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Methods of Thermochemical and Mechanical Activation of Fillers of Polymer Composite Materials

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The methods of thermochemical and mechanical activation of graphite particles and carbon fibers for creating effective fillers of polymer composite materials with high wear resistancehave been described.

Key words:polymer composite, graphite, filler, ash, carbon fibers.

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Introduction

During the development of technology and structure of composite polymer materials, design and processing them into products, recommendations for certain conditions of exploitation need to know the dependences of physical and mechanical, physical and chemical, thermophysical, tribological etc. properties of composites from nature, type, shape and size distribution of particles of disperse and fiber fillers [1-4] and polymer – matrix.The research results of influence the nature and distribution of particles on physical and mechanical [1-5], tribological [6, 7, 25], thermophysical [5, 6, 8-13, 25] etc. properties once again confirm the need to solve these research problems and technology. Especially important to solve these problems during creating of antifriction polymer materials based on thermostable, thermo-resistant and temperature resistant polymers [14-16] and carbon fillers – dispersive graphites and carbon fibers [17-21, 25].

The relationof antifriction and thermophysical properties of polymer composites in dependence on the composition of fillers is given in [6, 22, 28], and antifriction properties of polymer composites based on heat resistant polymers, graphite and carbon fibers during friction without or with limited lubrication in [23, 24]. Theoretical basis of the size distribution of particles of carbon fibers and graphites are given in [26-28].

I. The Phenomenon of Improving of Turbostrate Structure of Carbon Fibers during Dynamic Contact of Surfaces of Solid States

The phenomenon of improving of turbostrate (two-dimensional ordered) structure – decreasing interlayer distance and increasing the thickness and length of the packets layers of carbon hexagon of carbon fibers. The fibers were obtained by thermal treatment at temperature of 723 - 2673 K of final thermal influence on hydrate cellulose, polyacrylonitrile or copolymer organic fibers in an inert atmosphere, such as nitrogen, inert gases, methane or natural gas. The fibers were chemically processed before or after thermal treatment by compounds of phosphorus and boron, for example, sodium tetraborate and diammonium phosphate. After thermal treatmentthe fibers were subjected to mechanical activation in knife crusher for 2000 - 12000 rev./min. or in dismembrator or disintegrator for 2000 - 25000 rev./min. Additionally the fibers were subjected to thermal, complex deformation and tense influence during dynamic contact surfaces of solid states in the bound dispersion with polymer matrix in the node of friction or in the free dispersion, for example, in ball mill for 50-3050 hours.

The effect of improving the structure of fibers differs from three-dimensional ordered (crystalline) structure of artificial or natural graphite in the same conditions, for which interlayer distance increases and the length and thickness of the carbon hexagon packets decreases.

By results of researches found such regularities:

1. The three-dimensional ordered crystal structures of graphite during chemo-mechanical action, especially during friction and wear, the part becomes amorphous and the most part transforms in the two-dimensional ordered (turbostrate) structure.

2. It has opened the phenomenon of improving of turbostrate (two-dimensional ordered) structure (decreasing interlayer distance and increasing the thickness and length of the packets layers hexagon) of carbon fibers, obtained by chemo-thermo-mechanical activation in the presence of boron-containing and phosphorus-containing

compounds during intensive mechanical action. This effect the most appears for carbonated fibers at temperature of 1123 - 2073 K.

3. It has proposed the hypothesis: it is likely that only at certain perfection of turbostrate structure of carbon fibers and graphites (interlayer distance, thickness and length of the packets layers hexagon) and simultaneously during the leaking of tribochemical, chemo-physico-mechanical and other triboprocesses can achieve the effect of low friction and small magnitude wear.

II. The Effect of Particle Size Distribution of Graphite on the Properties of Polymer Composites

There are the results of studies of the effect of parameters of particle size distribution of fillers (natural graphite different bands) on physical and mechanical properties of polymer composites based on aromatic polyamide (APA) fenilon C-2. The fillers differed by ash content, moisture and grinding fineness (dispersion). The particle size of the filler and polymer for the theoretical gamma-distribution parameters (perimeter, thickness and diameter) have different values. The particles of graphite have similar values with aromatic polyamide particleson the perimeter.The particles of graphite and aromatic polyamide have the same average value that determines composition on these materialson the effective diameter of roughly.

The physical and mechanical properties of polymer composites based on aromatic polyamides are highly dependent on dispersion, of ash content and the graphite particles concentration of dispersed phase. Graphite is named the high-ash with 5 - 15 % ash content. And graphite is named the low-ash with 0.05 -2.5 % ash content.

