The Selection of Plasticizer for Creating Oil-Filled Composites of Tribotechnical Designation Based on Aromatic Polyamide Phenylone C-2

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Abstract. It is proposed to use oil-filled polymers, so-called «oilyanites» for units and parts of tribotechnical designation based on polymer matrices. Materials of the given class can generally be considered as a three-component system consisting of a polymer binder, a plasticizer and multifunctional additives-fillers. Common to these materials is the «self-lubrication» effect, stemmed from the polymer plasticization. The aromatic polyamide Phenylone C-2 was used as the composite matrix. F4MB polytetrafluoroethylene powder (tetrafluoroethylene and hexafluoropropylene copolymer) and MgAl₂O₄ spinel nano additive were used as nanodimensional fillers and additives respectively. PMPS (polymethylphenylsiloxane), cylinder oil C-52, and VGO (vacuum gasoil) were used as a plasticizer, increasing the elasticity and plasticity of the material during processing and operation. The selection of the given oils and technical liquids is due to their ability to maintain their lubricating properties in high-temperature operating conditions, as the molding temperature of Phenylone samples is 300-320°C.

1. Introduction
The exploitation of composite materials for units and parts of tribotechnical designation based on polymer matrices is emanated from the functional modification of base matrices with components characterized by diverse composition, dispersion, habit and activity. The approach developed by the authors of the given paper originates in improving the formation mechanism of the tribocontact surface as an aftermath of a purposeful modification of the polymer nanocomposite properties [1-4]. To form the multilevel structures on the tribounit surface, it is proposed to use oil-filled polymers, i.e. «oilyanites». Oilyanit is a multifunctional, versatile inhibitor of tribosystem wear specified by intelligence properties, i.e. the ability to adjust its own functional properties at friction process dynamically. It means the ability to plate selectively the most worn out parts of the rubbing surface being affected by the frictional energy, which initiates the physical and chemical processes of primary and secondary restructuring of its polymer matrix structure.

Aromatic polyamide Phenylone C-2 was used as a polymer matrix. It is a linear heterocyclic copolymer containing in the macromolecule main chain the amide group -HNCO-, connected on both sides by phenyl fragments (obtained by the emulsion polycondensation of metaphenylenediamine with
dichlorohydrides of isophthalic and terephthalic acids, taken in the ratio of 3: 2). In friction units Phenylone C-2 withstands loads up to 25 MPa and operating temperatures up to 250°C. Phenylone is distinguished by sufficiently high stress-strain properties, high wear resistance, chemical resistance to aggressive media, and form stability in a wide temperature range. However, the possibilities of using this material in friction units are limited by the sufficiently high value of the coefficient of friction [5].

A promising method to change Phenylone C-2 functional properties is the introduction of various types of nanodimensional fillers and additives into the polymer matrix. Some of them utilize the ability of minerals (such as magnesium hydroxides (a layered structure), aluminosilicates (a framework structure) and mixed oxides (a spinel-type structure)) to compose coordination-type chemical compounds in friction or under special external conditions. While the others (such as polytetrafluoroethylene), due to a chemical reaction, provide the formation of a frictionally transferred film, thereby reducing the coefficient of friction, wear and prevent seizure.

As for a plasticizer that increases the material elasticity and plasticity during processing and operation, there were used higher fatty acids (oleic, stearic, and ricinoleic acid), oils containing them (cottonseed, corn, and castor oil), as well as spirits, ethers and other compounds having a diphilic structure (polar group and long carbon chain). The use of the above-mentioned components makes it possible, on the one hand, to be a plasticizer for the polymer, on the other hand, to form polymer-metal lubricating films on the friction surfaces [6-8]. PMPS-4 (polymethylphenylsiloxane), cylinder oil C-52 and VGO (vacuum gasoil) were chosen as a plasticizer. The given oils and technical fluids were selected due to their ability to maintain their lubricating properties in high-temperature operating conditions, since the molding temperature of Phenylone C-2 based samples is 300-320°C.

Test samples were produced by powder pressing. After combining the powders of Phenylone C-2 and the filler, the resulting mixture was impregnated with a heated plasticizer for 2 hours.

