ISSN 1995-4212, Polymer Science, Series D, 2023, Vol. 16, No. 2, pp. 420–426. © Pleiades Publishing, Ltd., 2023.
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Imide-Containing Compositions for Tribotechnical Coatings Based on Polytetrafluoroethylene

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Received December 20, 2021; revised March 3, 2022; accepted April 28, 2022

Abstract—Results of the experimental studies on the development of the compositions of composite tribotechnical materials based on polytetrafluoroethylene modified with imide-containing reagents with enhanced parameters of the stress–strain and tribotechnical characteristics and conventional production and processing technology are presented. The developed compositions can be used for the fabrication of products for structural and tribotechnical use applied in the friction joints of machines, mechanisms, and process equipment without external lubrication.

Keywords: carbon-reinforcing filler, polytetrafluoroethylene, products of thermo-oxidative degradation of oligomers, oligomaleimidophenylene, tetramaleimide, *N*,*N*'-bisimides of unsaturated dicarboxylic acids, dry lubricant

DOI: 10.1134/S1995421223020429

A large number of composite materials used for the fabrication of parts operated in tribosystems are known. These are composites based on polymeric, carbon, and metal ceramics matrices. The main requirements to such materials are determined by the fact that the maximum or set values of the strength, rigidity, durability, and service-life parameters; minimum weight and energy losses; high processability; minimum cost; and convenience of installation and maintenance should be provided when fabricating and operating the structural elements of friction joints.

The choice of materials for the fabrication of products of tribosystems is executed with respect to a set of parameters. To maximally satisfy the operational requirements, polymeric composite materials consisting of a polymeric matrix, modifying additives, and strengthening fillers are mainly used.

Composite tribotechnical materials based on polytetrafluoroethylene (PTFE), which contain a carbon filler and a dry lubricant have been long known [1] and are being currently developed [2–8]. Dispersed particles of coke, carbon fiber (CF), technical carbon (carbon black), fullerenes, and carbon nanotubes are used as the carbon filler that is introduced in the amount of 0.1 up to 20 wt %. Graphite, molybdenum disulfide (MoS_2), salts of fatty acids, and layered silicates (micas, clays) are used as the dry lubricant. The concentration of the dry lubricant in tribotechnical materials based on polytetrafluoroethylene does not exceed 10 wt %.

Because of this, when producing products from composite tribotechnical materials based on polytetrafluoroethylene with the total concentration of fillers and modifiers over 5 wt %, special methods increasing the adhesion interaction at the PTFE–filler interface should be used to achieve increased parameters of stress–strain and tribotechnical characteristics. For this purpose, various modification methods are applied, one of which is plasma-chemical treatment of CF in a medium of fluorine-containing compounds, e.g., tetrafluoroethylene [9], in solutions of Foleoks and Epilam fluorine-containing oligomers [3, 10].

However, despite achieving a certain effect in the case of applying modified CFs, it turns out to be impossible to take full advantage of the reinforcing properties of this high-strength wear-resistant filler to the extent required for practical application. This negative effect is determined by the inertness of carbon fibers to the processes of adsorption interaction which is determined by the characteristic features of their production technology, in the case of which conditions are not fulfilled for the formation of functional groups including polar ones in the surface layer of CF which are capable of forming chemical and physical bonds with the macromolecules of polymeric and oligomeric matrices including PTFE [3, 7, 8].

To reinforce composites based on PTFE, the most optimum approach is using a carbon filler—fragments of carbon fiber with a size of 50–150 μm—as a reinforcing material and graphite as a dry lubricant. This

Table 1. Ratio of the components of the used carbon-containing reinforcing filler

Name of component	Concentration, wt %
Thermo-oxidative degradation products of oligoimides	0.1–20
Dry lubricant	0.1–10
Polytetrafluoroethylene	Other

material is industrially produced under the Flubon, Fluvis-LO, and Fluvis brands [11].