The influence of ash content and graphite dispersed phase on friction strength APA was investigated. Both factors affect about the same. The regularities for strength during stretching and compression, the specific impact strength, elongation at break were determined. There are discovered to the tribological properties too, which was found in the limit loads mode. The relative durability of samples of colloidal systems based on graphite is growing with a decrease in ash content and dispersity for low-ash graphite and with a increase in ash content and dispersity of high-ash graphite ($\frac{1}{I_C}$ / $\frac{1}{I_P}$ = $\frac{I_P}{I_C}$, where I_C, I_P – the intensity of wear of polymer composites and polymer matrix, respectively). A minimum of frictional strength observed by 1.5 - 5 % ash content. The durability of polymer composite have a reliable relationship with a set of bulk mechanical properties according to the research by selected samples.

The linear correlationwas determined between the relative durability ($y = I_P/I_C$) on the first (S_1) and second (S_2) friction stages and the gamma distribution θ and λ parameters on the basis of the results to predict areas of application and performance properties of polymer composites. Perimeter particles of graphite was the most informative parameterin polymeric composites. The non-linear correlation was discovered between the wear rate and the distribution parameters of graphite particles.

III. Properties of Films based on Copper Complex Adduct of Monoglycidyl Ethers Oxydiarylmethanes

This research is devoted to realization of the phenomenon of random transport of copper in dynamic contact of solid bodies, and also achievement of quasi anti-wear effect through creation of films on the surfaces of friction pair. Friction properties of films were studied using friction apparatus according to the friction scheme "plane surface – plane surface" of epoxy-filled composite, reinforced non-metallized and copper plated carbon fiber material (Cu^0-CFM).

Parameters of tribological testing: sliding speed 0.54 m/s, normal load to one sample 100 N, specific load 3 MPa; run-in path 0 - 20 km, stationary friction path 40-100 km, parameters of effectiveness assessment of lubrication material – specific volume wear rate I x 10^{-6} mm^3 / (N·M). The scheme of contact of unidirectional composite NNNN and NLNN in contact with the surface of steel 45 counterbody (LD 4.5 ± 0.2 Hpa; R_a = 0.30 ± 0.05 micron); steel surface temperature 383 ± 10 K.

For investigation of friction pair anti-frictional properties, we have selected the following lubricants with and without copper compounds:

a) glycerin [Gl.]; [Gl.] with admixture of 5 % disperse graphite [Gl. + Gr.]; [Gl.] with admixture of 5% copper graphite [Gl. + Cu^0 – Gr.]; [Gl.] with admixture of 5% organic copper compound MKF-18 [Gl. + MKF-18]; [Gl.] with admixture of 5% $(CH_3COO)_2Cu$ [Gl.+CA];

b) plastic lubricant SMT-5 with disperse copper powder content [SMT-5];

c) mineral (compressor) oil KS-19 [KS-19]; [KS-19] with admixture of SMT-5 [KS + SMT-5]; [KS-19] with admixture of MKF-18 [KS-19+MKF-18];

d) copper complex of epoxidated benzyl phenol (EBP) adduct, polyethilenepolyamine (PEPA), $(CH_3COO)_2Cu$ (CA) [EBP+ PEPA+CA].

The received results enabled making up minorant series according to wear intensity:

a) for composite with non-metalized CFM: [KS + MKF-18] > [KS + SMT-5] > [Gl.] > [KS-19] > [EBP+ PEPA-CA] > [Gl. + Gr.] > [SMT-5] > [Gl.+CA] > [Gl. + MKF-18] > [Gl. + Cu^0 – Gr.];

b) for composite with copper plated CFM: [KS-18] > [KS + MKF-18] > [KS + SMT-5] > [Gl. + CA] > [SMT-5] > [Gl. + MKF-18] > [Gl.] > [Gl. + Gr.] > [Gl. + Cu^0 – Gr.] > [EBP+ PEPA+CA].

These results have proved high efficiency of films on the surfaces of dynamic contact composite steel consisting of copper complex adducts of oxydiarylmethane, polyethilenepolyamine and copper acetate monoglycidyl ethers.

Conclusions

1. During mechanical activation of filler particles (carbon fibers) of polymer composite is observed phenomenon of improving of two-dimensional ordered structure of carbon fibers, which leads to the effect of low friction and high wear resistance of polymer composite.

2. Correlation analysis revealed that between the relative wear resistance of polymer composites and parameters of the gamma distribution by size of filler particles (graphite) there is reliable nonlinear relationship.

3. Metallization by copper of filler (carbon tissue) of polymer composite leads to its high wear resistance during friction in liquid lubricant, herewith this effect increases if the liquid lubricant contains copper compounds.

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Методи термохімічної та механічної активації наповнювачів полімерних композитних матеріалів

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Описані методи термохімічної та механічної активації частинок графіту та вуглецевих волокон для створення ефективних наповнювачів полімерних композитних матеріалів із високою зносостійкістю.

Ключові слова: полімерний композит, графіт, наповнювач, зольність, вуглецеві волокна.