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THE EFFECT OF PRE-ENCAPSULATING DISPERSED FILLER ON THE RHEOLOGICAL PROPERTIES OF HIGHLY FILLED PASTE-LIKE COMPOSITIONS BASED ON OLIGOMERIC RUBBER

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The article presents the results of the study on the past-like highly filled compositions and the assessment of their rheological properties using a rotational viscometer of a cone-plane system. Dispersed filler in the initial form of potassium chloride or in its surface-modified form (prepared by the precipitation of the oligomeric products of glycerolysis of polyethylene terephthalate on the surface of the particles) was introduced into the paste-like composition as a main component. The composition also included an additional filler (fine aluminum powder), oligomeric rubber SCDN-N together with a plasticizer as a binder and a surfactant. The effects of the preparation technology, composition and nature of the components on the viscosity of the compositions were evaluated in the range of the shear stresses of 1 to 30 kPa and the temperatures of 293 to 323 K. Along with the use of a surfactant and the addition of dioctylphthalate as a plasticizer, the developed modification of the filler surface (by means of pre-encapsulating its particles with oligomeric glycerolysis products of polyethylene terephthalate) allows significantly increasing the degree of filling of the paste-like composition, the dynamic viscosity close to the viscosity of the original oligomeric rubber being maintained.

Keywords: highly filled pasty compositions, oligomeric rubber, surface modification, oligomeric products, glycerolysis, polyethylene terephthalate, rheology.

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Introduction

Up-to-date missile technology involves the use of pasty fuel which allows providing a regulated mode of operation of propulsion systems. The advantage of such engines is the possibility of multiple start and stop as well as easy control of traction characteristics of operational maneuvering along the flight path [1,2]. As for the characteristics of the paste-like fuels themselves, they are convenient for production [3] and safer than liquid and solid fuels [4,5]. The use of this fuel allows multiple changes (up to 80 times) in the energy parameters during regulation [6,7] which is due to the nonlinear law of fuel consumption versus pressure drop because of the non-Newtonian flow of the system.

The main requirements for paste-like fuels were established in papers [1,6] as follows: high degree of filling to ensure high energy characteristics (up to 90 wt.%) while maintaining uniformity and flow ability under load; high density; compositional resistance in the temperature range from 263 to 323 K; sedimentation stability during storage; and low sensitivity to shock-kinetic effects.

An oxidizer is the main component in the composition of paste-like fuel. Currently, highly dispersed ammonium perchlorate is the most effective oxidized taking into account high oxygen balance and sufficient physicochemical stability. A significant disadvantage of this oxidizing agent is an environmental threat of the process of fuel combustion due to the release of a large amount of hydrogen chloride.

This oxidizer is used in a mixture with the combustible-binding polymer component which, unlike solid fuel systems, is an uncured plasticized polymer with either low or high molecular weight. Such a system is capable of flowing under load and has properties of a non-Newtonian fluid. To increase the energy characteristics, pasty fuel can also contain metals (mainly aluminum) or other powdery and

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liquid substances in a highly dispersed form with high enthalpy of formation. The composition may additionally include some technological additives [8] to provide the required rheological characteristics, a certain burning rate, etc.

Despite the existing scientific approaches to the creation of systems based on dispersive particles with a binder material [5,9], the problem of the ability to flow under load for the paste-like fuel compositions can be solved chiefly by experiment because of the qualitative diversity of the components their content, the size and shape of filler particles and the state of their surface [6].

This study was aimed to evaluate the possibility of the production of paste-like compositions with a maximum degree of filling capable of flowing at a predetermined operating temperature range.

