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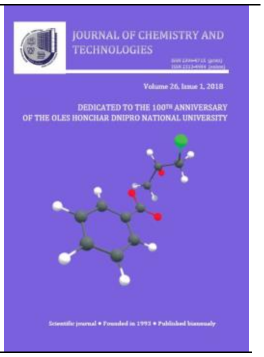

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THE EFFECT OF SURFACE MODIFICATION OF PARTICULATE KCL FILLER ON RHEOLOGICAL BEHAVIOUR OF ITS PASTE-LIKE COMPOSITES

Alexander B. Surovtcev[1], Anton M. Polivyanii[1], Viktor S. Tokarev[2], Mikhail P. Dyachenko[1],
Oleh M. Shevchuk[2], Stanislav V. Tokarev[2]

[1]*Oles Honchar Dnipro National University, 72 Gagarin Ave., Dnipro, 49010, Ukraine*
[2]*Lviv Polytechnic National University, Ukraine, 12 S. Bandery Str., Lviv 79013, Ukraine*

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Abstract

The paste-like composites of particulate KCl filler in a liquid rubber were prepared and their rheological properties were studied using a cone-and-plate rotation viscometer. Effects of the nature and concentration of surfactant added to composite, as well as the surface modification of KCl particles by functional polyperoxide on rheology of the paste prepared are discussed in this paper. In case of unmodified filler, an enhanced temperature and surfactants added brought about some reduction of the paste viscosity, while effect of the KCl surface modification by functional polyperoxide was more complicated. At room temperature such modification brought about essential reduction of the paste viscosity (by 1.5–2 times) imparting them flowability; however after heating, these pastes demonstrated a manifold growth in viscosity because of interaction of functional polyperoxide with macromolecules of liquid rubber and the formation of interphase chemical bonds. Thus, preheating of the pastes containing polyperoxide-modified filler allows to control their rheological properties.

Keywords: rheological properties, high-filled paste-like composites, particulate filler, surface modification of filler, liquid rubber, surfactants, polyperoxide.

ВПЛИВ ПОВЕРХНЕВОЇ МОДИФІКАЦІЇ ДИСПЕРСНОГО НАПОВНЮВАЧА KCL НА РЕОЛОГІЧНІ ВЛАСТИВОСТІ ЙОГО ПАСТОПОДІБНИХ КОМПОЗИЦІЙ

Олександр Б. Суровцев[1], Антон М. Полив'яний[1], Виктор С. Токарєв[2], Михайло П. Д'яченко[1],
Олег М. Шевчук[2], Станіслав В. Токарєв[2]

[1]*Дніпровський національний університет імені Олеся Гончара, пр. Гагарина, 72, м.Дніпро, 49010, Україна*
[2] *Національний університет «Львівська політехніка», вул. С. Бандери, 12, м. Львів, 79013, Україна*

Анотація

Отримано високонаповнені пастоподібні композиції на основі дисперсного KCl і рідкого каучуку, вивчено їх реологічні властивості з використанням ротаційного віскозиметра на системі конус-площина. У роботі розглянуто вплив на реологію пастоподібних композицій природи і концентрації поверхнево-активної речовини, а також поверхневої модифікації частинок KCl функціональним поліпероксідом. У разі немодификованного наповнювача підвищення температури і наявність поверхнево-активних речовин приводить до зниження в'язкості пасти, в той час як ефект модифікації поверхні KCl функціональним поліпероксідом складніший. За кімнатної температури така модифікація приводить до істотного зниження в'язкості композицій (у 1.5–2 рази), забезпечуючи більш високу текучість; а попереднє термостатування цих композицій за більш високих температур приводить до істотного зростання в'язкості через взаємодію функціонального поліпероксіда з макромолекулами рідкого каучуку і утворенню міжфазних хімічних зв'язків. Таким чином, попередній нагрів пастоподібних композицій, що містять модифікований поліпероксидом наповнювач, дозволяє контролювати їх реологічні властивості.

Ключові слова: реологічні властивості, високонаповнені пастоподібні композиції, порошкоподібний наповнювач, поверхнева модифікація наповнювача, рідкий каучук, поверхнево-активні речовини, поліпероксид.

**Corresponding author: Tel.:*+380676333617; *e-mail address: absurov55@gmail.com*

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ВЛИЯНИЕ ПОВЕРХНОСТНОЙ МОДИФИКАЦИИ ДИСПЕРСНОГО НАПОЛНИТЕЛЯ KCL НА РЕОЛОГИЧЕСКИЕ СВОЙСТВА ЕГО ПАСТООБРАЗНЫХ КОМПОЗИЦИЙ

Александр Б. Суровцев[1], Антон М. Полывяный[1], Виктор С. Токарев[2], Михаил П. Дьяченко[1], Олег М. Шевчук[2], Станислав В. Токарев[2]
[1]*Днепровский национальный университет имени Олеся Гончара, пр. Гагарина, 72, г. Днипро, 49010, Украина*
[2] *Национальный университет «Львiвська полiтехнiка», ул. С. Бандеры, 12, г. Львов, 79013, Украина*

Аннотация

Получены высоконаполненные пастообразные композиции на основе дисперсного KCl и жидкого каучука, изучены их реологические свойства с использованием ротационного вискозиметра на системе конус-плоскость. В работе рассмотрено влияние на реологию пастообразных композиций природы и концентрации вводимого поверхностно-активного вещества, а также поверхностной модификации частиц KCl функциональным полипероксидом. В случае немодифицированного наполнителя повышение температуры и наличие поверхностно-активных веществ приводит к снижению вязкости пасты, в то время как эффект модификации поверхности KCl функциональным полипероксидом более сложен. При комнатной температуре такая модификация приводит к существенному снижению вязкости композиций (в 1.5–2 раза), обеспечивая более высокую текучесть; а предварительное термостатирование этих композиций при более высоких температурах приводит к существенному росту вязкости из-за взаимодействия функционального полипероксида с макромолекулами жидкого каучука и образования межфазных химических связей. Таким образом, предварительный нагрев пастообразных композиций, содержащих модифицированный полипероксидом наполнитель, позволяет контролировать их реологические свойства.

Ключевые слова: реологические свойства, высоконаполненные пастообразные композиции, порошкообразный наполнитель, поверхностная модификация наполнителя, жидкий каучук, поверхностно-активные вещества, полипероксид.

Introduction

Promising and actual direction in development of rocket technology is the creation of propulsion systems working on the paste-like composite propellants to provide their controllable operating mode. These engines are well suited for multiple restarts and shutdowns, as well as controlling the traction characteristics required for high manoeuvrability along the flight trajectory [1–3]. Interest in paste-like propellants is maintained also due to easier adaptability of their production [4] and higher safety in comparison to liquid and solid propellants [5–7]. The use of such propellant enables tochange manifold (up to 80 times) their energetic parameters during regulation [8; 9]that is achieved via a nonlinearity of the propellant consumption versus pressure applied, which, in its turn, obeys the non-Newtonian fluid flow law.

