New Materials Based on Polytetrafluoroethylene and Modified Filling Materials in Mining Industry

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Abstract. Investigation into properties of polymer composite materials based on polytetrafluoroethylene and natural zeolites modified with F-42 and F-2M fluoroplastics is proposed in the present paper. It is shown that different zeolite modification techniques govern performance of composites. In the mechanical activation process a small amount of F-2M bearing filler improves Young’s modulus and relative tensile elongation of composites under rupture by 20-50%. Introduction of F-2M modified filler in amount of 5% by weight provides 380-fold increase in durability as compared to polytetrafluoroethylene. F-42 fluoroplastic used as a modifier of zeolite enables to gain 2-2.75-fold lower plastic yield of composites. The present research findings make it possible to consider the composites as promising materials in the mining industry.

1. Introduction

At present the materials based on polymer composites and their products are widely used in the mining industry. The materials are polymer matrices with specific distribution of filling agents in them. Future-oriented polymers applicable in the mining industry are fiberglass and basalt-plastics consisting of glass (basalt) filler permeated with thermoreactive or thermoplastic polymer binders. The binding agent can be polyester, epoxy, phenol-formaldehyde, silicon resins, etc. The filling agent of the study composites can be glass and basalt plastic fibers in the form of thread, bundle, glass-cloth, glass mats, chopped glass fibre. Mine anchors, grid to reinforce walls and roof of mine workings, rotors, ground pump bodies, impeller of flotation machines, mill lining, blades and lower classifier base, reinforcing and sealing members, pipes, etc. are usually made of polymer composites [1].

It is also known that in Russian North territories the actual challenges deal with low reliability and durability of mining machinery operating under long-term effect of extremely low temperatures and high intensity of mining equipment used to develop northern mineral deposits, because the open-air performance of mining machinery tends to lower 1.5–2 times in arctic winter period. The trouble-free life cuts down 1.6–2.4 times, the actual operation life is usually 2.5–3.5 times less, at repair rate and labor intensity of maintenance rises up more than 2.5–3 times [2]. The customary failures dealing with friction knots of bearings, gear transmission, pillars, piston and liner of cylinders, sealing, collar bush, machine parts contacting with frozen ground lead to annual losses as great as milliard Rubles. The perspective industrial development of Russian northern territories will lead to respective increase in losses due to imperfection of available mining machinery. Thus, expenses for repair and maintenance of open-pit equipment exceeds manifold its costs. Intensity of repair and maintenance of most
building, road-building machines and open-pit equipment in the course of their operation life exceeds approximately 15 times the labor intensity to manufacture new machines, thereto, high frictional losses in equipment knots dominate. More than half of fuel consumed by trucks, diesel locomotive and other transportation vehicles is directed to overcome friction in movable joints. Friction loss and respective expenses amounts to 1%–4% of the total domestic product of the Russian Federation, thus appreciably affecting the economy of the country, and arctic territories, in particular.

In view of the above the development of new materials on the basis of frostproof polymers with improved properties including frost and wear resistance, chemical durability, stiffness, etc. can appreciably improve functioning capacity of machinery at low temperature and cut down repair expenses as well as downtime costs.

2. Materials, methods of research and results

Fluoropolymer composites known for their unique properties hold the outstanding position among numerous antifriction and sealing polymer materials applicable under extreme conditions. They are distinguished for the package of unique properties: superior chemical stability, high thermo-, frost- and fireresistance, prominent mechanical dielectrical, electroinsulating antifrictional properties as well as their capacity to preserve all the cited properties within a wide range of temperatures, pressures, high environmental and wear durability under conventional conditions, so the guaranteed service and storage life exceeds 20 years [3,4].

Thanks to exclusive chemical inertness polytetrafluoroethylene (PTFE) is good at storing and hauling in the highly aggressive media. PTFE-based composites are the promising materials to use in friction joints such as bearings, sleeve bearings, their adequate elasticity allows their application as movable sealers with the efficiency comparable to that of elastomeric analogues [5].

The rank of PTFE as rebellious adhesive-inert polymers makes it rather difficult to introduce any filling agents into their volume and implies the necessity to make novel technological solutions, capable to intensify adhesive interaction at polymer-filler phase interface, thus reducing the effect of negative factors on structure and operation characteristics of the study composites [6]. Modification of polymers and fillings agents involves the increasing use of physical techniques in order to provide activation of materials and higher resultant performance characteristics. The perspective trend in improvement of physical and chemical properties of the composites is simultaneous mechanical activation of components [7, 8].