Experimental

Materials

To prepare model paste-like compositions, the following initial components were used: SCDN-N rubber (OJSC «Efremov Synthetic Rubber Enterprise»), potassium chloride (Sigma-Aldrich), finely dispersed aluminum, dioctylphthalate (DOP, Farmchim), polypropylene glycols with a molecular weight from 260 to 1000 (laprols, Armcorp), and the glycerolysis products of the degraded PET (PGO-1÷5). The non-functionalized low-molecular cis-butadiene rubber SCDN-N (a liquid product of polymerization of butadiene under the action of a catalytic system based on nickel salts and organoaluminum compounds) with a molecular weight of 2500 and a content in the composition, was used as the main component of the binder in pasty compositions according to the approach which was set forth in the study devoted to polybutadiene chain of 70÷80% of cis-1,4 units [6]. A plasticizer, dioctylphthalate, was added into the binder in some cases.

Oligomeric polyoxypropylene glycol (PPG) with the general formula $HO[CH_2(CH_3)CHO]_nH$ was used as a surfactant [10]. PPGs had a molecular weight (M_W) of 260, 480 and 1000; they are transparent liquids without color and odor.

A highly disperse inert component, potassium chloride (KCl), was used as the main filler that simulates a real oxidizer in the fuel compositions (i.e. ammonium perchlorate). In addition, highly dispersed aluminum (grade ASD-4, manufactured by «New Tech») with an average particle size of 12.4 μm was introduced into the fuel compositions as a high-energy additive [1].

The oligomeric products of glycerolysis of degraded PET were high-viscosity plastic or solid masses of yellowish color with a maximum softening point of 333 K. These products have high adhesion to various materials [11] and can be used as a component of a polyurethane coating, a film backing material and an adhesive [13].

The products were obtained by chemical modification of PET via recycling process [13] which included the following sequence of the processes: (i) the degradation of the main chain of polyethylene terephthalate under the action of the degradation agent, glycerol, (ii) the synthesis (transesterification), and (iii) the intermolecular exchange with the formation of oligomeric products of branched structure (Fig. 1).

The characteristics of the PGO samples used in the work are given in Table 1.

Preparation of pasty compositions

We experimentally prepared the model paste-like compositions and determined their viscosity in the temperature range of 293–323 K. For the preparation of the compositions, the constituent components other than the main filler do not require any preliminary preparation.

The preparation of the main filler KCl assumed its coarse grinding in a ball mill followed by screening on sieves, further drying to achieve a constant weight at 393 K, cooling and storage in sealed conditions to avoid contact with moisture of the air due to hygroscopicity. To produce the pasty compositions, KCl samples with the following granulometric dimensions were used: a fraction up to 45 μm and a fraction from 45 μm to 63 μm in a weight ratio of 1:1.

Table 1

Characteristics of PGO samples

Designation	Reagent ratio PET/PEG-400 in the process of synthesis (in parts by weight)	Characteristics
PGO-1	75/25	Solid is brown at 298 K, the viscosity is 30 Pa·s at 323 K
PGO-2	70/30	Solid is brown at 298 K, the viscosity is 28 Pa·s at 323 K
PGO-3	60/40	Pasty substance of white color, the viscosity is 24 Pa·s at 323 K
PGO-4	50/50 (at 503 K)	Pasty substance of white color, the viscosity is 18 Pa·s at 323 K
PGO-5	60/40	Pasty substance of yellow color, the viscosity is 20 Pa·s at 323 K