The briquetting of the fusion mixture was carried out without heating at a pressure equal to 50 MPa. The obtained briquette was dried at 200°C for an hour. Hot briquettes were placed in a preheated mold and held for 1 minute. Next stage includes 1-minute pressing at a temperature of 320-340°C and a pressure of 50 MPa. Finally, the obtained sample was cooled together with the mold to 100 °C and pressed out.

The test samples thus obtained were used to conduct the comparative studies of physical, mechanical and tribological properties of oil-filled antifriction self-lubricating polymer composites carried out to assess the effect of the selected plasticizer.

2. Study of Tribological Properties of Composites

The impact of the introduction of various plasticizers on the tribological properties of the composite was studied on a laboratory friction machine of Amsler II 5018 type according to the «finger-roller» scheme at a constant rotational velocity of 0.4 m / s. Composite samples were made in the shape of a 10-mm diameter cylinder. The counterbody is a 40-mm diameter and 10-mm width steel roller. When carrying out tribological tests, the rapid test method was used. It implies the stepwise load applied to the finger (209N, 310N, 420N, 520N, 620N, 720N, 820N, 920N, 1020N). The load remains constant for 30 minutes for each test stage. During the entire test period, a continuous recording of the friction torque on the lower shaft of the machine was performed. The test results made it possible to determine the mass wear value (Table 1), to calculate the samples’ coefficient of friction and to construct generalized coefficient of friction-time- variable loading conditions diagram. According to the data obtained, the introduction of VGO plasticizer into the composite material contributed to the greatest reduction of the coefficient of friction in the entire range of loads, regardless of the method used to prepare the composite.
Table 1. Mass wear of laboratory samples after tribological tests.

| Material                                                                 | Mass before testing, g | Mass after testing, g | Mass wear    |
|-------------------------------------------------------------------------|------------------------|-----------------------|--------------|
| 1. Phenylone C-2 + 7% cylinder oil (C52)                                 | 11.3773                | 11.3417               | 0.0356       |
| 2. Phenylone C-2 + 10% F4MB + 5% cylinder oil (C52)                      | 11.4070                | 11.3940               | 0.0130       |
| 3. Phenylone C-2 + 10% F4MB + 7% cylinder oil (C52)                      | 11.5487                | 11.5296               | 0.0191       |
| 4. Phenylone C-2 + 10% F4MB + 3.5% spinel + 3.5% cylinder oil (C52)     | 11.3783                | 11.3556               | 0.0227       |
| 5. Phenylone C-2 + 10% F4MB + 10% (spinel + cylinder oil (C52))         | 10.9481                | 10.9344               | 0.0137       |
| 6. Phenylone C-2 + 3% spinel + 7% cylinder oil (C52)                     | 11.1833                | 11.1804               | 0.0029       |
| 7. Phenylone C-2 + 5% PMPS*                                              | 10.9352                | -                     | -            |
| 8. Phenylone C-2 + 10% F4MB + 5% PMPS                                    | 10.8620                | 10.7090               | 0.153        |
| 9. Phenylone C-2 + 10% F4MB + 10% PMPS                                   | 10.7446                | 10.5573               | 0.1873       |
| 10. Phenylone C-2 + 5% VGO*                                              | 11.1205                | -                     | -            |
| 11. Phenylone C-2 + 10% F4MB + 5% VGO                                    | 11.5980                | 11.5912               | 0.0068       |
| 12. Phenylone C-2 + 10% F4MB + 10% VGO                                   | 11.0208                | 11.0055               | 0.0153       |
| 13. Phenylone C-2 + 5% (VGO + ADDP)*                                     | 10.8964                | -                     | -            |
| 14. Phenylone C-2 + 10% F4MB + 5% (VGO + ADDP)                           | 10.7809                | 10.7457               | 0.0352       |

* - the sample was destroyed during the test

Based on the data presented in Table 1 and the calculated values of the coefficient of friction, samples № 2, 5, 6, 11 and 12 were selected for further resource tests. Resource tests were carried out at a load of 1020 N and rotational velocity of 0.4 m / s for 7 hours. Figure 1 shows «Phenylone C-2 + 10% F4MB + 5% VGO» sample coefficient of friction diagram.
3. Specification of physical and mechanical properties

