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Study of structure and properties of modified Armenian minerals for composite polymer-based self-lubricating materials

Key words

Mineral filler, fluoroalcon, friction coefficient, surface energy, solubility.

Summary

Research results of the modification mechanism of the Armenian minerals with fluorocontained oligomers are given. It is shown that, when treating of mineral fillers with fluoroalcon, a modified product is formed saving the structure of fillers with developed layers of fluoroalcon in which chlorine atoms are located on its periphery. It was established that the developed composites based on heterochained polymers and modified fillers are characterised by higher wear resistance, low friction coefficient, and improved strength properties.

1. Introduction

It is known that the modified Armenian mineral fillers (MAMF) have a significant impact on the structure and properties of heterochained polymers. It was established that the developed composites are characterised by higher wear resistance, lower friction coefficient, and improved strength properties [1-9].

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These mineral fillers are cheap and widespread in Armenia, and using for them modification fluoroalcon (FA) is the waste of the polytetrafluoroethylene synthesis with the temperature of the melting and boiling $T_m=65-670^{\circ}\text{C}$, $T_b=80-1740^{\circ}\text{C}$, density $\rho=1.67-1.72 \text{ g/sm}^3$ and common formula $\text{H}(\text{CF}_2)_n\text{Cl}$, where $n=7-14$, the molecular mass 316.5-596.5, possesses high anti-friction properties and low viscosity of the melt as well as high thermo stability and workability, and good solubility in organic solvents [6-10].

The aim of the study is the investigation of the regularities of the mechanism of modification of Armenian mineral fillers with fluorocontaining oligomers such as fluoroalcon, as well as the study of the structure and properties of the developed materials.

2. Experimental

For modification of the mineral filler (travertine, bentonite, marble or tuff felsite), its powder was mixed for a minute in the eccentric mixture type ML-30 with the FA at frequency of 100 Hz producing lubricating properties.

The lubrication of MAMF was evaluated on a friction machine I-47 using Trust Washer scheme through their tests between the two rubbing metal (steel 1H13) surfaces with a stepped increase of the sliding speed. As a criterion of lubricating ability, the limiting sliding speed was chosen, which precedes rapid increase of the friction coefficient. The analysis of the samples' wettability using two liquids (water and methyleniodide) means of the instrumental MMI-2 microscope has been carried out. The structure of the initial mineral fillers, fluorocontaining oligomers, and modified mineral fillers by X-ray method on the DRON-1 diffractometer has been studied. The interaction of FA with the mineral filler by methods of mass spectrometry (MS-30), sol-gel analysis and electron paramagnetic resonance (EPR) has been studied.

3. Results and discussions

Test results showed (Fig. 1) that the modification of mineral fillers by FA led to the significant decrease (4...5 times) of the friction coefficient, forming 0.07...0.08 for a mixture of travertine+FA. The increase of the sliding velocity up to 0.4 m/s has no significant effect on the friction coefficient of the basic travertine. However, its further increase leads to the rapid increase of the friction coefficient, which is associated with an increase of the temperature at the friction contact. The similar phenomenon is observed for a mixture travertine+FA, but with a sliding velocity of more than 1.0 m/s, which indicates an increase in load capacity of the MAMF. Modification of mineral fillers (Table 1) leads to a decline of the free surface energy of 35.84 (43.65) to 26.97

(38.33) J/cm², respectively, for travertine and tuff. The polar component of the wettability contact angle of surface free energy of the mixture of travertine (tuff)+FA after washing out of FA is not reduced, approaching the value characteristic of the initial filling, but rather increases to a value of 1.02 (1.32) J/m², indicating the special structure of the obtained product, where the polar chlorine atoms are located on the periphery of the grafted layer.