A Flubon material (and its analogue, Fluvis) possess quite high wear resistance, outperforming with respect to this parameter other analogues (F4K20, F4G10) that contain dispersed particles of a carbon filler—coke or graphite. An advantage of this material over the analogues is the minimum abrasive action of the filler on the conjugate metal counterbody, which makes it possible to use the products made of it in the friction joints, the shaft of which is fabricated from unquenched carbon or doped steels as well as nonferrous metals (Ti, Al) and alloys based on them (brass, bronze).

A series of disadvantages are characteristic of composite tribotechnical materials based on tetrafluoroethylene, the most important of which are

a low tensile strength of 17–20 MPa, which is substantially lower than the initial strength of PTFE (30–32 MPa), and the complex production technology of the filler, which includes an operation of fiber graphitization and three-stage grinding of the semifinished product with significant power costs [1, 11].

The specified disadvantages are determined by the inertness of CF fragments to the processes of adsorption interaction with the matrix (PTFE), as a result of which a defect low-strength layer is formed at the matrix–filler interface. In addition, binder-free cluster structures are formed in the composites from the particles of the dispersed fiber that are macrodefects of the composite structure, and the difference in the shape of the particles of PTFE and fragments of CF prevents homogenization of the mixture upon its stirring in paddle-type units.

The aim of this work is the development of the compositions of a composite tribotechnical material based on polytetrafluoroethylene with increased parameters of stress–strain and tribotechnical characteristics that possesses a simple production and processing technology.

To achieve the aim, products of thermo-oxidative degradation of oligoimides chosen from a group of oligomaleimidoaminophenylene, oligohydroxymaleimidophenylene, oligoaminophenylene, tetramaleimide, and *N*,*N*'-bismaleimide of unsaturated dicarboxylic acids obtained at 350–380°C for 8–20 h were used as the carbon-containing reinforcing filler; the ratio of the components is presented in Table 1.

The structure of the macromolecules of the oligoimides chosen for the preparation of a composite material based on polytetrafluoroethylene includes various functional groups such as –CH=CH–, –OH, $-NH_2$, and >C=O which possess increased activity in the processes of adsorption interaction with different components to form physical and chemical bonds. These groups are also capable of interacting with a $-CF_2-$ group that constitutes a polytetrafluoroethylene macromolecule to form bonds of the adsorption and chemisorption types. Because of this, introducing dispersed particles of oligoimides into the composition of a composite tribotechnical material based on polytetrafluoroethylene will make it possible to form a structure with an increased strength.

In the process of sintering (monolithization) of a product or semifinished product made of a composite material based on PTFE with the use of Flubon and Fluvi materials [11], long-term action of increased temperatures of 350–380°C for 8–20 h occurs, which provides the formation of a structure with the set parameters of stress–strain and tribotechnical characteristics.

Such an energy action determined by the technology of fluorocomposites induces processes of structuring and thermo-oxidative degradation of the dispersed particles of oligoimides which lead to the formation of a cross-linked carbon structure with an increased strength that contains active functional groups. In the process of thermal treatment of a semifinished product made of the composite material, the supplied thermal energy is consumed not only for sintering of the particles of the matrix polymer (PTFE), but also for the formation of reinforcing carbon particles that are substantially superior to carbon particles of other types with respect to activity: CF, carbon black, and coke. Because of this, the reinforcing effect of the introduction of the products of thermo-oxidative degradation of oligoimides is substantially higher when compared to the use of carbon particles obtained by other technologies because the particles of these products are not inferior to other fillers with respect to strength, while they are superior to them with respect to activity in the processes of interaction with the matrix.

In addition, the shape and sizes of the initial particles of oligoimides and, hence, particles of the products of their thermo-oxidative degradation are similar to the shape and sizes of PTFE particles. Because of this, in the process of mixing of the components in