There are several main requirements to paste-like propellants, namely, a high degree of filling (up to 90 wt.%) to achieve high energy characteristics, while maintaining a uniform distribution of mineral particles in an organic binder; pastes should also have flowability under loading, high density, compositional resistance in a temperatures range from -10 °C to +50 °C, sedimentation stability during storage, low sensitivity to shock-kinetic effects [1; 8].

In the paste-like propellants, the main component by content has to be an oxidizer (oxygen-containing highly dispersed component), among which ammonium perchlorate is the most effective because of a high oxygen balance and sufficient physicochemical stability. The latter is mixed with combustible preferably organic binder(e.g. with either an uncured low molecular polymer or highly plasticized polymer) which has the properties of a non-Newtonian fluid and provide the ability of the composite to flow under loading. To improve the energetic characteristics, the pasty propellant may also contain up to 15 wt.% of powdered metals (e.g. Aluminium, Magnesium, Titanium, Boron) or other powdery and liquid substances with a high enthalpy of formation of oxidized products. Technological additives [10] can be also added to pastes to provide the required rheological characteristics and an appropriate burning rate.

Despite the scientific approaches developed for the systems based on highly dispersed mineral particles and a binder material that finds reflection in [11; 12], for paste-like composite propellants, the problems of rheological behaviour can be solved mostly via their experimental studies because of a variety of the nature of components used, their content, size and shape of the filler particles and the state of their surface [13].

High energy characteristics of paste-like propellants are achieved at a complete combustion of their components (i.e. at zero oxygen balance) that requires as high as possible filling degree of composites by an oxidizing agent. It is a big technological problem to reach high filling degree because of insufficient wetting of the mineral filler surface by organic binder, aggregative and sedimentation instability of highly filled composites and a sharp deterioration of their rheological properties.

Some improvements in the filler mineral surface wettability, aggregative and sedimentation stability, as well as rheological properties of highly filled composites can be achieved via adding the proper surfactants and the filler surface modification. This paper is aimed at investigation of the effect of the surfactant nature and the filler surface modification by polyperoxide on the rheological behaviour of the pastes with a high filling degree modelling a composite propellant. As a model of paste-like propellants in this investigation a composition with a high filling degree (80 wt.%) based on a low-polarity liquid rubber and particulate Potassium chloride was chosen. This model was used to estimate the possibility of obtaining highly filled composites that have a sedimentation stability and flowability at ambient temperatures due to a prior surface modification of the filler in combination with the use of surfactants, added to improve wetting of the mineral filler surface by a binder, as well as to reduce viscosity of the composites. This approach was thought to allow increasing the volume fraction of an oxidizer and metal powder that in turn should increase the specific impulse of propellants, hence improving both the processability and the performance properties of the paste-like propellants.

Experimental

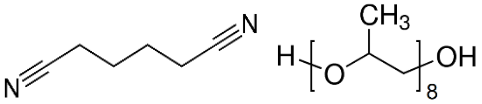
The experimental evaluation of the rheological properties of the paste-like model composites was performed with the use of Potassium chloride (KCl) instead of a real highly dispersed oxidizer. In accordance with [10; 14], the former one is an inert filler with the physicochemical characteristics similar to ammonium perchlorate. As it was aforementioned, for rheological investigations the composites comprised a low-polarity liquid rubber, particulate Potassium chloride (either pristine or surface-modified), and surfactant were used.

Materials. KCl was purchased from Sigma-Aldrich. It was dried at 100 °C to constant weight, ground and fractionated before the use. For the preparation of model pasty composites, the fraction with the particle size of 45–63 µm (as a base) was exploited. Same fraction of Potassium chloride (45–63 µm) was also used for the preparation ofa surface-modified filler in accordance with the approach outlined in [15; 16] and applyingthe procedure described below.

As an additive improving the energy characteristics of propellant an Aluminium powder ASD-4 with an average particle size of 12.3 µm was used in the work.

The hydroxyl terminated liquid rubber SKD-HTR with molecular weight of 2900 Da was appliedas a binder in the model composites [17].

Adipic acid dinitrile (AAD) and poly(propylene glycol) with a molecular weight of 480 Da (PPG) were assessed as surfactants in the model composites.



AADPPG480

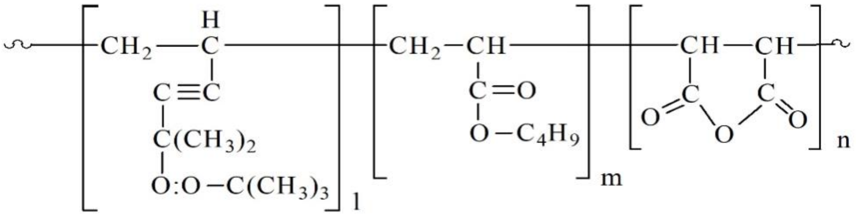
Monomers: butyl acrylate (BA, Merck) was purified by double vacuum distillation; maleic anhydride (MA, Merck) was purified by recrystallization from chloroform; peroxidic monomer 5-tert-butylperoxy-5-methyl-1-hexene-3-yne (PM) was synthesized via method described elsewhere [18] and vacuum distilled before the use.

Synthesis of the functionalized polyperoxides. Functionalized polyperoxide (FPP) with the structure shown in Figure 1 was synthesized via radical terpolymerization of PM, BA and MA at the total monomer concentration of 3.5 mol/l in acetone in the presence of lauroyl peroxide as an initiator as described elsewhere [19]. The structure, composition and some characteristics of FPP are given in Figure 1.

The content of MA subunit in FPP was determined by a reverse potentiometric titration of carboxylic groups [20]. The content of peroxide groups in FPP was calculated from the results of gas-chromatographic analysis of the final decomposition products obtained at the FPP thermolysis at 483 K in a sealed ampoule under argon blanket [21].