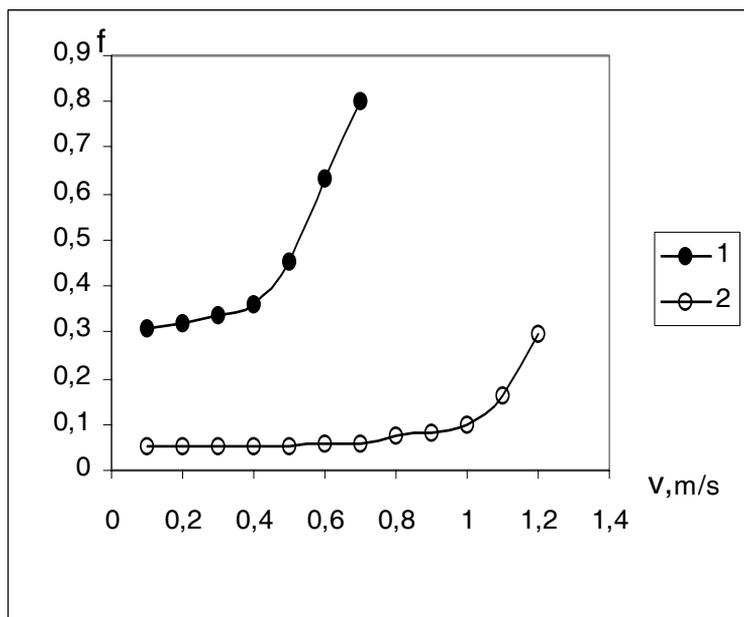


Fig. 1. The influence of the sliding speed on the friction coefficient of the travertine (1) and of the mixture travertine + 3wt.% FA (2)

To study the MAMF sample structures, the X-ray analysis of FA, of basic travertine and of the mixture travertine + FA after treatment in a vibratory mill was carried out, which results are shown in **Fig. 2**. On the diffractogram of FA (**Fig. 2,a**), the figures are marked by 1-6 reflection orders corresponding to the main reflections ($d_1 = 17.80 \text{ \AA}$). Besides, it marked reflex $d_2 = 5.60 \text{ \AA}$ and a large maximum in the term of 2θ from 32 to 44° . This diffraction is similar to the diffraction of the paraffin and other substances with a layered structure. Period $d_1 = 17.80 \text{ \AA}$ is the interlayer and characterises the thickness of one layer. The system of parallel sections of streamlined and extends for considerable distances (**Fig. 3**). The reflection corresponding to $2\theta = 18.15^\circ$ ($d_2 = 5.60 \text{ \AA}$) is intralayer not interlayer. The interplanar distance $d_2 = 4.90 \text{ \AA}$ and a large maximum $2\theta = 32 \dots 44^\circ$ characterise the intermolecular distances within the layer.

Table 1. Surface energy of the basic and modified mineral filler [10]

Indicator, 10 ⁻³ J/m ²	Travertine (tuff)	Travertine (tuff) + 3wt.% FA	Travertine (tuff) + 3 wt. % FA (after extraction)
Dispersion component, Y _{sd}	35.84 (43.65)	26.23 (37.28)	27.64 (37.75)
Polar component, Y _{sh}	0.48 (0.72)	0.74 (1.05)	1.02 (1.32)
Surface energy, Y	36.32 (44.37)	26.97 (38.33)	28.66 (39.06)

The comparison of diffractograms shows that, as the result of processing in the vibratory mill of the mixture travertine+FA, the travertine lines have not changed. With regard to the FA lines, the major change in them lies in the fact that all orders of reflection associated with the interlayer period $d_1 = 17.80 \text{ \AA}$ disappeared. At the same time, the intralayer reflex $d_2 = 5.60 \text{ \AA}$ is preserved and clearly visible on the diffractogram (**Fig. 2c**). The disappearance of the interlayer reflection and preservation of the intralayer means that the layers themselves (or at least a substantial part of them) survived, but their packages are destroyed. This indicates that, after processing in a vibratory mill of the mixture, the structure of FA is not in the form of particles, consisting of layer packets but in the form of individual monolayers. It is natural to assume that such structural changes, because the individual FA monolayers, were distributed on the borders of the travertine particles. Consequently, the structure of the mixture after treatment in a vibratory mill can be represented in the form of particles of travertine, covered with a thin film of FA (**Fig. 3**). Such FA monolayers prevent the direct friction of the travertine particles. The results [8-10] indicate that the modification of travertine by FA prevents the travertine crystals from the destruction.

