectra of modified polyamides, a decrease in the optical density of the absorption band of 3,100 cm^{-1} (— NH). As a result of the modification of the amide groups of polyamide 6 in them, there is a redistribution of electron density and a decrease in the probability of rupture under the thermal-oxidative effect on the macromolecule of the weak α-methylene bond, which is most susceptible to destruction. This results in an increase in the resistance of polyamide 6 to thermal-oxidative environments (Fig.3-5).

A more effective method of alloying turned out to be diffusion stabilization of PA6 blocks with an alcohol or acetone solution of LBS and VD, which makes it possible to protect the surface layer of the product from the effects of a thermal-oxidative environment. The study of the dependence of the breaking tension stress on the duration of thermal oxidation at 423 K shows that the oligomers of VD and LBS are quite effective antioxidants. At the same time, the VD oligomer is more effective than the LBS, which is obviously due to the presence of a large amount of residual formaldehyde in it, which increases the possibility of interaction between PA6 macromolecules and the oligomer.

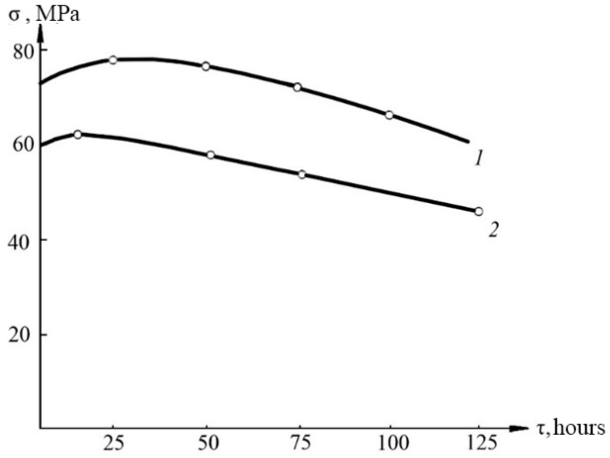

Fig. 2. Dependence of tensile stress (σ) on thermal oxidation time (τ) in air at 423 K of polyamide 6 treated with solutions LBS-3 (1) and VD (2)

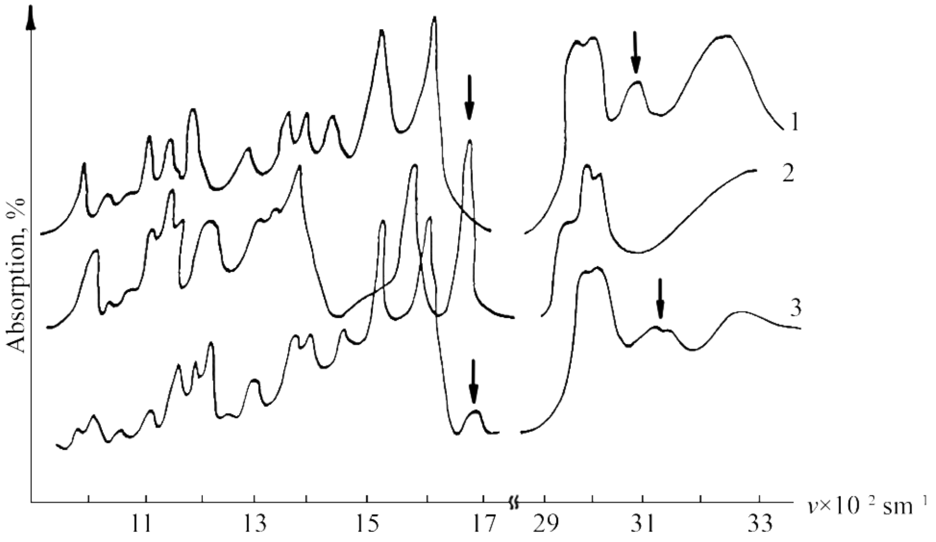

Fig. 3. IR spectra of PA6 (1), VD (2), PA6+VD (3)