Number-average molecular weight of FPP was determined by Gel Permeation Chromatography

(GPC) using a Polymer Standard Service system (PSS, Mainz, Germany) with MDS RI detector, a 50 mm GRAM precolumn and two 300 mm GRAM columns(particle size – 10 µm) in DMF containing 1 g/l LiBr. Polystyrene standards were used for calibration of this GPC setup.



l=19.1 mol%, m=34.9 mol%, n=46.0 mol%,

$[O_{act}]=1.5\cdot10^{-3}$ mol/g, M_n=12.7 kDa

Figure 1. Structure and properties of functional polyperoxide FPP

Surface modification of Potassium chloride. The surface modification of the ground KCl was achieved via FPP adsorption from its solutions in ethyl acetate (EA) at the weight ratio of KCl to the FPP solution as 1 : 4 and concentration of FPP (C_{FPP}) of 0.050 or 0.125 mg per 1 g EA (Table1). The process was carried out at ambient temperature for 1 hour under continuous vigorous stirring using a magnetic stirrer. Afterwards a liquid phase was decanted out; the precipitate of KCl modified was rinsed with a portion of pure ethyl acetate, separated by decantation and dried till constant weight under ambient conditions. The amount of FPP adsorbed at the surface of ground KCl (A_{FPP}) was determined using elemental [C, H] analysis and controlled by gravimetry.

Table 1

Characteristics of ground KCl modified by FPP

C_{FPP} in a solution, mg/g of EA	FPP : KCl ratio in solution, mg/g	A_{FPP}, mg/g_{KCl}	Content of peroxide groups $[O_{act.}]\cdot10^6$, mol/g_{KCl}
0.050	2.0	2.0	3.1
0.125	5.0	4.9	7.5

Preparation of highly filled paste-like composites. The procedure for preparation of pasty composites involved several subsequent stages:

- pre-heating of a batch of the liquid rubber SCD-HTR at 50 – 60 °C to reduce its viscosity;
- addition of a pre-weighted amount of surfactant to the rubber heated under vigorous stirring of the mixture by a paddle stirrer with an electric drive for 10 – 20 minutes and maintaining temperature in the range of 50 – 60 °C;
- slow feeding by a small portions (totally 4–5 portions) of required amounts of ground KCl and aluminum powder into aforementioned mix under continuous stirring and heating at 50 – 60 °C for 30–40 minutes until obtaining a mixture with a visually even distribution of all components;
- vacuum treatment of the final composites at 50 °C for 2 hours under residual pressure of 0.04 MPa.

From the point of view of the methodology in order to obtain the reproducible results, such aspects as vacuumization and storage time of composites prior to evaluating their rheological properties are of high importance. Recently we have found [22] that vacuumization of composites brought about a decrease in their viscosity due to the removal of gaseous inclusions. At the same time, prolonged storage of composites caused an insignificant increase in their viscosity, probably because of a some structurization occurred in these systems. Taking into account the above, the rheology tests for all composites were carried out under the same conditions, namely, one day after their preparation and subsequent vacuumization.

Rheology tests of the highly filled paste-like composites. Rheological studies of the composites were carried out using a Reotest 2 rotational viscosimeter with a cone-plane system intended to study flows of highly viscous liquids in the shear stress range of 135 – 87000 Pa in the thermostating cell maintaining a discrete sample temperatures of 30, 40 and 50 °C [22].

Results and discussions

When preparing the paste-like composites based on the low-polar liquid rubber SCD-HTR and the pristine ground KCl filler, it was established that the highest filling degree, at which these composites had satisfactory values of plasticity and flowability, reached 80 wt. %.

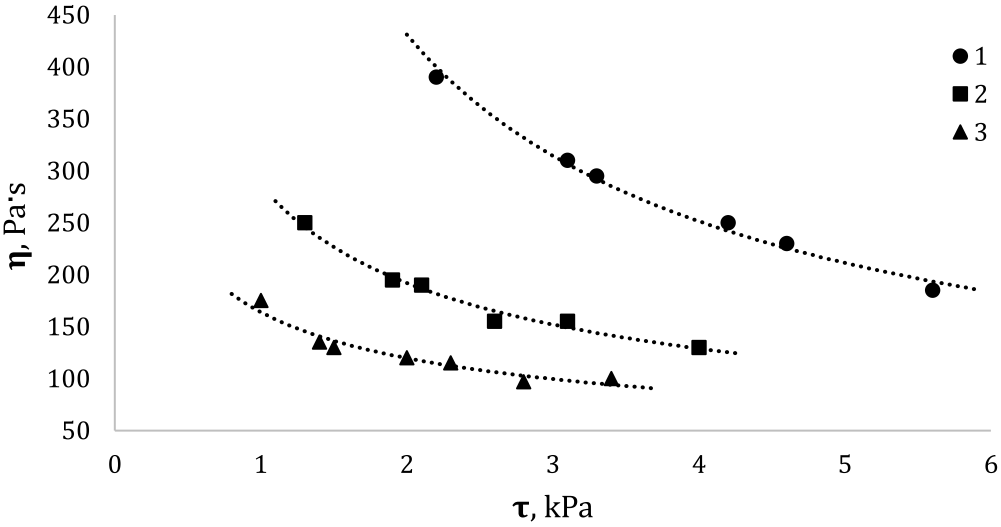


Figure 2. Dependence of dynamic viscosity of the paste-like composites filled by pristine KCl on shear stress at temperatures:1 – 30 °C; 2 – 40 °C; 3 – 50 °C.

At a higher filling degree, the composites became crumbly, non-uniform in appearance and lost their plastic flowability. All further investigations were performed for composites with the total filling degree of 80 wt. %. The effect of temperature in the range of 305 °C on viscosity of the composites has been estimated (Figure 2). The shape of rheological curves is a typical for non-Newtonian fluids; dynamic viscosity of composite drops down with increasing shear stress. Temperature has a similar effect; the composites become thinner at enhanced temperatures.

The effect of surfactants on the viscosity of composites. To increase plasticity of the composites owing to enhancement of the mineral filler surface wetting by a polymer binder (i.e. for improvement of particle wettability), introduction to their compositions of two alternative surfactants, namely AAD and PPG, which differ in their polarity essentially ,were considered. Each of these surfactants was added to the composites in the amounts ranged from 0.1 to 1.0 wt. % with respect to overall composition weight with the total filling degree of 80 wt. % (including 65 wt. % KCl and 15 wt. % Al). Figures 3 and 4 demonstrate effect of the surfactants added on rheological behaviour of the composites.

In both cases, a graduate decrease in the composite viscosity with increasing amount of surfactants added are clearly recognizable. It can be supposed that both surfactants AAD and PPG are readily adsorbed on the surface of mineral filler reducing its surface energy thus improving wettability by the organic binder SKD-HTR. That causes formation of solvated layers around of the filler particles and in turn weakening of an interaction between filler particles, some lubrication effect; that is reflected in the paste viscosity decrease.

The effect of surfactant amounts added on the rheology of composites is shown in Figure 5 for both surfactants to compare their effectiveness under the same conditions (T=30 °C and shear stress τ=4 kPa). The surfactant content was varied in the range of 0.1–1.0 wt. part. Analysing the experimental data, it can be concluded that introduction of any of surfactants in the amounts exceeding 0.5 wt. part has no sense, since only a slight decrease in the viscosity is observed with a higher surfactant loading. AAD demonstrate a better performance as compared to PPG.