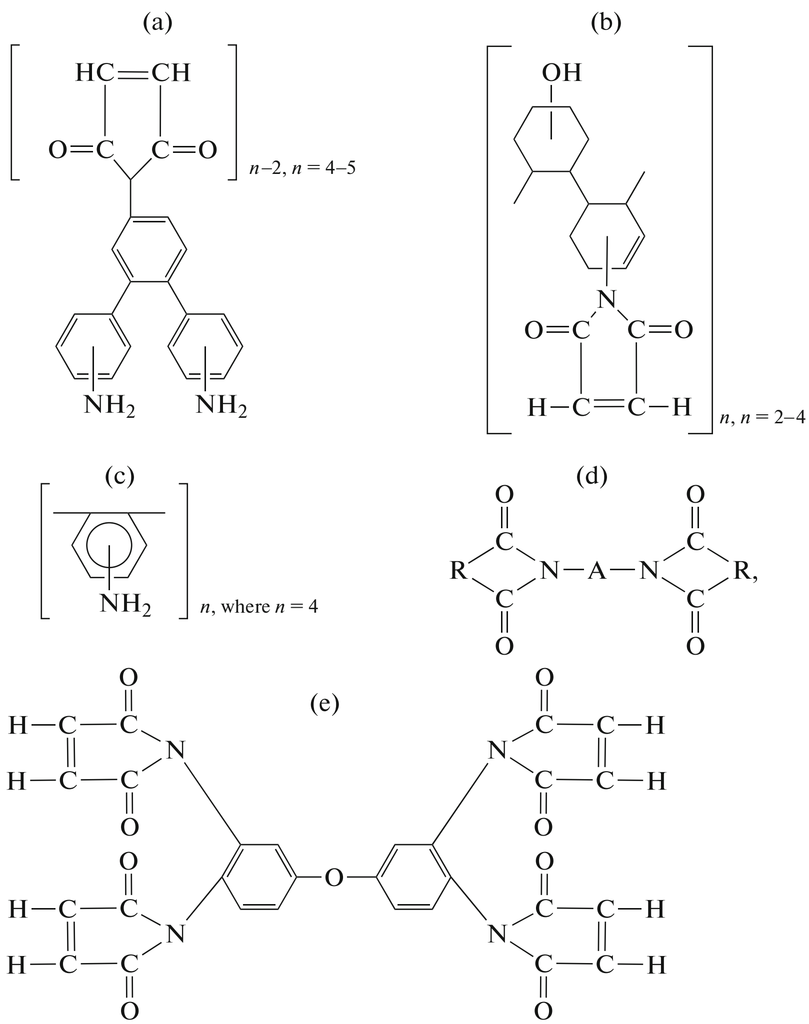


Fig. 1. Structural formulas of the oligoimides: (a) OMIAP, (b) MIG-3, (c) OAP, (d) *N*,*N*'-bismaleimides of unsaturated dicarboxylic acids, and (e) TMI.

paddle-type mixers, compositions with higher homogeneity are formed without the formation of cluster structures of the filler that are defects decreasing the strength parameters of the composite.

The following components were used to obtain compositions of composite tribotechnical materials based on polytetrafluoroethylene:

polytetrafluoroethylene of the F-4 brand (F4PN, F4TN) in the state of industrial supply;

carbon-containing reinforcing fillers;

dispersed fragments of carbon fiber obtained by grinding of a semi-finished product in the form of ribbons and cloths of the LO-1-12N brand produced at OAO Svetlogorsk Khimvolokno [10];

dry lubricants:

atomized or colloidal graphite of the C-1 brand;

oligoimides:

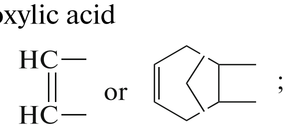
oligomaleimidoaminophenylene (OMIAP) (see Fig. 1a);

oligohydroxymaleimidophenylene (MIG-3) (see Fig. 1b);

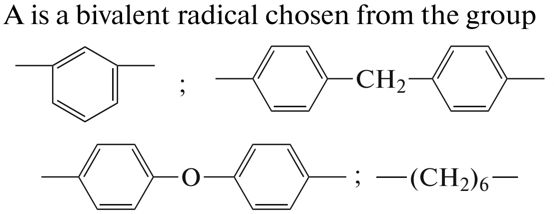
oligoaminophenylene (OAP) (see Fig. 1c);

tetramaleimide (TMI) (see Fig. 1d);

N,*N*'-bismaleimides of unsaturated dicarboxylic acids (see Fig. 1e), where R is the residue of an unsaturated dicarboxylic acid



A is a bivalent radical chosen from the group



The oligoimides were obtained by common procedures based on the interaction of stoichiometric amounts of anhydrides of corresponding dicarboxylic acids and diamines in a medium of polar solvents followed by the cyclization of the obtained products.