Thus, the method of X-ray analysis revealed that, during the mechanical treatment of the FA particles, composed of package layers, they are divided into individual monolayers. This division apparently is easy, since the intermolecular forces between the individual layers of the FA molecules with structures similar to the structure of PTFE must be very weak. Monolayers of FA, distributing on the borders of the travertine particles, preserve the travertine particles and the structure of the whole mixture from mechanical influence. It was assumed that in the thin FA layers are possible as physical and physicochemical phenomena.

The sol-gel analysis of the mixture travertine+FA revealed that, after the joint vibrating grinding, the part of FA (**Fig. 4**) was not washed out by the chloroform solvent. The amount of undissolved FA depends on the duration of the grinding, reaching the equilibrium value at 90% after 60 s of the action.

To investigate the nature of the processes occurring on the surface of the travertine during mechanical action, the mass spectrometric study of the basic

FA and of the mixture travertine + FA before and after vibrating grinding was conducted (**Table 2**). The study of the basic FA showed that the most intensively extracting chlorine-containing species in the mass spectrum are the ions $(CF_2)_mCl$, where $m=1...4$. In the mass spectrum, there are all products of the sequence splitting of this ion.

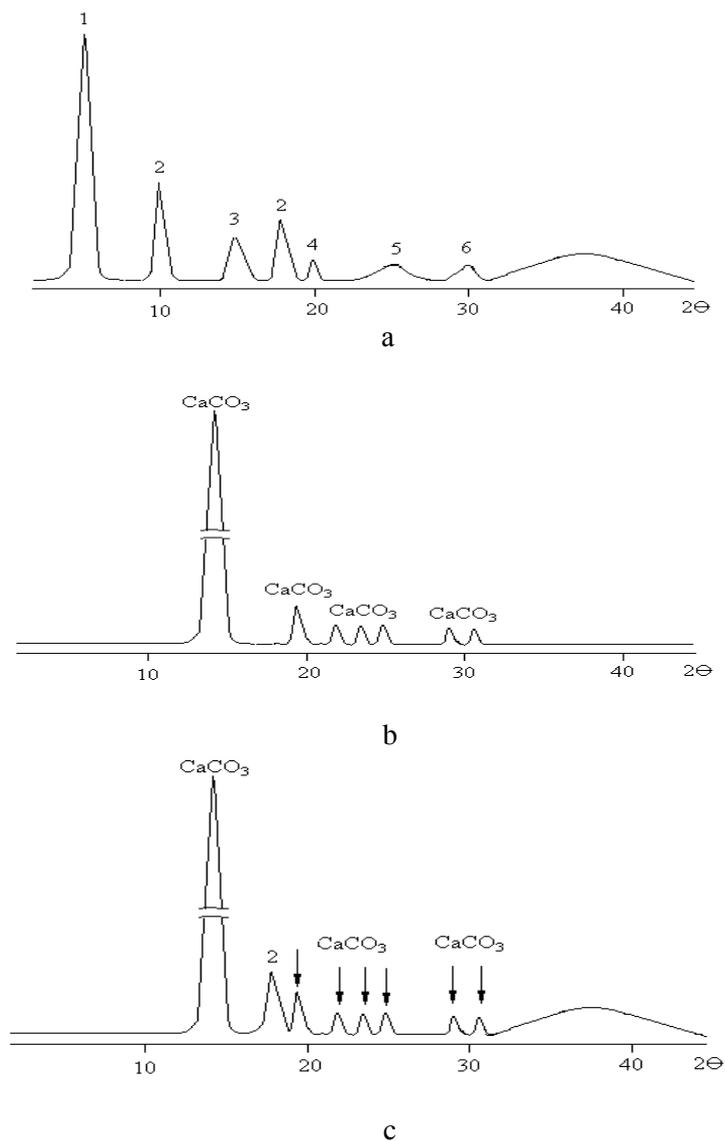


Fig. 2. Diffractograms of FA (a), basic travertine (b) and mixture travertine + 3wt.% FA after treatment in a vibratory mill (c)