The study of physical and mechanical properties of oil-filled polymer composite materials was carried out in accordance with the methodology, described in [1], on NanoTest 600, a complex designed to determine physical and mechanical properties of the materials. A diamond indenter of conical shape with a cone angle of 90° and the radius of curvature 25 µm at the vertex was used during the experiment. Each nanoindentation test included 25 tip penetrations divided into 5 columns. The distance between the indents in the column and the distance between the columns was 100 µm. The maximum value of the indentation force was set to 150 mN. After testing, there was build a diagram, depicting the dependence of the load on the penetration depth of the indenter. The data obtained helped to calculate the values of the microhardness $H$, modulus of elasticity $E$, and the ratios $H/E$ and $H^3/E^2$. The given values are presented in Table 2.

| Material | Microhardness $H$, GPa | Modulus of elasticity $E$, GPa | $H/E$ | $H^3/E^2$ |
|----------|------------------------|-------------------------------|-------|------------|
| 1. Phenylene C-2 + 7% cylinder oil (C52) | 0.3 | 4.526 | 0.066 | 0.001323 |
| 2. Phenylene C-2 + 10% F4MB + 5% cylinder oil (C52) | 0.302 | 4.172 | 0.073 | 0.002 |
| 3. Phenylene C-2 + 10% F4MB + 7% cylinder oil (C52) | 0.264 | 4.062 | 0.065 | 0.001142 |
| 4. Phenylene C-2 + 10% F4MB + 3.5% spinel + 3.5% cylinder oil (C52) | 0.289 | 4.692 | 0.062 | 0.001112 |
| Material | Microhardness $H$, GPa | Modulus of elasticity $E$, GPa | $H/E$ | $H^3/E^2$ |
|----------|------------------------|-------------------------------|------|-----------|
| 5. Phenylone C-2 + 10% F4MB + 10% (spinel + cylinder oil (C52)) | 0.32 | 4.815 | 0.066 | 0.001486 |
| 6. Phenylone C-2 + 3% spinel + 7% cylinder oil (C52) | 0.287 | 4.711 | 0.061 | 0.001081 |
| 7. Phenylone C-2 + 5% PMPS | 0.302 | 4.383 | 0.069 | 0.001448 |
| 8. Phenylone C-2 + 10% F4MB + 5% PMPS | 0.326 | 4.279 | 0.076 | 0.001934 |
| 9. Phenylone C-2 + 10% F4MB + 10% PMPS | 0.210 | 2.465 | 0.085 | 0.001579 |
| 10. Phenylone C-2 + 5% VGO | 0.332 | 5.149 | 0.064 | 0.001382 |
| 11. Phenylone C-2 + 10% F4MB + 5% VGO | 0.288 | 4.123 | 0.070 | 0.001420 |
| 12. Phenylone C-2 + 10% F4MB + 10% VGO | 0.295 | 4.042 | 0.073 | 0.001589 |
| 15. Phenylone C-2 + 5% (VGO + ADDP) | 0.324 | 4.473 | 0.072 | 0.001738 |
| 16. Phenylone C-2 + 10% F4MB + 5% (VGO + ADDP) | 0.333 | 4.243 | 0.079 | 0.002081 |

The analysis of the findings show that the composite with VGO plasticizer possesses the most stable properties, since the values of microhardness and modulus of elasticity did not change much while varying its percentage (the difference did not exceed 2%). As for other plasticizers, these indices decreased with increasing their mass fraction in the composite. The values of $H/E$ and $H^3/E^2$, which characterize the materials’ frictional wear resistance and the plastic strain resistance, respectively, on the average were the highest in the composite with the VGO plasticizer as well. Taking into consideration the entire set of properties, the sample containing 5% PMPS-4 plasticizer with added 10% polytetrafluoroethylene filler was the most advantageous.

4. Conclusion
The given paper is aimed at studying physical, mechanical and tribological properties of oil-filled antifriction self-lubricating polymer composite materials with various plasticizers. Based on the results obtained, a number of samples characterized by the highest values of the coefficient of friction and mass wear, as well as mechanical parameters, were selected. These samples were used to conduct resource tests, the results of which demonstrated that composites with VGO plasticizer were the best to exploit in heavy loaded friction units.

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5. References
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