The synthesis of OMIAP was executed by a three-stage method, first, obtaining oligoaminohydroxyoxyphenylene and, then, carrying out its interaction with maleic anhydride followed by imidization of the formed oligoamidoacid.

The synthesis of OAP was performed by the condensation of *p*-phenylenediamine in a nitrogen flow in the presence of *p*-toluenesulfonic acid.

MIG-3 was obtained by the reaction of hydroxyl-containing oligoaminophenylene and maleic anhydride followed by chemical imidization.

TMI was obtained by low-temperature polycondensation of tetraaminodiphenyl ether with maleic anhydride followed by imidization of tetramaleamidoacid.

The obtained oligomers were variously colored powders (from dark brown to black) with a particle size of 5–10 μm.

Composite tribotechnical materials based on polytetrafluoroethylene were obtained by mechanical mixing of the components in a paddle-type mixer until obtaining uniform consistency. The blanks (specimens) for the tests were fabricated according to a conventional technology [8] which includes the operation of production of blanks by cold pressing and subsequent sintering in a furnace with a temperature of 350–380°C for 8–20 h (depending on the dimensions of the blank). In the process of sintering (monolithization) of the specimens made of composite materials based on polytetrafluoroethylene, thermo-oxidative degradation of the dispersed particles of oligomers occurs, which leads to the formation of a carbon-containing product with a cross-linked three-dimensional structure.

The data of IR spectroscopy evidence the occurrence of the processes of cross linking by the place of functional >C=O groups and –C=C– unsaturated bonds that are determined by oxidation and structuring processes. Based on the data of DTA, a conclusion has been drawn about the formation of an adduct with high thermal stability that exceeds the thermal stability of the initial oligomers and polytetrafluoroethylene. Here, occurrence of the processes of interaction of the $-CF_2-$ groups of a PTFE macromolecule and the functional groups present in the initial structure of the oligomers with the formation of bonds of various types is possible in the process of thermal treatment of the dispersed particles of the oligomers in a medium of PTFE.

The time of thermal treatment of the dispersed particles of the oligomers was 8 or 20 h, which is enough for practical completion of the processes of structuring and removal of volatile products formed during the formation of the three-dimensional structure. Due to this, the relative concentration of carbon in the products of thermal treatment increases, which transforms the initial oligomer into a cross-linked structure based on carbon.

The treatment temperature of the dispersed particles of the oligomers of 350–380°C provides the process of formation of a carbon-containing product with a three-dimensional structure and does not induce deep degradation that would lead to its destruction and formation of volatile products.

At lower treatment temperatures (250–300°C), processes of structuring of the particles of the oligomers predominantly occur without an increase in the relative fraction of carbon in the product. Such particles in the composition of the composite increase the coefficient of friction, because they do not possess the characteristic properties of carbon fillers.

Increasing the treatment temperature of the particles of the oligomers up to 400–450°C in air leads to the formation of a large amount of volatile products of thermal and thermo-oxidative degradation, which sharply decrease the strength characteristics of the structured particle and prevent the formation of a defect-free structure of the composite material.

The determination of the parameters of the stress–strain characteristics was performed on specimens in the form of rings and columns. The tribotechnical characteristics were determined on a KhTI-72 friction machine under friction of three specimens with a hemispherical head over a polished surface of a steel disc under a normal load on three specimens of 300 N and linear sliding speed of 1.0–3.0 m/s.

The compositions of the declared tribotechnical materials based on polytetrafluoroethylene and a prototype are presented in Table 2, and the parameters of the stress–strain, tribotechnical, and process characteristics are presented in Table 3.

As it follows from the data presented in Tables 2 and 3, the developed compositions of the composite tribotechnical materials based on polytetrafluoroethylene at the same concentration of the reinforcing carbon filler (20 wt %) are substantially superior to the analogue with respect to the strength parameters under tension, compression at 10% deformation, and wear resistance. Here, the process of fabrication of products from the developed compositions does not require special dispersion and activation operations, which substantially decreases the energy consumption of the process and cost of the final product.