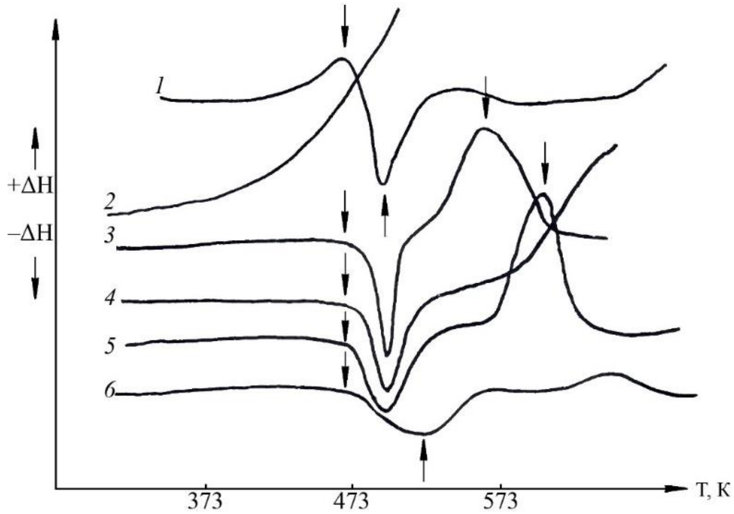

Fig. 4. DTA curves of PA6 (1), monomers FA (2), N,N'-phenylene-bis-maleimide (3) and compositions PA6+1 wt% FA (4), PA6+5 wt% N,N'-phenylene-bis-maleimide (5), PA6+5 wt% N,N'-phenylene-bis-maleimide after heat treatment at 523 K (6)

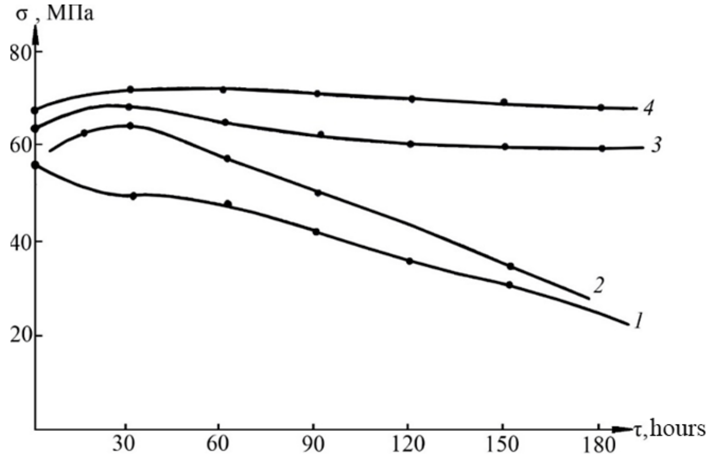

Fig. 5. Dependence of tensile breaking stress (σр) on thermal oxidation time (τ) in air at 423 K PA6 initial (1), modified 1 wt.% of FA (2), 5 wt.% (3) and 10 wt.% N,N'-phenylene-bis-maleimide (4)

Modification of PA6 0.5-7.0 wt. % of the FA monomer reduces the intensity of thermal-oxidative processes in the volume of the polymer. This is confirmed by the decrease in the area of the exothermic effect in the temperature range of 453-473 K on the DTA curves. Polyamide 6 doped in this way retains the tensile strength σ at 40-45 MPa after exposure of 100 hours at 423K. The original polyamide loses 80-90% of its strength under the same processing conditions [13].

The achieved effect makes it possible to use modified polyamide as a binder for anti-friction materials, products made of which are used for a long time under the influence of high temperatures (373-423 K) at [pV]≤0.1-0.5 MPa·m/s.

Oligoimides of unsaturated dicarboxylic acids capable of nucleophilic attachment reactions turned out to be more effective modifiers of aliphatic polyamides. Studies have shown that the use of N,N'-bis-imides for modification has a complex effect on polyamides [14]. At the injection of 0.5-10.0 wt. % of the modifier increases strength characteristics, resistance to thermal-oxidative environments, stabilizes the coefficient of thermal expansion, increases the heat and heat resistance of polyamides [14].

The data of DTA, IR and EPR spectroscopy made it possible to establish that in the process of processing by injection molding, polyamide macromolecules are cross-linked by the mechanism of nucleophilic addition of N,N'-bis-imides, which interact with amide and terminal amino groups (Fig. 4). The effective (apparent) activation energy of thermal-oxidative destruction of oligoimide-modified polyamide at the same conversion rate is 124.7 kJ/mol at 84.5 kJ/mol for the original polyamide. This indicates an increase in the thermal stability of polyamide.