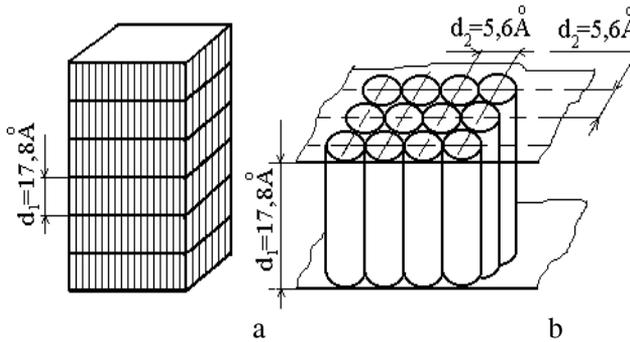


Fig. 3. Schemes of the FA crystallite structure, consisting of parallel layers (a) and one layer (b)

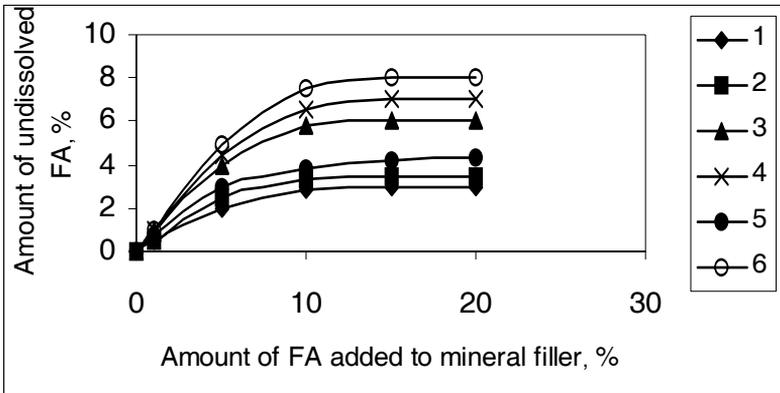


Fig. 4. Sol-gel analysis of modified FA mineral fillers:
1-travertine, 2-bentonite, 3-marble, 4-tuff felsite, 5-heat-treated travertine,
6-heat-treated tuff felsite

The mass spectrometric analysis of thermal decay products indicates the destruction of the FA under the electron impact proceeds with the break of the less strength C-C bonds of the FA chain and the formation of active radicals. The strength of the C-F bonds prevents the transition of the atom F with one radical to another, leading, as in the case of PTFE, to the appearance of m/z 100 (CF_2)₂.

The decay of the mixture travertine+FA in contrast to the basic FA is characterised by significant reduction in "large" products of disintegration, indicating the interaction of the travertine with FA in the process of joint vibrating grinding. For a more detail study of the obtained products, the washed out products by the chloroform part of FA and the residue after washing were analysed. The mass spectrometric analysis the part of the mixture travertine+FA dissolved in chloroform shows the full reproduction of the basic FA. The lower decrease in the amount of "large" particles of disintegration probably indicates

only a partial destruction of FA remaining in the unbound state. However, in the balance, after the washing out of the FA, there is a change of the liberated "large" products compared to the basic mixture. The spectra of this product of mass spectrometric results show a significant increase in the amount of ions $(CF_2) mCI^+$ on fluorine. This suggests that the interactions with the modification of travertine by FA occur due to the radical products formed during the destruction of C-C bonds of the FA chain, rather than by chemisorptions on the fluorosulphate group.