The exceedance of the optimum concentration of the thermo-oxidative degradation products of oligomers (composition VI) or its decrease (composition V) either does not provide an additional effect or decreases the strength and wear resistance parameters.

A positive effect manifests itself in the case of the use of thermo-oxidative degradation products of both

Table 2. Compositions of composite tribotechnical materials based on polytetrafluoroethylene

Component	Concentration, wt %													
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Reinforcing carbon filler:														
Carbon fiber	–	–	–	–	–	–	–	–	–	–	–	–	–	5
Thermo-oxidative degradation products of oligomers:														
N,*N*′-*m*-phenylene bismaleimide (PBMI)*	–	–	–	–	–	–	10	–	–	–	–	5	–	–
N,*N*′-4,4′-diphenyloxide bismaleimide (DPOMI)*	–	–	–	–	–	–	–	10	–	–	–	–	–	–
Oligoaminophenylene (OAP)**	–	–	–	–	–	–	–	–	–	–	–	–	5	–
Oligomaleimidoaminophenylene (OMIAP)**	–	–	–	–	–	–	–	–	10	–	–	–	–	–
Oligohydroxymaleimidophenylene (MIG-3)**	–	–	–	–	–	–	–	–	–	10	–	–	–	–
Tetramaleimide (TMI)**	0.1	5	10	20	0.05	25	–	–	–	–	10	5	5	5
Dry lubricant:														
Colloidal graphite	0.1	5	5	10	0.05	15	5	5	5	5	–	5	5	5
Molybdenum disulfide	–	–	–	–	–	–	–	–	–	–	5	–	–	–
Polytetrafluoroethylene of the F-4M brand	99.8	90	85	70	99.9	60	85	85	85	85	85	85	85	85

* Samples made of composite tribotechnical materials based on polytetrafluoroethylene with these oligomers are obtained by monolithization (sintering) of the blanks obtained by cold pressing at 350–380°C for 8 h;
** Samples made of composite tribotechnical materials based on polytetrafluoroethylene with these oligomers are obtained by monolithization (sintering) of the blanks obtained by cold pressing at 350–380°C for 20 h;
*** A Fluvis-20 (Flubon-20LO) composite tribotechnical material based on polytetrafluoroethylene produced by OAO Grodnenskii mekhanicheskii zavod (TU (Technical Specification) 6–05-14-69–79) and OAO Grodno Azot (TU (Technical Specification) 03535279.071–99) is chosen as the prototype.

Table 3. Parameters of the stress–strain, tribotechnical, and process characteristics of the composite tribotechnical materials based on polytetrafluoroethylene

Characteristic	Code of the composition													
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Tensile strength, MPa	32	35	40	44	28	45	42	44	42	43	43	44	42	35
Strength at 10% deformation, MPa	25	28	30	33	20	35	31	32	31	33	30	32	32	34
Coefficient of friction	0.12	0.13	0.13	0.13	0.11	0.13	0.12	0.13	0.11	0.13	0.13	0.13	0.13	0.13
Wear intensity, 10^{-7} mm^3 N^{-1} m^{-1}	3.6	2.0	1.5	0.52	4.7	0.50	1.7	1.9	1.7	1.4	1.5	1.8	2.0	1.8
Need for preliminary activation (treatment) of the filler	Activation of the reinforcing filler is executed in the process of monolithization (sintering) of the product (blank)													

individual oligomers (compositions I–XI) and their mixtures (compositions XII, XIII) and in the case of the use of a mixture of reinforcing carbon fillers of different types—CF + thermo-oxidative degradation products of TMI oligomer (composition XIV).

CONCLUSIONS

Therefore, compositions of tribotechnical composite materials based on polytetrafluoroethylene are characterized by a high level of stress–strain and tribotechnical characteristics and are more technology-savvy in fabrication and processing into products.

The developed compositions of composite tribotechnical materials based on polytetrafluoroethylene have been tested at OAO Grodnenskii Mekhanicheskii Zavod and OAO Grodno Azot, which produce fluoro composites and products made from them for their own needs and for sale to consumers from various industrial sectors.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Boltukhina