Elastomeric nanocomposite for recovery of worn-out basic parts of agricultural machinery

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Abstract. Due to the high specific surface area of nanoparticles, in comparison with micro-sized particles, a significant improvement in the consumer properties of polymer nanocomposites is achieved at relatively low concentrations of nanoscale fillers (up to 5%). Research and subsequent development of new polymer nanocomposites are of great scientific and practical interest, as they provide further development of promising high-performance technologies for restoring landing holes, increasing the post-repair life of basic parts and reliability and significantly reducing the cost of repairing agricultural machinery. The article describes the influence of metal nanoparticles on the thermophysical and mechanical properties of elastomers, presents the results of experimental studies of the deformation-strength and adhesive properties of a nanocomposite based on F-40 elastomer filled with nanoscale copper and aluminum particles as well as its optimal composition. Comparative data on the heat and heat resistance of the F-40 elastomer and the nanocomposite based on it are presented.

1. Introduction

Body parts are basic and the most material-intensive and expensive parts whose resource determines the durability of the units and the reliability of the machine as a whole. Restoration of worn-out basic parts allows you to significantly reduce the cost of repairing of automotive equipment. In comparison with the production of new parts, when similar parts are restored 20-30 times less metal is used. By eliminating the metallurgical cycle, when restoring 1 ton of steel parts, 180 kWh of electricity, 0.8 tons of coal, 0.5 tons of limestone, and 175 m\textsuperscript{3} of natural gas are saved [1, 2].

Modern methods of restoration provide not only compensation for wear in the part, but also a significant increase in its post-repair service life, increasing the reliability of equipment after restoration [3–8]. One of the main defects that causes discarding of body parts of automotive equipment is the wear of the landing holes for rolling bearings. This defect is eliminated by applying electroplating coatings, electric contact welding of steel tape, various methods of surfacing and other methods whose main disadvantages are: the complexity of the technological equipment and process, energy consumption, the need for mechanical processing of holes. Methods for restoring basic parts with polymer materials favourably differ in simplicity, low energy consumption and costs, significantly increase the resource of basic parts, bearing units of shafts and gears [9–11].
Development of polymer composites is a promising direction that provides a high efficiency of restoring the landing holes of basic parts. Due to the filling of the polymer matrix with highly dispersed particles, consumer properties of the material are significantly increased and its price decreases [12–17].

Domestic manufacturers currently offer a large list of nanoparticles made of various materials that differ in shape and size. Due to the high specific surface area of nanoparticles there are a much larger number of nanoparticles per unit volume of the polymer matrix in comparison with micro-sized particles. Therefore, a significant improvement in the consumer properties of polymer nanocomposites is achieved at relatively low concentrations of nanoscale fillers (up to 5%) [18–21].

Research and subsequent development of new polymer nanocomposites are of great scientific and practical interest, as they provide further development of promising high-performance recovery technologies of landing holes that increase the post-repair life of basic parts, their reliability and significantly reduce the cost of repairing of automotive equipment.

The polymer materials used to restore the landing holes in the basic parts of the transmission units of automotive equipment are subject to specific requirements. In order to have a high service life, taking into account the operating temperature of the bearing assembly, thermal cycling, the need for heat removal from rubbing bearing parts, alternating dynamic loads, assembly conditions, the material must have increased heat resistance, thermal conductivity, high adhesive and cohesive strength, endurance and other consumer properties [16, 17].

The objective of the research is the influence of metal nanoparticles on thermophysical and mechanical properties of the elastomer F-40, determining the optimal composition of elastomeric nanocomposite for restoration of planting holes in parts of automotive engineering (the study was performed with the financial support of RFFR, research project No. 19-38-90227/19).

2. Materials and methods

Metals of variable valence can be catalysts for some types of rubber and inhibitors of chain radical oxidation processes for other types of rubber. The nature of the catalytic action of a metal of variable valence determines the structure of rubber. Studies of K. B. Piotrovsky and Yu. A. Lvov revealed that copper is a catalyst for natural rubber and for butadiene-nitrile rubbers, this metal is an inhibitor of the oxidation process [22, 23]. In the work of A. E Mikhailuk it was found that the introduction of nanoparticles of metals of variable valence into the elastomer increases the activation energy of the thermal degradation process of the polymer material, i.e. increases the composite heat resistance [19]. The stabilizing effect during the thermal destruction of the elastomer is caused by the appearance of chemisorption bonds between metal nanoparticles and polymer macromolecules. The metals that were used as fillers, according to the degree of increase in the heat resistance of the elastomer to high-temperature destruction, can be arranged in the following sequence:

$$Bi < Pb < Ni < Cu.$$ 

The F-40 elastomer is based on SCN-40 butadiene-nitrile rubber, copper has the highest ionization energy in the list of metals, so it should be expected that copper nanoparticles form strong chemisorption bonds with the SCN-40 rubber macromolecules which results in increase in heat resistance of the F-40 elastomer-based nanocomposite [24].