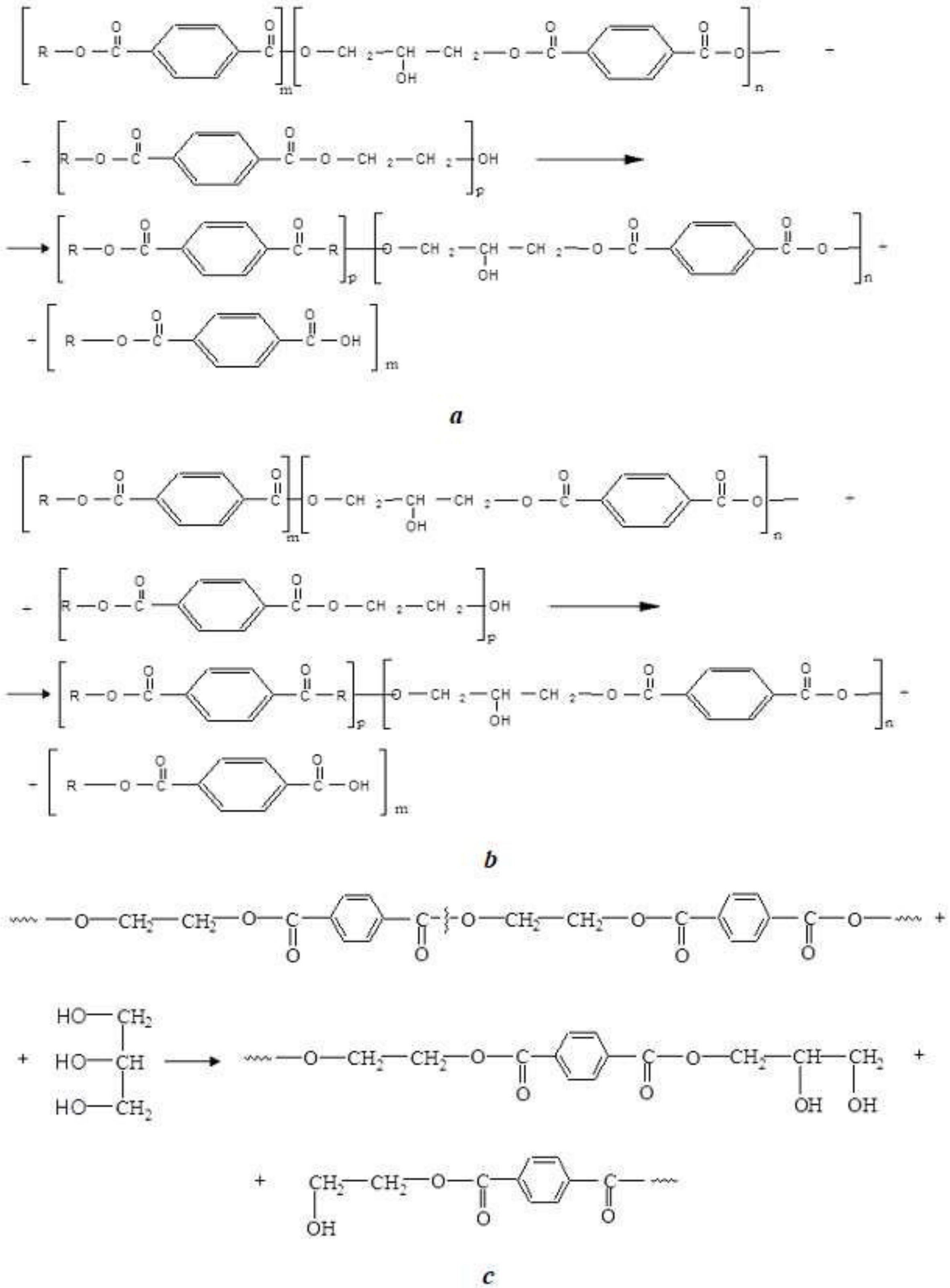

Fig. 1. Chemical modification of PET: a – the degradation of the main chain under the action of the glycerol; b – synthesis (transesterification); c – the intermolecular exchange with the formation of oligomeric products of branched structure

To produce the modified filler, the PGO sample (PET recycle) in an amount of 2% by weight of the filler mass was dissolved in acetone and the solution was mixed with the prepared KCl sample. The resulting mixture was subjected to vigorous stirring and heating to 333 K in a flask with a direct condenser to condense the acetone to be removed. Then, the modified filler was dried to a constant weight at 293 K for complete removal of acetone and sieved to produce the compositions with a particle size of up to 63 μm. Thus, a small amount of a fraction of the aggregated filler particles adhering due to the oligomeric PGO on their surface was separated.