At the same time, the effect of the stabilizing effect of N,N'-bis-imides on polyamides was noted. For example, the value of the tensile breaking stress of PA6 films containing 5–20 wt. % N,N'-phenylene-bis-maleimide remains at the level of 60-70 MPa in air even after 210 hours of thermal aging at 423 K, while the original polyamide loses 60-70 % of strength under similar conditions (σ = 18.6 MPa) (Fig. 5). Blocking amide groups responsible for adhesive interaction during frictional contact with metals [15] helps to reduce the coefficient of friction and increase the wear resistance of modified polyamides. Polyamides doped with oligoimides have been used to create heat- and heat-resistant anti-friction materials.

Oligomers selected from the group of aminophenylene oligomaleimic acid, tetramaleinimidic acid diphenyloxide, oligomaleimideic acid aminohydroxyylphenylene and N,N′-bis-maleimidic acid aromatic diamide were used to modify industrial polytetrafluoroethylene (F-4M) (Tab. 1).

Table 1. Composite materials based on polytetrafluoroethylene modified with oligoimides

Component	Content				
	I	II	III	IV	V
1. N,N′-m-phenylene-bis-maleamidoacid (PBMAA)	10				
2. N,N′-4,4′-diphenyloxide-bis-maleamidoic acid (DPOMAA)		10			
3. Oligoaminophenylene (OAP)			5		
4. Aminophenylene oligomaleimidic acid (APOMA)				10	
5. Tetramaleimidic acid diphenyl oxide (TMACDPO)					10
6. Dry lubrication: colloidal graphite, molybdenum disulfide	5	5	5	5	5
7. Polytetrafluoroethylene F-4M	85	85	85	85	85

It has been established that the introduction of oligomers in the amount of 0.1–20.0 wt. % allows to significantly increase the parameters of deformation-strength and tribological characteristics (Tab. 2). Taking into account that the samples were obtained using the traditional technology of fluorocomposites processing, including mixing of components, cold pressing and hot sintering of blanks at temperatures of 623–653 K, the effect is due to the formation of a specific structure formed by a thermoplastic matrix and cross-linking oligomers. At the same time, the cross-linked oligomeric structure is subjected to intensive thermal oxidation at sintering (monolithization) temperatures, which increases the activity of interaction with the matrix polymer.

Table 2. Characteristics of composite materials based on polytetrafluoroethylene modified by oligoimides

Characteristic	Parameter				
	I	II	III	IV	V
1. Tensile strength, MPa	43	45	43	44	44
2. Strength at 10% deformation, MPa	31	32	32	30	30
3. Coefficient of friction	0.12	0.13	0.13	0.13	0.13
4. Intensity of wear, 10^{-7} mm^3/N·m	1.5	1.8	1.9	1.2	1.4

The conducted research made it possible to develop compositions of composite materials based on industrial thermoplastics (polyamides and polytetrafluoroethylene) with increased performance parameters for the manufacture of functional products for various purposes [16].

Composite materials have been tested in the manufacturing processes of products used for the manufacture of driveshafts of trucks, sealing and sealing units of equipment for the production of compressed and liquefied gases, and have shown high reliability and manufacturability.

Conclusions

The features of the formation of the structure of composite materials based on industrial thermoplastic matrices - polyamide 6 and polytetrafluoroethylene F-4M, modified by oligomers of cross-linking resins of various composition and structure are considered. It has been shown that the introduction of cross-linking resin oligomers into thermoplastic polymers – methylol derivative of dimethylvinylethinylphenol (VD), phenylformaldehyde resin oligomer (PFR), a mixture of furfurylidenate and difurfurylidenacetone (FA monomer), oligoimids (N,N'-m-phenylene-bis-maleamidoacid, N,N'-4,4'-diphenyloxide-bis-maleamidoacid, oligoaminophenylene, oligomaleimideic acid aminophenylene, tetramaleimidic acid diphenyloxide) allows to achieve a synergistic effect of increasing the parameters of deformation-strength, tribological characteristics and resistance to the effects of thermal-oxidative environments. The probable mechanism of the effect is the interaction of the active sites of thermoplastic macromolecules with functional groups of oligomeric modifiers and the formation of a cross-linked structure.

The developed compositions of composites are recommended for the manufacture of products using traditional technologies used in the construction of automotive components, sealing and sealing devices for the production of compressed and liquefied media.

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