A higher effectiveness of ADD can be explained by the presence in its molecule of two highly polar nitrile groups, which obviously should have a better affinity towards the mineral filler surface compared with the less polar hydroxyls present in PPG macromolecules. Thus, ADD molecules should interact more strongly with the filler surface, forming a denser adsorption layer, and improving the filler surface wettability by molecules of low-polar SKD-HTR rubber.

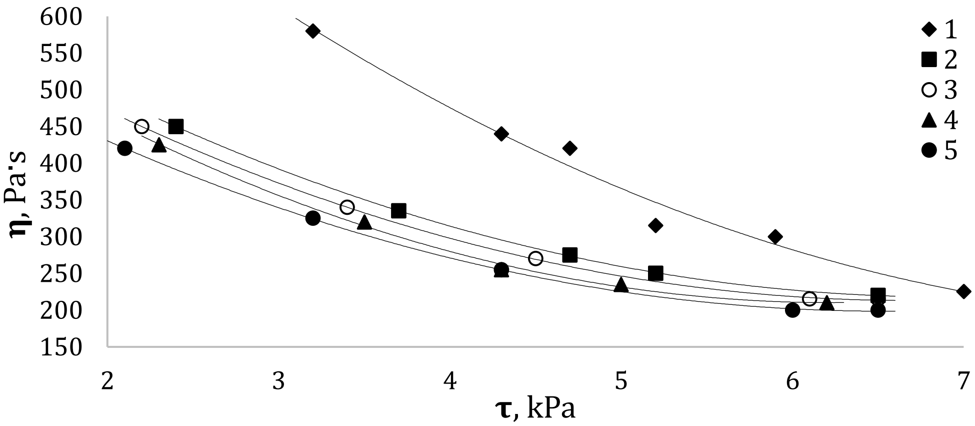


Figure 3. Dependence of dynamic viscosity of the paste-like composites filled by pristine KCl on shear stress at different amounts of PPG added (wt. part): 1 – 0; 2 – 0.1; 3 – 0.3; 4 – 0.5; 5 – 1.0

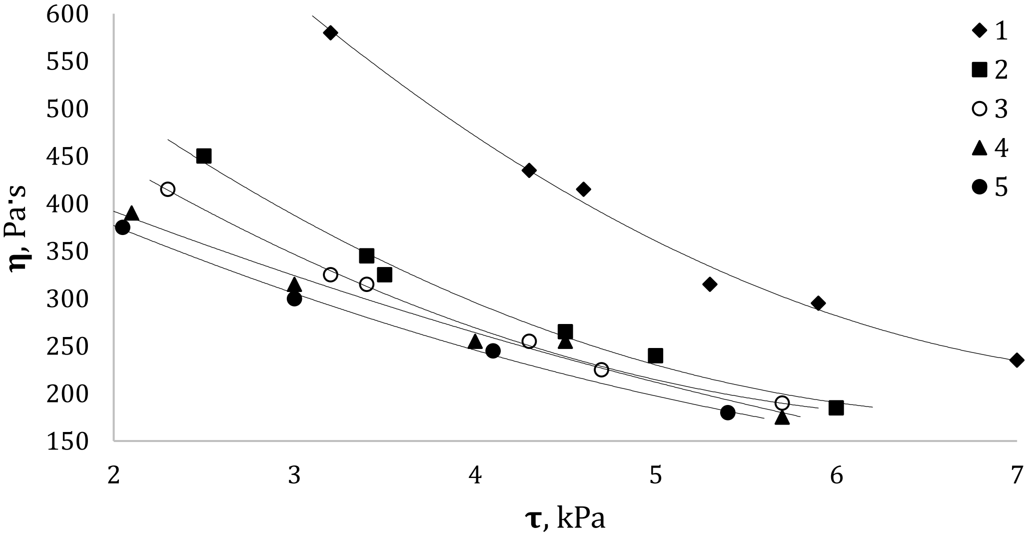


Figure 4. Dependence of dynamic viscosity of the paste-like composites filled by pristine KCl on shear stress at different amounts of AAD added (wt. part): 1 – 0; 2 – 0.1; 3 – 0.3; 4 – 0.5; 5 – 1.0

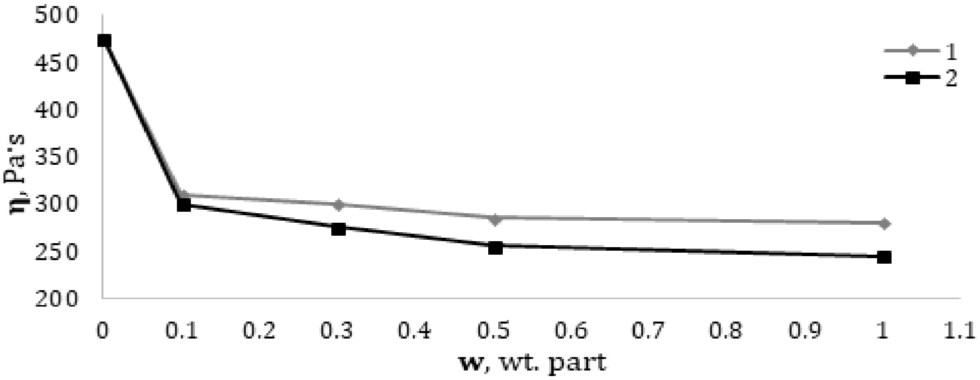


Figure5. Dependence of dynamic viscosity measured at 30°C and τ=4 kPa for the paste-like composites filled by pristine KCl on the nature and content of surfactants: 1 – PPG, 2 – AAD.

Based on these results, in further investigations, AAD in an amount of 0.5 wt. part was introduced into all compositions as a surfactant.

Effect of the filler surface modification by polyperoxide on rheological behaviour of composites. To study the effect of the filler surface modification on the rheology of composites, we have prepared two samples of the ground KCl modified by FPP, which differ in the amounts of the adsorbed polyperoxide, namely 2.0 and 4.9 mg per 1g of filler (Table 1). Using these samples and a sample of pristine ground KCl (all of the same granulometric characteristics), three model paste-like composites with similar compositions and the total filling degree of 80 wt. % have been prepared, which include 65 wt. % KCl (either modified or pristine), 15 wt. % Al powder, 20 wt.% SKD-HTR rubber, and 0.5wt.part of ADD added with respect tooverall composition weight.