The present paper sets forth the research results on development of the process for modification of a filling agent with fluoropolymers with the purpose to produce novel composite materials based on polytetrafluoroethylene.

The study objects are polytetrafluoroethylene (PTFE) (brand PN GOST 10007-80) and composites based on it. Natural zeolite rock originated from Kemptendyasky deposit, Republic of Sakha (Yakutia) is selected as a filler of polymer composite materials (PCM). Zeolites are aluminosilicates of general formula \( \text{Me}_2/n\text{O} \times \text{Al}_2\text{O}_3 \times x\text{SiO}_2 \times y\text{H}_2\text{O} \), where \( \text{Me} \) is alkali of alkali-earth metal, \( n \) is degree of its oxidation. Adsorption properties of zeolites get evident after water molecules are removed from pores in calcination process. Water is removed from zeolite crystals under heating without failure of silico-oxygen carcass structure, thereto, the crystals become porous [9]. Zeolites are ranked as sorbents with microporous structure, zeolites exhibit high adsorption activity and molecular-sieve properties. In all the cases the mechanically activated zeolite was used in order to gain homogeneous fraction composition and higher chemical reactivity.

Fluoropolymers F-2M and F-42 were used as modifiers of filler surface. F-2M fluoropolymer (TU 6-05-1781-84) is polyvinylidene difluoride modified by hexafluoropropyne having melting temperature within 155–165°C. It exhibits high mechanical strength, hardness, lack of cold flow under load. Two processes are used to compound zeolites with F-2M fluoropolymer, They are mechanical activation in Pulverizette 5 planetary mill (Fritz Co.) at rotation rate of 200 rpm for 2 minutes and a simple blending in an impeller mixer. The test specimens are manufactured by cold pressing and sintering at a predetermined mode.
Table 1 demonstrates the test data on properties of PCM based on PTFE and zeolite modified by F-2M fluoropolymer provided that compounding of components is carried out in an impeller mixer.

**Table 1.** Strain-strength and tribotechnical characteristics of PCM based on PTFE and zeolite with F-2M in agitation at an impeller mixer

| Composition                  | Ratio F-2M:zeolite by mass | $\Sigma$, MPa | $\varepsilon_t$, % | $E_t$, MPa | $\rho$, g/cm$^3$ | $I$, mg/h | f     |
|------------------------------|-----------------------------|---------------|-------------------|--------|----------------|--------|------|
| PTFE                         | -                           | 19            | 310               | 469    | 2.19           | 161.9  | 0.20 |
| PTFE + 1% (F-2M:zeolite)     | 1:1                         | 17            | 391               | 594    | 2.19           | 5.66   | 0.18 |
| PTFE + 2% (F-2M:zeolite)     | 1:1                         | 15            | 408               | 637    | 2.19           | 2.53   | 0.25 |
| PTFE + 5% (F-2M:zeolite)     | 1:1                         | 10            | 5                 | 826    | 2.13           | 0.87   | 0.19 |
| PTFE + 1% (F-2M:zeolite)     | 1:2                         | 14            | 429               | 652    | 2.19           | 3.72   | 0.19 |
| PTFE + 2% (F-2M:zeolite)     | 1:2                         | 17            | 431               | 612    | 2.18           | 2.30   | 0.25 |
| PTFE + 5% (F-2M:zeolite)     | 1:2                         | 14            | 395               | 639    | 2.14           | 0.78   | 0.21 |
| PTFE + 1% (F-2M:zeolite)     | 2:1                         | 18            | 392               | 559    | 2.18           | 5.35   | 0.19 |
| PTFE + 2% (F-2M:zeolite)     | 2:1                         | 17            | 405               | 552    | 2.16           | 3.00   | 0.25 |
| PTFE + 5% (F-2M:zeolite)     | 2:1                         | 9             | 7                 | 704    | 2.09           | 0.88   | 0.19 |
| PTFE + 2% F-2M+2% zeolite    | -                           | 12            | 231               | 596    | 2.12           | 1.64   | 0.20 |
| PTFE + 2% F-2M+3% zeolite    | -                           | 11            | 176               | 577    | 2.12           | 0.89   | 0.21 |

Note: $\sigma_t$ – ultimate tensile strength; $\varepsilon_t$ – relative tensile elongation; $E_t$ – Young’s tensile modulus; $\rho$ – density; $I$ – mass wear rate, mg/h; $f$ – friction factor.