Table 2. Products of thermal decay of FA and modified mineral filler [7, 10]

Ion , m/z	Decomposition products	Intensity of liberation, %		
		FA	Travertine (tuff)+FA	Travertine (tuff) + FA (after washing FA)
31	CF	0.83	0.56 (0.65)/0.45 (0.58)	0.08 (0.09)/0.062 (0.072)
50	CF ₂	0.9	0.42 (0.48)/0.35 (0.40)	0.06 (0.07)/0.038 (0.05)
51	CF ₂ H	4.8	0.82 (0.93)/0.68 (0.76)	0.16 (0.17)/0.12 (0.152)
85	(CF ₂)CI	5.9	1.20 (1.26)/1.02 (1.05)	0.84 (0.90)/0.53 (0.690)
87	(CF ₂)CI	4.8	0.80 (0.84)/0.62 (0.68)	0.66 (0.72)/0.57 (0.062)
100	(CF ₂) ₂	4.8	0.64 (0.70)/0.44 (0.57)	0.12 (0.13)/0.08 (0.103)
101	(CF ₂)H	2.0	0.24 (0.29)/0.16 (0.22)	0.04 (0.05)/0.02 (0.030)
119	(CF ₂)F	4.8	0.86 (0.92)/0.58 (0.75)	0.15 (0.16)/0.09(0.141)
131	(CF ₂)CF	4.8	0.98 (1.05)/0.70 (0.88)	0.31 (0.38)/0.22 (0.352)
135	(CF ₂)CI	3.6	0.51 (0.56)/0.32 (0.41)	0.34 (0.39)/0.23 (0.363)
137	(CF ₂)CI	2.8	0.43 (0.51)/0.20 (0.34)	0.27 (0.35)/0.19 (0.310)
150	(CF ₂) ₃	4.8	0.78 (0.85)/0.52 (0.65)	0.23 (0.28)/0.15 (0.24)
151	(CF ₂) ₃ H	0.3	0.08 (0.09)/0.05 (0.07)	0.02 (0.03)/0.01 (0.02)
185	(CF ₂) ₃ CI	0.9	0.12 (0.13)/0.080 (0.11)	0.08 (0.09)/0.04 (0.07)
187	(CF ₂) ₃ CI	1.1	0.15 (0.16)/0.11 (0.14)	0.10 (0.11)/0.05 (0.08)
200	(CF ₂) ₄	0.7	0.20(0.18)/0.16(0.12)	0.32(0.28)/0.26(0.24)
201	(CF ₂) ₄	0.14	0.23(0.16)/0.17(0.11)	0.36(0.32)/0.27(0.23).
235	(CF ₂) ₄ CI	0.28	0.20(0.18)/0.16(0.12)	0.30(0.26)/0.23(0.18)
237	(CF ₂) ₄ CI	0.14	0.22(0.18)/0.15(0.12)	0.35(0.30)/0.28(0.22)

Notes: in numerator the data of the initial, and in denominator – of the heat-treated filler are indicated.

In this regard, co-grinding products were investigated by EPR (**Fig. 5**). The grinding of each of the components (travertine and FA) in the selected conditions did not lead to the formation of paramagnetic centres (PMC). This is probably due to the rapid recombination of the products of a radical type. EPR signals characteristic to the fluorocontaining radicals (major constants of the hyperfine interaction with the atoms of F) are absent in the mixture travertine+FA. However, there is a significant amount of paramagnetic particles. This is probably due to the fact that the PMC were formed by the reaction of FA radicals with the surface of travertine.

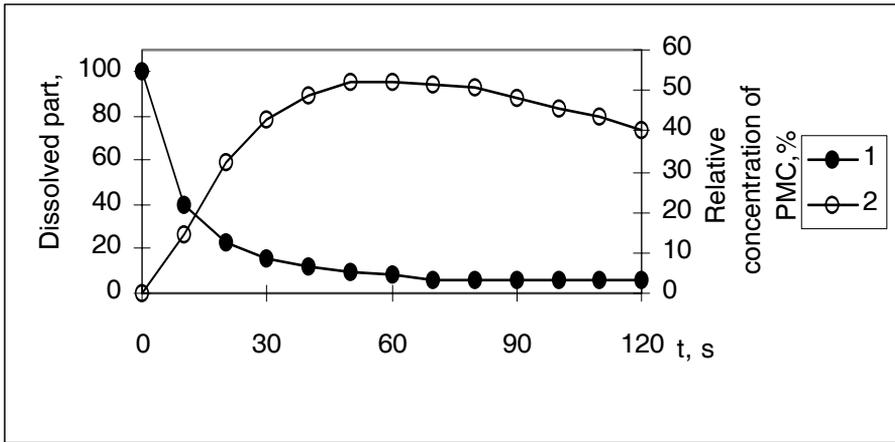


Fig. 5. The influence of the duration of vibrating grinding of MAMF on the solubility of the FA (1) and the concentration of PMC (2)