A surface-modified sample of KCl of the same granulometric composition was used for the preparation of pasty compositions: a fraction up to 45 μm and a fraction of 45 μm to 63 μm in a weight ratio of 1:1. The original filler KCl differed from the modified filler KCl by the fact that the latter was completely insoluble in water which confirmed the deposition of a hydrophobic PGO modifier on the surface of filler particles resulted from the effect of encapsulating these particles.

The proposed version of the surface modification of the model dispersed potassium chloride filler is simpler than the variant described in ref. [15] which implies performing a surface modification of KCl particles with a functional polyperoxide by carrying out the process of terpolymerization at the phase boundary of an organic solvent, a dispersed filler.

The preparation of model paste-like compositions was performed in a water bath (temperature of 323 K) by the addition of the specified amounts of surfactant, plasticizer, modifying additives and fillers to the sample of rubber. Then the mixture was thoroughly stirred for 20 minutes using a vane-type mixer with an electric drive to achieve an even distribution of all components by volume of composition for subsequent visual evaluation of mixing quality. The resulting compositions were held for 30 minutes to remove air inclusions remaining in the mass while stirring [10] in a vacuum chamber (the residual pressure was 50 mm of Hg and the temperature was 323 K).

The estimation of the viscosity of paste-like compositions was carried out using a rotational viscometer «Rheotest-2» by the cone-plane system in the range of shear stresses of 1–30 kPa and the temperatures of 293–323 K. The error of viscosity measurement was not more than 1%).

Results and discussion

We considered the following approaches to the evaluation of the influence factors on the rheological properties of pasty systems:

– the sequence of introduction of components;

– the influence of the type and quantity of surfactants;

– the surface modification of the filler by forming an oligomeric shell on the surface of its particles (i.e. encapsulation);

– the introduction of a plasticizer into the system.

To evaluate the effect of the surfactants, three options were considered: preliminary introduction into the phase of rubber; preliminary application of KCl and simultaneous introduction to the mixture of all components. The optimal way to introduce surfactants (for example of polyoxypropyleneglycols, M_w=480) in the preparation of paste-like

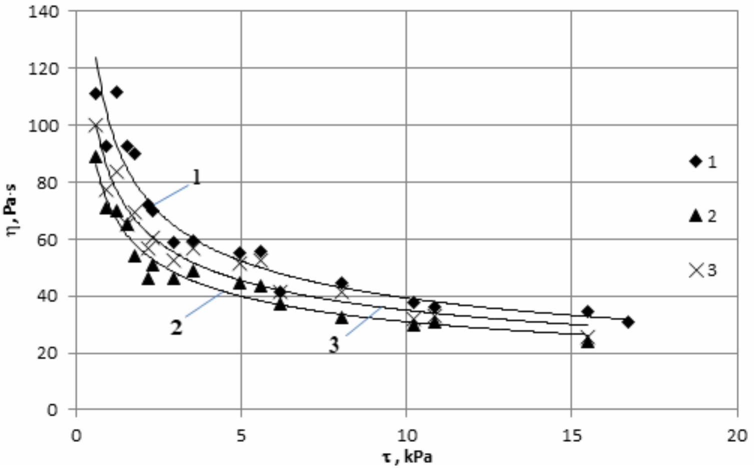

Fig. 2. The effect of the order of the introduction of a surfactant (polypropylene glycol, M_W=480, 0.5 wt.%) on the viscosity of a pasty composition based on SCDN-N rubber with a degree of filling of 80 wt.%. 1 – the KCl filler, 2 – simultaneously a mixture of all components of the composition, 3 – into the phase of rubber. Temperature 323 K

compositions was determined from the results of the measurements of the viscosity of compositions of the same content (Fig. 2).