The increase in concentration of a modified filler up to 5% by mass in ratios 1:1 and 2:1 in the polymer under agitation in an impeller mixer leads to higher stiffness and brittleness of test composites and reduced strength. The mass wear rate tends to lower versus increase in filler concentration.

**Table 2.** Strain-strength and tribotechnical characteristics of PCM based on PTFE and zeolite modified by F-2M fluoropolymer in the mechanical activation process

| Composition                  | Ratio F-2M:zeolite by mass | $\Sigma$, MPa | $\varepsilon_t$, % | $E_t$, MPa | $\rho$, g/cm$^3$ | $I$, mg/h | f     |
|------------------------------|-----------------------------|---------------|-------------------|--------|----------------|--------|------|
| PTFE                         | -                           | 19            | 310               | 469    | 2.19           | 161.9  | 0.20 |
| PTFE + 1% act(F-2M:zeolite)  | 1:1                         | 15            | 347               | 543    | 2.19           | 3.51   | 0.18 |
| PTFE + 2% act(F-2M:zeolite)  | 1:1                         | 13            | 325               | 592    | 2.17           | 1.89   | 0.25 |
| PTFE + 5% act(F-2M:zeolite)  | 1:1                         | 12            | 258               | 575    | 2.12           | 0.67   | 0.19 |
| PTFE + 1% act(F-2M:zeolite)  | 1:2                         | 15            | 356               | 548    | 2.17           | 2.36   | 0.18 |
| PTFE + 2% act(F-2M:zeolite)  | 1:2                         | 11            | 203               | 674    | 2.19           | 0.89   | 0.25 |
| PTFE + 5% act(F-2M:zeolite)  | 1:2                         | 12            | 248               | 579    | 2.15           | 0.43   | 0.21 |
| PTFE + 1% act(F-2M:zeolite)  | 2:1                         | 15            | 353               | 579    | 2.17           | 4.71   | 0.18 |
| PTFE + 2% act(F-2M:zeolite)  | 2:1                         | 10            | 134               | 791    | 2.16           | 3.36   | 0.20 |
| PTFE + 5% act(F-2M:zeolite)  | 2:1                         | 12            | 240               | 547    | 2.09           | 0.93   | 0.20 |
Table 2 reports the research data on properties of PCM based on PTFE and zeolite modified by F-2M fluoropolymer in the process of simultaneous mechanical activation. Small amount of the filler higher Young’s modulus and relative tensile elongation of composites by 20–50% at concurrent reduction in tensile strength parameter. Introduction of the modified filler in amount of 5% in mass at ratio 1:2 provides 380-fold improvement of wear durability as compared to that for PTFE. Perspectiveness is shown for application of the mechanical activation process to improve tribotechnical properties of PCM.

The effect of zeolite modified by F-42 fluoropolymer on strain-strength and tribotechnical characteristics of PTFE-based PCM is demonstrated in Table 3. F-42 Fluoropolymer (GOST 25428-82) is a co-polymer of vinylidene difluoride with tetrafluoroethylene of melting temperature within 150–160°C. It exhibits high strength and chemical durability, antifriction properties, light aging resistance.

| Composition | Ratio F-42: zeolite by mass | Σt, MPa | Et, % | Et, MPa | ρ, g/cm³ | I, mg/h | f |
|-------------|----------------------------|---------|-------|---------|---------|---------|---|
| PTFE        | -                          | 19      | 310   | 469     | 2.19    | 161.9   | 0.20 |
| PTFE + 1% act(F-42: zeolite) | 1:1                  | 14      | 318   | 594     | 2.18    | 7.66    | 0.18 |
| PTFE + 2% act(F-42: zeolite) | 1:1                  | 14      | 375   | 647     | 2.18    | 2.9     | 0.21 |
| PTFE + 5% act(F-42: zeolite) | 1:1                  | 9       | 5     | 860     | 2.15    | 2.54    | 0.17 |
| PTFE + 1% act(F-42: zeolite) | 1:2                  | 15      | 343   | 562     | 2.18    | 7.92    | 0.18 |
| PTFE + 2% act(F-42: zeolite) | 1:2                  | 11      | 296   | 713     | 2.17    | 3.31    | 0.19 |
| PTFE + 5% act(F-42: zeolite) | 1:2                  | 10      | 4     | 1002    | 2.19    | 2.58    | 0.17 |
| PTFE + 1% act(F-42: zeolite) | 2:1                  | 14      | 305   | 617     | 2.18    | 27.96   | 0.17 |
| PTFE + 2% act(F-42: zeolite) | 2:1                  | 11      | 4     | 1037    | 2.18    | 6.86    | 0.20 |
| PTFE + 5% act(F-42: zeolite) | 2:1                  | 11      | 14    | 773     | 2.14    | 3.43    | 0.17 |