The important features of the surface-modified KCl are a lower tendency to aggregation and better flowability, in contrast to the unmodified sample, that was observed when preparing the composites. It is worth mentioning that the KCl particles are not completely encapsulated by a polymer shell in the result of their surface modification. The complete and rather rapid solubility of the surface-modified KCl in water confirms this statement, indicating that the FPP polymer shell is not tight (nonporous), at least for the modification degree at the level of 2.0 and 4.9 mg/g. These results are in good agreement with the conclusions of our previous investigations that polyperoxides '*...do not occupy the adsorbent surface tightly; even in the case when the adsorbed layer reaches saturation, the underground is particularly reachable for water molecules*' [23]. Nevertheless, such a modification has a significant effect on therheology of composites with a high filling degree (80 wt. %), as shown in Figure 6.

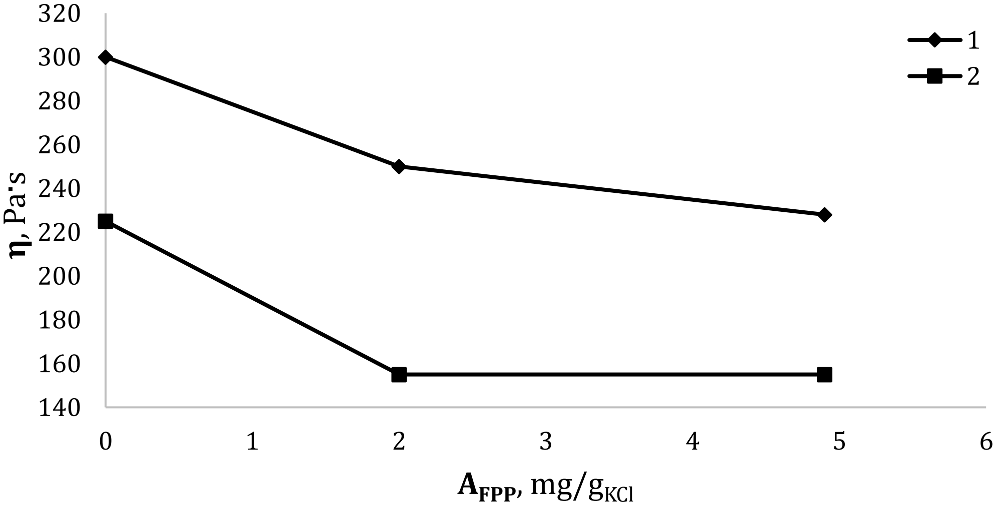


Figure6. Effect of surface modification of KCl filler by FPP on the dynamic viscosity of the paste-like composites at 30 °C, under different shear stresses: 1 – 2 kPa; 2 – 4 kPa.

Figure 6 illustrates the summarized results of a comparative rheological study of the composites filled by the surface-modified and pristine KCl fillers. As is clearly seen, an adsorption of FPP on the surface of KCl particles brings about a decrease in viscosity of the paste-like composites by about one-quarter to one-third.

Such reduction is achieved already at a low modification degree (2.0 mg/g); while the increasing degree of the KCl modification up to 4.9 mg/g has a much lower gain in further thinning of the composites. FPP contains reactive peroxide groups, as it follows from its structure shown in Figure 1. It can be supposed that the FPP adsorbed at the filler surface can interact under certain conditions with the macromolecules of matrix SKD-HTR in composites through radical mechanism. As the results, grafting of the SKD-HTR macromolecules onto the surface of modified KCl particles as well as cross-linking of the matrix can occur. The probability of these reactions is as higher as higher is temperature of preheating of the composites prepared. Figure 7 illustrates the effect of preheating temperature of the prepared composite, filled by the surface-modified particulate KCl with FPP content of 2.0 mg/g, on their rheology.

It is clearly seen a graduate increase in the dynamic viscosity with enhancing the preheating temperature; the viscosity of the paste-like composite filled by FPP-modified KCl (2.0 mg/g) is more than doubled if the thermostating temperature is enhanced from 50 °C to 100 °C. The effect of preheating on the paste viscosity is more pronounced for the KCl filler with a higher degree of modification (Figure 8).

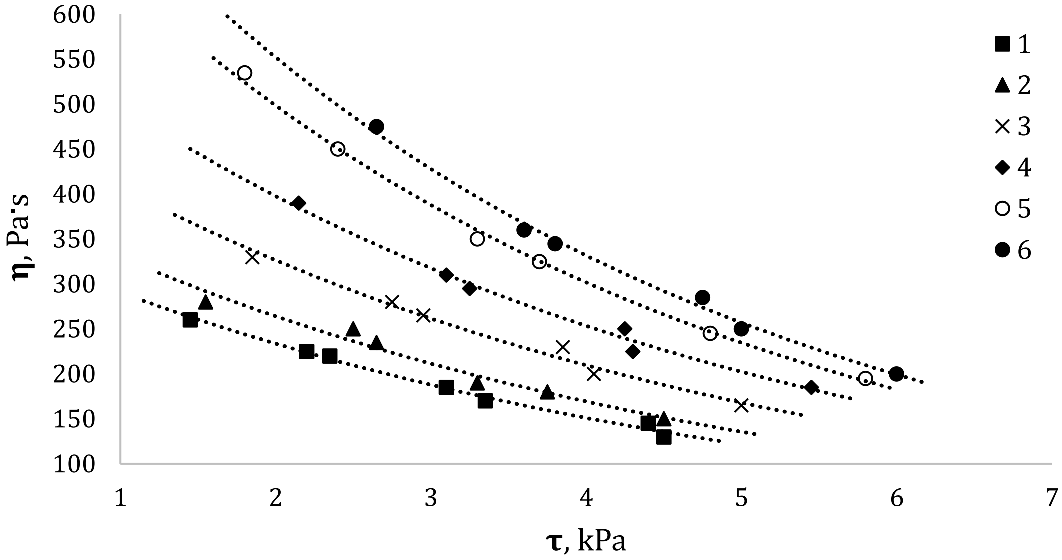


Figure 7. Plots of dynamic viscosity (at 30 °C) vs. shear stress for the paste-like composite filled by FPP-modified KCl (2 mg/g) after thermostating at different temperatures: 1 – 50 °C; 2 – 60 °C; 3 – 70 °C; 4 – 80 °C; 5 – 90 °C; 6 – 100 ˚C