Module of elasticity of an elastomeric nanocomposite

In nanocomposites, when the polymer interacts with a filler particle, an adsorbed layer (interfacial area) is formed on the surface of the latter, which has properties that are significantly different from the polymer matrix. There is a "freezing" of the molecular mobility of the polymer in the interphase areas, i.e., near the surface of the filler nanoparticles. Filler particles and interfacial regions are the reinforcing element of the elastomeric nanocomposite, which increases its elastic module. The work of G. V. Kozlov investigates a composite based on styrene-butadiene rubber filled with nanosungite. It was found that the elastic module of the interfacial layer is only 23-45% lower than the similar parameter of the filler, but it is up to 8.5 times higher than the elastic module of the polymer [25]. The introduction of highly dispersed aluminum, manganese and iron particles lyophilized to rubber has
vulcanizing and strengthening effect on composites based on chloroprene and butadiene-nitrile rubbers [26].

The introduction of metal nanoparticles into the elastomer solution increases its viscosity. The reason for the increase in viscosity and flow resistance is the interphase areas with the "frozen" molecular mobility of the polymer in these (interphase) areas. Due to the high specific surface area of nanoparticles, the effective saturation of polymers with filler (achieving extreme deformation and strength properties) is achieved at low concentrations, up to 5 wt. h.

**Peculiarities of increasing the strength and crack resistance of elastomeric composites**

The influence of polymer adhesion to the filler is considered in the work of S. S. Voyutsky. The adhesive theory of elastomer reinforcement considers a composite as a set of microscopic adhesive compounds of the elastomer-particle filler type. It is established that there is a linear dependence of the strength of composites on the values of adhesion, which confirms the correctness of the adhesive theory of elastomer reinforcement. The increase in the strength of the elastomeric composite, which contains chain structures is due to the presence of polymer molecules in the gap surrounding the contact point, each of which is firmly bound to at least two filler particles provided but not due to the contact of the filler particles with each other [27].

There are four main factors of strengthening of elastomers: equalization of stresses at the break of the elastomer-filler bonds, blunting of growing cracks in the material, increasing energy dissipation in the volume of the material along the break line, and the formation of chain structures of filler particles among themselves [28].

Rubbers based on chloroprene and butadiene-nitrile rubbers with highly dispersed metal particles are characterized by increased deformation and strength properties. The reason is the strong rubber-metal bonds formed at the moment of opening of the double bonds. Aluminum has the highest specific surface energy of destruction. The use of aluminum particles as a filler of polymer materials increases the surface energy of destruction, strength, crack resistance and endurance of composites. Therefore, filling the F-40 elastomer based on SCN-40 butadiene-nitrile rubber with aluminum nanoparticles will increase the strength and durability of the nanocomposite [29].

Increase in heat resistance and thermal conductivity of the elastomer composite when introducing metal nanoparticles

In comparison with anaerobic sealants, acrylic and cyanoacrylate adhesives elastomers GEN-150 (B), sealant 6F, lacquers F-40 and F-40C are characterized by relatively low heat resistance. The heat resistance of the sealant 6F, lacquers F-40 and F-40 C, having approximately the same base is about 100° C [9]. Considering the fact that the bearings of the usual design are heated during operation to temperatures of 70 ... 90 °C, it is necessary for polymer materials to have a large temperature margin for heat resistance to restore the landing holes in the basic parts.

Filling polymer materials with micro-sized metal particles practically does not change the heat resistance and glass transition temperature of the composite [30]. The heat resistance of the microcomposite is actually determined by the heat resistance of the polymer matrix.

A completely different picture is observed in polymer nanocomposites. Filling the polymer matrix with metal nanoparticles leads to the formation of mesh formations with nanoparticles in the nodes. For this reason, the molecular mobility of the polymer chains decreases, and the heat resistance increases accordingly. In nanocomposites, when the polymer interacts with a filler particle, an adsorbed layer (interfacial region) is formed on the surface of the latter, which has properties significantly different from the polymer matrix.