It is known [10], that one of main problems to be solved by introducing filling agents into polymer matrices deals with increase in polymer stiffness, which can be described by elasticity modulus magnitude. Specimens of compositions PTFE + 2% by mass (F-42: zeolite) at mass ratio 2:1 and PTFE + 5% by mass (F-42: zeolite) at ratio 1:2 demonstrated 2-2.5 times higher elasticity moduli as compared to the initial polymer, thus indicating the appreciable enhancement of material stiffness.

![Figure 1. Isochronal stress–relative elongation curves after t=1000 h.](image)
Creeping negatively affects the exploitation properties of load-bearing structural elements, as it leads to possible development of critical strains in them and elimination of their further application. Creeping is a process of ever-increasing residual strain in time under constant load and temperature. This property specific even for rather stiff polymers is induced by development of both plastic and quasiplastic deformations [11]. In the figure the isochronal curves are shown for dependence of relative elongation versus stress of the initial PTFE and polymer composites after 1000 h period. Creep of the test composites reduced 2–2.75 times as compared to that of the initial polymer. It is important to point out that the test specimens did not fail during 1000 h tests, none of cracks were observed at their surface thus justifying their less predisposition to brittle failure regardless of the low strain-strength parameters.

3. Conclusions
To conclude, the present research justifies perspectiveness of simultaneous mechanical activation of components with a view to modify surface of zeolites. It is found that a small amount of F-2M-based filling agent improves elasticity modulus and respective tensile elongation of a composite by 20-50% at smallish reduction in strength index under tension. Introduction of a filler modified by F-2M in the amount of 5% by mass provides 380-fold boosting of wear resistance as compared to PTFE. F-42 fluoroplastic used as a modifier of zeolite induces higher stiffness and consequently 2-2.75-fold lower creep of composites. The composites with zeolites modified by F-2M fluoroplastic developed on the basis of the present research evidence can be considered as promising sealing and anti-friction materials. The composites with F-42 modified zeolites can be used as constructional materials.

References
[1] Baskakov VP and Uvarova VA 2014 Polymeric composites in mining, their fire and environmental safety Safety of Work in the Industry No 6 pp. 63–68
[2] Ishkov AM and Vikulov MA 2015 Operation of mining-transport cars at North pits. Moscow: Forum
[3] Buznik VM 2008 Russian fluoropolymer chemistry and industry of fluoropolymer materials. Russian Chemical Journal Vol 52 No 3 pp 7–12
[4] Kondakov LA and Golubev AI et al. 1986 Consolidations and sealing technique Moscow: Mechanical Engineering
[5] Okhlopkova AA Adrianova OA and Popov SN 2003 Modification of polymers by ultradispersed connections Yakutsk: Yakut branch of Publishing house of the Siberian Branch of the Russian Academy of Sciences
[6] Dhanumalayan E and Joshi GM 2018 Performance properties and applications of polytetrafluoroethylene (PTFE)-a review. Advanced Composites and Hybrid Materials Vol 1 pp 247–268
[7] Boldyrev VV Avvakumov EG Boldyрева EV et al 2009 Fundamental bases of mechanical activation, mechanosynthesis and mechnochemical technologies Novosibirsk Publishing House of the Siberian Branch of the Russian Academy of Sciences
[8] Ammosova OA et al 2017 The modified polymeric and composite materials for northern conditions Novosibirsk Publishing House of the Siberian Branch of the Russian Academy of Sciences
[9] Movsumzade EM Pavlov ML Uspensky BG and Kostina ND 2000 Natural and synthetic zeolites, their production and application Ufa: Reactant
[10] Kryzhanovsky VK 2009 Engineering choice and identification of plastic St Petersburg: Scientific bases and technologies
[11] Cherednichenko VS 2006 Materials science Technology of structural materials Moscow: Omega-L