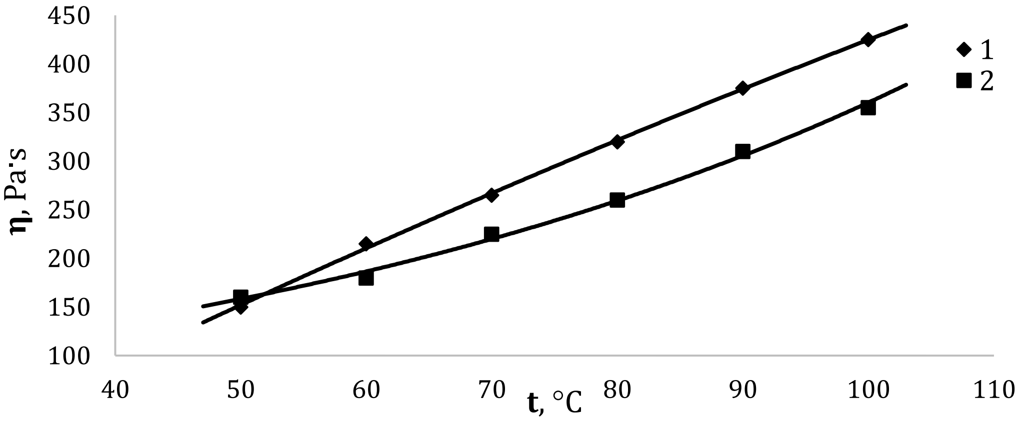


Figure8. The effect of the thermostating temperature on dynamic viscosity (at shear stress of 4 kPa) of the paste-like composites filled by the modified KCl containing different amount of FPP adsorbed: 1 – 4.9 mg/g, 2 – 2.0 mg/g.

To interpret the obtained results (Figures 6, 7, 8), the following explanations should be taken into account.

At the temperatures of preparation of paste-like composites (50 – 60 °C,), the peroxide groups of FPP remain quite stable, and under these conditions a polymer shell, formed on the surface of the KCl particles via FPP adsorption, improves their wettability by the SKD HTR rubber and reduces an internal friction in this highly filled system. Both these phenomena reveal themselves as a decrease in the composite viscosity (Figure 6).

A situation changes drastically when the paste-like composites with modified KCl undergo preheating at elevated temperatures (60 – 100 °C) for a longer time. Under this condition, peroxide groups decompose forming free radicals, including the polymeric free radicals immobilized at the surface of KCl filler particles. Further reactions of the free radicals formed with double bonds present in macromolecules of the SKD HTR rubber cause their grafting onto the surface of particles and partial cross-linking of the rubber matrix. Both these phenomena reveal themselves as an increase in the composite viscosity and the higher the preheating temperature, the higher the viscosity (Figure 7 and 8). A slight effect of preheating temperature on the viscosity of composites filled by the pristine particulate KCl confirms the scenario described above. The similar effect of the mineral filler modification by polyperoxides on rheological behaviour of the melt of polypropylene (PP) composites filled by $Mg(OH)_2$was described in [24]. The composites of a pure PP filled by the surface modified $Mg(OH)_2$ filler demonstrated an essentially higher melt flow as compared with the similar composites filled by the pristine $Mg(OH)_2$ filler. There was also shown, that an introduction of unsaturated compounds with double bonds into PP compositions with the surface modified $Mg(OH)_2$ filler brings about an appreciable decrease of their melt flow.

It should be noted that both effects, namely, viscosity reduction and viscosity increase, are more pronounced when the degree of the surface-modification of the filler is higher; however, it is more appropriate to increase the degree of modification of the filler surface in order to thicken the composition, but not for improving its flowability. The possibility of correcting the rheological properties can play a significant role, as noted in [25], when using ready-made paste-like fuel compositions in practice.

Conclusions

1. The highly filled paste-like composites flowable at temperatures of 30 °C and above have been obtained on the base of the liquid rubber SKD-HTRwith thetotal filling degree of 80 wt. % using AAD as a surfactant in the amount of 0.5 wt. part.

2. The surface modification of particulate filler by functional polyperoxide demonstrates two very distinguishing effects on the rheological behaviour of paste-like composites, depending on conditions of their preparation. In the paste-like composites filled by modified particulate KCl and prepared at 50 – 60 °C, the FPP adsorbed on KCl particles improves their wettability by the SKD HTR rubber and reduces an internal friction thus significantly reducing viscosity of the composites. But when these pastes undergo preheating at temperatures in the range of 60 – 100 °C, decomposition of FPP followed by a sequence of radical reactions causes the grafting and partial cross-linking of the rubber matrix, that is reflected in a graduate increase of the composite viscosity with enhancing preheating temperature. Both abovementioned effects are more pronounced when the degree of the surface-modification of the filler is higher.

3. Thus, the surface-modification of the mineral fillers by the functional polyperoxide and subsequent preheating of their composites with SKD HTR rubber is a new powerful approach to control the rheological properties of paste-like composites over a wide range that can be used for preparing the rocket composite propellants with improved characteristics.

Bibliograhpy

[1] Rocket propulsion elements / Eds. G. P. Sutton, O. Biblarz. – 8th ed. Pub: John Wiley & Sons, Inc., Hoboken, New Jersey.– 2010. –785 p.
[2] Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics / T. B. Brill; Wu-Zhen Ren; Vigor Yang // Progress in Astronautics and Aeronautics, AIAA, NY, Vol. 185. Pub. Reston, Virginia.–2000. – 999 p.
[3] Recent Advances in Research on Solid Rocket Propulsion/ Y. Fabignon, J. Anthoine, D. Davidenko [et al] //AerospaceLAB Journal. – 2016, N 11. –P. 1-15.
[4] Bondarenko S. G. Rocket propulsion using unitary paste-like propellant. Experimental investigation of paste-like propellant and results of PRM fire tests /S. G. Bondarenko, V. I. Eliseev, Yu. V. Protsan // Prog. of 61-th International Astronautical Congress (IAC-10.C44.1.9.).–2010. Prague. Czech Republic.–P. 27.
[5] Sarner S. F. Propellant chemistry / S. F. Sarner. – New York, Reinhold.– 1966. – 417 p.
[6] Lipanov A.M. Survey of Solid Rocket Propulsion in Russia/ A.M. Lipanov, V.E. Zarko. In: De Luca L., Shimada T., Sinditskii V., Calabro M. (eds) Chemical Rocket Propulsion. – Springer Aerospace Technology. Springer, Cham, 2017. – 144 p.
[7] Chemical Rocket Propulsion: A Comprehensive Survey of Energetic Materials. / Eds. De Luca L., Shimada T., Sinditskii V. P., Calabro M. – Springer, 2016. – 1084 p.
[8] Varghese T.L. The Chemistry and Technology of Solid Rocket Propellants (A Treatise on Solid Propellants)/T. L. Varghese, V.N. Krishnamurthy// Pub: Allied Publishers.– New Delhi, 2017. – 324 p.
[9] Serdyuk A.I.Slurry-propellant rocket propulsion. Eco-safety and new power opportunities. Tests of new propellants (IAC- 2013, C4.3,11) / A.I.Serdyuk, Yu. V. Protsan, S.G. Bondarenko // Proc.of 64-th International Astronautical Congress.– 23-27 September, 2013. – Beijing, China.–9 p.
[10] Dependence of rheological characteristics of paste-like rocket propellant from dispersion of filler, concentration of filler and PEAHENS/ K. O. Tretiakov, O. V. Potupa, S. G. Oginski [et al] //Вопросы химии и химической технологии. –2006, N 3.– С.158–163.