There is a "freezing" of the molecular mobility of the polymer in the interphase regions, i.e., at the surface of the filler nanoparticles. The elastic module of the interfacial material is less than the similar parameter of the filler material, but it is many times higher than the elastic module of the matrix polymer [25]. Due to the high specific surface area of the filler nanoparticles, the proportion of interphase regions in the polymer nanocomposite is significantly higher than in the microcomposite. The "freezing" of the molecular mobility of the polymer in the interfacial regions, the increase in the
elastic module are the reason for the increase in the heat resistance of the nanocomposite in comparison with the non-filled elastomer.

Silver, copper, and aluminum particles have the highest thermal conductivity. Due to the very high price, the use of silver as a filler is not economically feasible. For this reason, to increase the thermal conductivity of a nanocomposite based on the F-40 elastomer, copper and aluminum nanoparticles should be used as fillers [31].

3. Results of the research

Research and optimization of the nanocomposite composition

At the initial stage of experimental studies, the strength and deformation of films of nanocomposites of four compositions were studied.

Composition number 1: elastomer f-40 – 100 mass. h, Al – 1.6 wt. h, Cu – 1.4 wt. h; composition No. 2: elastomer f-40 – 100 mass. h, Al – 1.8 masses. h, Cu – 1.6 wt. h; part 3: elastomer f-40 – 100 mass. h, Al – 2.0 wt. h, Cu – 1.8 wt. h; composition No. 4: elastomer f-40 – 100 mass. h, Al – 2.2 wt. h, Cu – 2.0 mass. h

The greatest strength is observed in composition No. 2. In comparison with non-filled elastomer, an increase of 23%, with compositions No. 3, No. 1 and No. 4, the strength is greater by 2%, 8% and 15%, respectively. With an increase in the concentration of aluminum and copper nanopowders, the deformation decreases from 62% to 54%.

The priori information established the nonlinearity of the dependence of the parameter on the composition of the nanocomposite. An active experiment on the compositional plan was implemented [32]. The specific work of destruction \( \alpha_p \), MJ/m\(^3\), was taken as the response function Y, and the independent factors were the content of aluminum nanoparticles, mass. h - the content of copper nanoparticles, mass. h.

The regression equation in natural units has the following form:

\[
Y = -15,296 + 18,903X_1 + 13,509X_2 - 0,15X_1X_2 - 5,08X_1^2 - 4,08X_2^2.
\]

The response surface and its two-dimensional cross-section are shown in Figures 1 and 2.

The optimal composition of the nanocomposite based on the F-40 elastomer is determined. The maximum specific work of destruction of 13.0 MJ/m\(^3\) has a composite film, the following composition: elastomer F-40 – 100 wt. h., aluminum nanopowder – 1.9 wt. h. and copper nanopowder – 1.8 wt. h. [29].

Investigation of the elastic modulus of a nanocomposite

The experiment showed that filling the F-40 elastomer with aluminum and copper nanoparticles increases the elastic modulus of the material: in tension – 1.2, compression – 1.3 times.

Investigation of the adhesion of a nanocomposite based on F-40 elastomer

The adhesion of polymer materials was evaluated by the strength of the bond between the material and the metal during the exfoliation of the samples. The compositions were studied: No. 1: elastomer F-40-100 wt. h., Al-1 wt. h., Cu-0.6 wt. h.; No. 2: F-40-100 wt. h., Al-2.0 wt. h., Cu-1.6 wt. h.; No. 3: F-40-100 wt. h., A1 – 3 wt. h., Cu – 2.6 wt.h. The coatings of elastomer F-40: coatings of composition No. 2 have the maximum adhesion. The adhesion index is and exceeds the same parameter of the unfilled elastomer 2.89 times, the coatings of composition No. 1 and No. 3 – 1.57 and 1.17 times.

Therefore, taking into account the results of the active experiment, the optimal composition of the nanocomposite was accepted: a solution of elastomer F-40 – 100 wt. h., aluminum nanopowder – 2.0 wt. h., copper nanopowder – 1.6 wt.h. This composition provides the highest deformation-strength and adhesive properties of the material.
Study of heat resistance of nanocomposites based on F-40 elastomer

The heat resistance of the polymer material is the most important operational characteristic that determines the maximum permissible temperature of the material use in real operating conditions.

Fig. 3 shows the temperature of the heat resistance of the coatings of the F-40 elastomer and the nanocomposite based on it.