It follows from the obtained data that the order of introduction of components into the composition influences the rheological properties. When the surfactant is preliminarily introduced into the rubber phase (Fig. 2, curve 3), a decrease in viscosity is observed to a great extent when compared with the introduction of the surfactant into the KCl filler phase (Fig. 2, curve 1) or in the simultaneous mixing of all components (Fig. 2, curve 2). This is obviously associated with the possibility of a more even distribution of this component in the composition. Considering this fact, the surfactant was introduced previously into the rubber in the preparation of subsequent model compositions.

Fig. 3 illustrates a comparative evaluation of the type of polypropylene glycol as a surfactant for the considered filled systems. The addition of a sample with a molecular weight of 1000 is more effective from the viewpoint of viscosity reduction. Hence, this additive was used in all further experiments.

In order to increase the adhesion interaction and sedimentation resistance of non-polar rubber and polar filler compositions, we examine the influence of the additive of oligomeric products of glycerolysis of the degraded PET (PGO) of substances with a low softening point (up to 333 K) on their rheological properties (Table 1). Two following options for introducing these additives were tested:

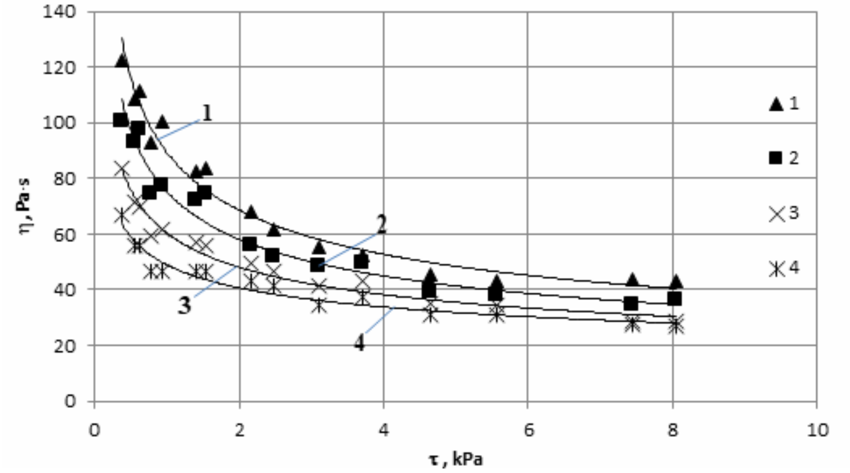

Fig. 3. The effect of the type of a surfactant (0.5 wt.%) on the viscosity of a pasty composition based on SCDN-N rubber with a degree of filling of 80 wt.%. 1 – no surfactant, 2 – PPG_1, 3 – PPG_2, 4 – PPG_3. Temperature 323 K

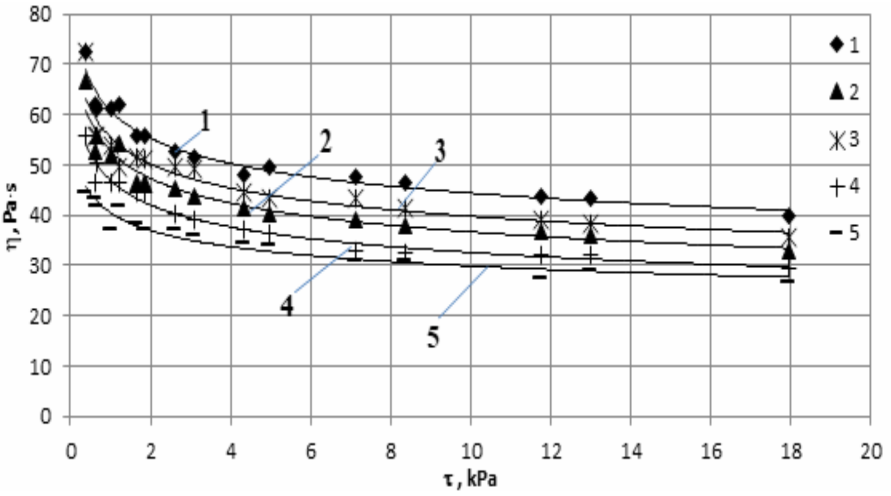

Fig. 4. The effect of the surfactant (PPG_3) with a degree of filling of 80 wt.% on the viscosity of the paste composition on the basis of SCDN-N rubber. 1 – PGO-1, 2 – PGO-3, 3 – PGO-2, 4 – PGO-5, 5 – PGO-4. The recycling additive (2 wt.%) was introduced directly into the composition on the viscosity. Temperature 323 K

directly into the binder phase and modification of the KCl filler by using a recycling additive to the surface of its particles. The results are shown in Fig. 4 and 5.