[11] Tadros T. F. Rheology of Dispersions: Principles and Applications/ T. F. Tadros. – Wiley-VCH, 2010. – 216 p.

[12] Bröckel U. Product, Design and Engineering: Formulation of Gels and Pastes, 1st Edition / U. Bröckel, W. Meier, G. Wagner – Wiley-VCH Verlag, Weinheim, Germany, 2013. – 355 p.

[13] Экспериментальное и численное исследование реологических характеристик пастообразных топливных композиций / В.И. Елисеев, С. Г. Бондаренко, А.Ф. Курочкин [и др.] // Вестник двигателестроения. Запорожье: АО «МоторСич». – 2012, N 1.–С. 26-31.

[14] Kurochkin A. F. High-filled compositions on the base on olygomeric rubber / A. F. Kurochkin,N. V. Dolmatova, A. B. Surovtcev//All materials. Encyclopaedic reference book Science and technology.– 2011.– Vol. 1. –P. 35–40.

[15] Modification of interface by polymeric peroxides - a new approach to the creation of composites / V. Tokarev, S. Voronov, V. Seredyuk [et al.] // Adsorption Sci. Technol. – 1996.– Vol. 14,N 4.– P. 239-249.

[16] Polyperoxide Surfactants for Interface Modification and Compatibilization of Polymer Colloidal Systems. 2. Design of Compatibilizing Layers. / S. Voronov, V. Tokarev, V. Datsyuk [et al.] // J. Appl. Polym. Sci. – 2000.– Vol. 76.– P. 1228-1239.

[17] Shankar R. M. Terminal functionalized hydroxyl-terminated polybutadiene: An energetic binder for propellant / R. M. Shankar, T. K. Roy, T.Jana // J. Appl. Polym. Sci.– 2009.– Vol. 114,N 2.– P. 732-741.

[18] Obtaining of dimethylvinylethynyl-methyltret-butyl peroxide / M. Vilenskaya, D. Karamov, E. Sorokin[et al.] // Khimicheskaya promyshl. – 1979, N 7.– P. 15–17.

[19] Polyperoxide Surfactants for Interface Modification and Compatibilization of Polymer Colloidal Systems. 1. Synthesis and Properties of Polyperoxide Surfactants /S. Voronov, V. Tokarev, K. Oduola,Yu. Lastukhin / J. Appl. Polym. Sci. – 2000.– Vol. 76.– P.1217-1227.

[20] The Effect of Structure of Compatibilizing Layer at the Mineral Filler Surfaces on Mechanical Properties of Premixes / V. Tokarev, O. Shevchuk, N. Bukartyk, U. Wagenknecht // Materials of International Symposium 'Technomer-2005', Chemnic, Germany.– 2005. AP5. – P. 1-10.

[21] Handbook of Maleic Anhydride Based Materials: Syntheses, Properties and Applications / Ed. Musa O. M. Publ.: Springer, New Jersey.– 2016.– 638 p.

[22] Influence of the nature of surface-active substances on rheology of high-filled paste-like compositions on a base on liquid diene rubber and disperse filler / A. Surovtcev, K. Kovalenko, N. Kuzmenko, S. Bondarenko //Bull. Dnipropetrovsk Univ. Ser. Chem. – 2014. – Vol. 22, N . – P. 76–81.

[23] Graft Polymerization from a Silica Surface Initiated by Adsorbed Peroxide Macroinitiators. I. Adsorption and Structure of the Adsorbed Layer of Peroxide Macroinitiators on a Silica Surface / O. Shafranska, V. Tokarev, A. Voronov[et al.] //Langmuir.– 2005.– Vol. 21,N 8.– P. 59-69.

[24] Flame-retardant polymer composites on the basis of modified magnesium hydroxide / O. Shevchuk, U. Wagenknecht, S. Wiessner[et al.] // Chemistry & Chemical Technology.– 2015.– Vol. 9, N 2.– P. 149-155.

[25] Rocket Propulsion Using Unitary Paste-like Propellant Analysis of Mass Efficiency for Applications in the Composition of Landing Units and Upper Stages of Launch Vehicles/Yu. Protsan, D. Maydaniuk, S. Bondarenko // Proceedings of International Forum on Special Equipments and Engineering Mechanics. – July 10-12, 2013. Nanjing, P. R. China. – P. 56-62.

References

[1] Sutton, G. P. Biblarz, O. (2010). *Rocket propulsion elements* / Eds. - 8th ed. Pub: John Wiley & Sons, Inc., Hoboken, New Jersey, USA.

[2] Thomas B. Brill, Wu-Zhen, Ren; Vigor, Yang. (Ed.). (2000). *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics* / Eds. - Progress in Astronautics and Aeronautics, AIAA, NY, Vol. 185. Pub. Reston, Virginia, USA.

[3] Fabignon, Y., Anthoine, J., Davidenko, D., Devillers, R., Dupays, J., Gueyffier, D., Hijlkema, J., Lupoglazoff, N., Lamet, J. M, Tessé, L., Guy, A., Erades, C. (2016). Recent Advances in Research on Solid Rocket Propulsion. *AerospaceLAB Journal*, 11, 1-15. https://doi.org/10.12762/2016.AL11-13

[4] Bondarenko, S. G., Eliseev, V. I., Protsan, Yu. V. (2010). *Rocket propulsion using unitary paste-like propellant. Experimental investigation of paste-like propellant and results of PRM fire tests. Prog. of 61-th International Astronautical Congress (IAC-10.C44.1.9.).* Prague. Czech Republic, 27.

[5] Sarner, S. F. (1966).Propellant chemistry. New York, USA: Reinhold.

[6] Lipanov, A.M., Zarko, V.E. (2017) *Survey of Solid Rocket Propulsion in Russia.* In: De Luca L., Shimada T., Sinditskii V., Calabro M. (eds) Chemical Rocket Propulsion. Springer Aerospace Technology. Springer, Cham. https://doi.org/10.1007/978-3-319-27748-6_43

[7] De Luca, L., Shimada, T., Sinditskii, V. P., Calabro, M. (Ed.). (2016). *Chemical Rocket Propulsion: A Comprehensive Survey of Energetic Materials.*Springer. http://www.springer.com/cn/book/9783319277462

[8] Varghese, T.L., Krishnamurthy, V.N. (2017). *The Chemistry and Technology of Solid Rocket Propellants (A Treatise on Solid Propellants).* Pub:, New Delhi, USA: Allied Publishers.