As follows from Fig. 3, the heat resistance of the unfilled elastomer F-40 is 100 °C. When elastomer was filled with copper and aluminum nanopowders, heat resistance increased in comparison with the non-filled elastomer 1.23 times and amounted to 123 °C.
Investigation of the thermal conductivity of F-40 elastomer and nanocomposite based on it

Polymer materials belong to the category of heat insulators, since their thermal conductivity differs in a smaller direction from the similar parameter of ferrous metals approximately 100 times. For this reason, it is possible that the heat sink in the restored bearing units may deteriorate under operating conditions.

In heavily loaded bearing assemblies of machinery, an increase in the temperature of the polymer material due to hysteresis losses, a difficult heat sink can cause a significant increase in the temperature of the bearing and the lubricant and, under certain conditions, a decrease in the durability of the bearing assembly.

The results of studies of the thermal conductivity of the F-40 elastomer and the nanocomposite based on it are shown in Fig. 4. As can be seen from Fig. 4, the value of the thermal conductivity coefficient of the F-40 elastomer samples was $\lambda_n = 0.56 W / m \cdot K$. The nanocomposite samples showed the value of the thermal conductivity coefficient. Due to the introduction of aluminum and copper nanoparticles into the elastomer, the thermal conductivity coefficient increased 38.9 times.

Study of the heat resistance of F-40 elastomer and nanocomposite based on it. Copper is an inhibitor of the oxidation process of butadiene-nitrile rubbers [24], so in our work it is proposed to fill the F-40 elastomer with copper nanoparticles, which will allow one to bind free radicals formed during thermal decomposition and increase the temperature resistance of the elastomer.
Studies of the thermal stability of the F-40 elastomer and its nanocomposite were carried out by measuring the strength and deformation of the material samples under uniaxial tension before and after aging, which was carried out under conditions of limited oxygen access at the temperature of 250 ° C for 2 hours.

Figure 5. Service life of polymer seats $t$ of bearing 209 with different thickness $h$ of a polymer coating made of nanocomposite based on F-40 elastomer, loaded with a cyclic radial load of 20 kN [31]

4. Conclusions
1. Due to high ionization energy copper nanoparticles interacting with macromolecules of SCN-40 butadiene-nitrile rubber form strong chemisorption bonds that provide a stabilizing effect during thermal destruction and increase the temperature resistance of the elastomer.

Filling the F-40 elastomer with copper and aluminum nanoparticles increases the elastic module, strength and durability of the material.

When metal nanoparticles are introduced into the polymer matrix, mesh formations with nanoparticles in polymer chains are formed. In this case, the molecular mobility of the chains decreases and the heat resistance of the nanocomposite increases. Copper and aluminum have the highest thermal conductivity. Therefore, filling the F-40 elastomer with copper and aluminum nanoparticles will increase heat resistance and thermal conductivity of the nanocomposite.

2. A regression model of the dependence of the specific work of destruction of nanocomposite films based on F-40 elastomer on the concentration of fillers is obtained. The optimal composition of the nanocomposite has the highest deformation-strength and adhesion properties: elastomer F-40-100 wt. h., aluminum nanopowder-2.0 wt. h. and copper nanopowder-1.6 wt. h. The nanocomposite has a high specific work of destruction of 12.9 MJ/m$^3$. In comparison with the non-filled elastomer, the elastic module of the nanocomposite increased to 1.65 times, and the adhesion - 2.9 times.

3. The heat resistance of the nanocomposite increased 1.23 times and amounted to 123 ° C in comparison with the non-filled elastomer.

Filling with aluminum and copper nanoparticles increases the thermal conductivity of the nanocomposite to $\lambda_c = 21.8 \frac{W}{m \cdot K}$, which is 38.9 times higher than the thermal conductivity of the F-40 elastomer. The aging coefficients of the nanocomposite are 1.8 times stronger and 1.4 times more deformed than those of the polymer matrix, which confirms the increase in the heat resistance of the nanocomposite.

4. Nanocomposite based on F-40 elastomer is recommended to restore the body parts of equipment with a diametrical wear of the bearing holes up to 0.25 mm. Filling the F-40 elastomer with aluminum and copper nanopowders increases the thermal conductivity of the material and significantly increases the heat dissipation from the parts of the restored bearing assembly. The temperature of the bearing assembly parts, with the fit restored by the F-40 elastomer nanocomposite, is lower to 16 ° C in comparison with the unfilled material.
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