The sol-gel analysis of the MAMF showed that, after joint vibrating grinding, the part of FA is not washed with solvent. With the increasing of the amount of FA introduced into the mineral filler, the undissolved amount of FA is also increased. This process is continued with the introduction of FA up to 10% for travertine, marble, bentonite, and 15% for the tuff. Further increasing of FA does not change the amount of undissolved FA, indicating a saturation of the mineral fillers by FA. The similar in nature, dependencies are observed with the heat-treated fillers [7, 10].

Conclusions

The joint vibrating grinding of the mineral fillers as travertine, bentonite, and tuff with fluoroalcon, the new anti-friction product MAMF is formed having improved lubricating properties and saving the structure of fillers with developed layers of fluoroalcon in which chlorine atoms are located on its periphery. The mass-spectrometry analysis showed the presence of chlorine-containing species such as $(CF_2)_mCl^+$, where $m=1..4$. The thermal decay of fluoroalcon resulted in the breakage of less low-strength C-C bonds and the formation of active radicals. The latter promoted enhanced adhesion between the filler and polymer, which resulted in increased wear resistance. The developed composites based on polymers were found to have higher wear resistance, a decreased friction coefficient, and improved strength properties. These attributes made them good candidates for application as friction units in machines.

References

- [1] Tribology in the USA and the Former Soviet Union: Studies and Applications /Ed. by Belyi V., Ludema K. and Myshkin N. New York, Allerton Press, 1993, 454p.
- [2] Pogolian A., Karapetian A., Oganessian K. Tribochemical Processes and Wear of Composite Polymer Materials // Wear of Materials ASME. Denver, USA, 1989, vol.2, pp. 521- 528.
- [3] Gribova I., Krasnov A., Chumaevskaya A. Chemical Structure of Polymers and Tribochemical Changes in Polymers and Filled Systems // Friction and Wear, 1997, vol.18, N 2, pp.258-279.
- [4] Pogolian A., Hovhannisyan K., Karapetyan A., Baghdasaryan A. Antifriction Composite Polymer Materials Based on Copolymer of Formaldehyde // Friction and Wear, 1998, vol.19, N1, pp.97-103.
- [5] Karapetyan A. Study of Tribochemical Processes at Friction of Aliphatic Polyamides // News of NAS RA and SEUA, Techn. Sciences Series, 2004, vol. 57, N3, pp.406-413 (In Russian).
- [6] Karapetyan A., Hovhannisyan K. Strained-Strength Properties of Modified Heterochained Polymers//Machine Dynamics Problems, Warsaw, 2004, vol.28, N 3, pp.151-156.
- [7] Pogolian A.K., Karapetyan A.N., Hovhannisyan K.V. Study of Physico-Chemical Modification Process of Heterochained Polymers by the Fillers Minerals // Tribologia, Warsaw, 2004, vol. 193, N 1, pp.63-73.
- [8] Pogolian A.K., Karapetyan A.N., Hovhannisyan K.V. Development of Composite Antifriction Materials Based on the Thermoplastic Polymers // Tribologia, Warsaw, 2005, vol. 203, N 5, pp.111-129.
- [9] Pogolian A., Bahadur Sh., Karapetyan A., Hovhannisyan K. Investigation of the Tribochemical and Physico-Mechanical Processes in Sliding of Mineral-Filled Formaldehyde Copolymer Composites Against Steel // Wear, 2006, vol. 260, N 6, pp. 662-668.
- [10] Karapetyan A., Gribova I., Krasnov A., Studnev Yu., Pogolian A., Hovhannisyan K. Study of the Structure and Properties of the Armenian Minerals Modified With Fluorocontained Olygomers // News of NAS RA and SEUA, Techn. Sciences, 2005, vol.58, N2, pp.243-250 (In Russian).

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