[9] Serdyuk, A.I., Protsan, Yu.V., Bondarenko, S.G. (2013) *Slurry-propellant rocket propulsion. Eco-safety and new power opportunities. Tests of new propellants (IAC- 2013, C4.3,11)*,Proc.of 64-th International Astronautical Congress, Beijing, China.

[10] Tretiakov, K. O., Potupa, O. V., Oginski, S. G., Kurochkin, A. F., Surovtcev, A. B. (2006). [Dependence of rheological characteristics of paste-like rocket propellant from dispersion of filler, concentration of filler and PEAHENS]. *Voprosykhimii I khimicheskoitekhnologii – Issues of Chemistry and Chemical Technology,* 3, 158–163. (in Ukrainian)

[11] Tadros, T. F. (2010). *Rheology of Dispersions: Principles and Applications.* Wiley-VCH,. http://197.14.51.10:81/pmb/CHIMIE/3527320032Rheology.pdf

[12] Bröckel, U., Meier, W., Wagner, G. (Ed.).(2013). Product, *Design and Engineering: Formulation of Gels and Pastes*, 1st Edition. Wiley-VCH Verlag, Weinheim,

Germany.https://www.amazon.com/Product-Design-Engineering-Formulation-Pastes/dp/3527332200

[13] Eliseev, V., Bondarenko, S., Kurochkin, A., Mayorskaya, T., Ustimenko, E., Surovtsev, A. (2012). [Experimental and numerical research reological descriptions of paste-like propellant compositions]. *Zaporogye, Vestnik dvigatelestroeniya*, 1, 26-30. (in Russian).https://cyberleninka.ru/article/n/eksperimentalnoe-i-chislennoe-issledovanie-reologicheskih-harakteristik-pastoobraznyh-toplivnyh-kompozitsiy

[14] Kurochkin, A. F., Dolmatova, N. V., Surovtcev, A. B. (2011). [*High-filled compositions on the base on olygomeric rubber*], All materials. Encyclopaedic reference book,Moscow: Science and technology, 1, 35–40. (in Russian).https://elibrary.ru/item.asp?id=16317613

[15] Tokarev, V., Voronov, S., Seredyuk. V., Kozar, M., Bednarska, O. (1996). Modification of interface by polymeric peroxides - a new approach to the creation of composites. *Adsorption Sci. Technol. 14*(4), 239-249. https://revolution.allbest.ru/chemistry/00453399_2.html

[16] Voronov, S., Tokarev, V., Datsyuk, V., Seredyuk, V., Bednarska, O., Oduola, K., Adler, H., Puschke, C., Pich, A., Wagenknecht, U. (2000).Polyperoxidic Surfactants for Interface Modification and Compatibilization of Polymer Colloidal Systems. 2. Design of Compatibilizing Layers. *J. Appl. Polym. Sci. 76*, 1228-1239. https://doi.org/10.1002/(SICI)1097-4628(20000523)76:8<1228::AID-APP3>3.0.CO;2-8

[17] Shankar, R. M., Roy, T. K., Jana, T. (2009). Terminal functionalized hydroxyl-terminated polybutadiene: An energetic binder for propellant. *J Appl Polym Sci, 114*(2), 732-741. https://doi.org/10.1002/app.30665

[18] Vilenskaya, M., Karamov, D., Sorokin, E., Petrovskaya, G., Puchin, V. (1979). [Obtaining of dimethylvinylethynylmethyltret-butyl peroxide. *Khimicheskaya promyshl*, 7, 15–17. (in Russian).

[19] Voronov, S., Tokarev, V., Oduola, K., Lastukhin, Yu. (2000) Polyperoxide Surfactants for Interface Modification and Compatibilization of Polymer Colloidal Systems. 1. Synthesis and Properties of Polyperoxide Surfactants. *J. Appl. Polym. Sci. 76*, 1217-1227. https://doi.org/10.1002/(SICI)1097-4628(20000523)76:8<1217::AID-APP2>3.0.CO;2-F

[20] Musa, O. M. (Ed.). (2016). Handbook of Maleic Anhydride Based Materials: Syntheses, Properties and Applications. Springer, New Jersey.https://www.springer.com/la/book/9783319294537

[21] Tokarev, V., Shevchuk, O., Bukartyk, N., Wagenknecht, U. (2005). The Effect of Structure of Compatibilizing Layer at the Mineral Filler Surfaces on Mechanical Properties of Premixes. *Materials of International Symposium 'Technomer-2005'*, Chemnic, Germany, AP5. 1-10. https://www.researchgate.net/profile/Viktor_Tokarev3/publication/316510013_The_Effect_of_Structure_of_Compatibilizing_Layer_at_the_Mineral_Filler_Surfaces_on_Mechanical_Properties_of_Premixes/links/590186d34585156502a09854/The-Effect-of-Structure-of-Compatibilizing-Layer-at-the-Mineral-Filler-Surfaces-on-Mechanical-Properties-of-Premixes.pdf

[22] Surovtcev, A., Kovalenko, K., Kuzmenko, N., Bondarenko, S. (2014). [Influence of the nature of surface-active substances on rheology of high-filled paste-like compositions on a base on liquid diene rubber and disperse filler]. *Bull. Dnipropetrovsk Univ. Ser. Chem.*, *22*(2), 76–81.(in Russian).https://doi.org/10.15421/0814156

[23] Shafranska, O., Tokarev, V., Voronov, A., Bednarska, O., Voronov, S. (2005).Graft Polymerization from a Silica Surface Initiated by Adsorbed Peroxide Macroinitiators. I. Adsorption and Structure of the Adsorbed Layer of Peroxide Macroinitiators on a Silica Surface. *Langmuir, 21*(8), 59-69.https://doi.org/10.1007/s10965-015-0807-2

[24] Shevchuk, O., Wagenknecht, U., Wiessner, S., Bukartyk, N., Chobit, M., Tokarev, V. (2015).Flame-retardant polymer composites on the basis of modified magnesium hydroxide. *Chemistry & Chemical Technology, 9*(2), 149-155.http://ena.lp.edu.ua:8080/handle/ntb/28323

[25] Protsan, Yu., Maydaniuk, D., Bondarenko S.(2013). Rocket Propulsion Using Unitary Paste-like Propellant Analysis of Mass Efficiency for Applications in the Composition of Landing Units and Upper Stages of Launch Vehicles. Proceedings of International Forum on Special Equipments and Engineering Mechanics. Nanjing, P. R. China, 56-62.