Upon the addition of glycerolysis products of the degraded PET, the viscosity of the highly filled composition is reduced (this effect is significantly expressed for PGO-4). This can be considered as an action of an additional surfactant that provides an increase in the fluidity in a system of nonpolar rubber and polar filler.

Comparative characteristics of the obtained results with the sample of the additive PGO-4 (Fig. 6) shows that the surface modification of KCl is a more effective way to reduce the viscosity of pasty compositions (Fig. 6, curve 1): the viscosity of the composition is reduced by about 1.5 times over a wide range of shear stresses.

A higher efficiency of the encapsulation of the filler with PGO-4 recycled to reduce the viscosity of pasty compositions is also confirmed by the results of the calculation of activation energies of viscous flow for the compositions based on SCDN-N rubber (Table 2) in the temperature range of 293–323 K.

The activation energy of the viscous flow and the viscosity of the melt of polymer systems obey the following equations [15]:

$$\eta = A \cdot e^{\frac{E}{RT}} \quad \text{or} \quad \ln \eta = \ln A + \frac{E}{RT}, \qquad (1)$$

where E is the activation energy of the viscous flow, kJ/mol.

The effect of temperature on the viscosity of a melt is determined from the equation:

$$\eta = K_0 \cdot e^{-b(T-T_0)}, \qquad (2)$$

where T is the absolute temperature, K; T_0 is the test temperature, K; K_0 is the coefficient of rheological dependence of shear stress (τ) on the nature of the polymer.

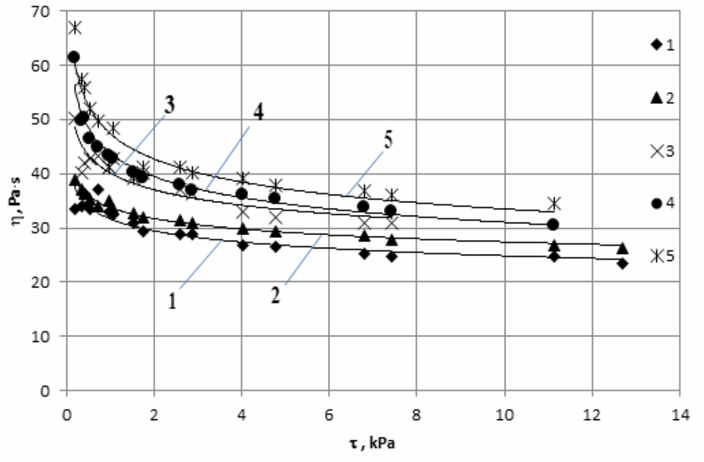

Fig. 5. The effect of encapsulated KCl (2% by weight of the recycling additive on the filler surface) on the viscosity of the paste composition on the basis of the SCDN-N rubber and 0.5 wt.% of the surfactant (PPG_3) at a filling degree of 80 wt.%. 1 – PGO-4, 2 – PGO-3, 3 – PGO-2, 4 – PGO-5, 5 – PGO-1. Temperature 323 K

Table 2

The activation energy of the viscous flow of compositions based on rubber SCDN-N

Temperature range, K	Activation energy of viscous flow E (kJ/mol) for the compositions based on rubber SCDN-N (wt.%)				
	SCDN-N	SCDN-N – 20 KCl – 80	SCDN-N – 20 KCl – 80 PPG_3 – 0.5	SCDN-N – 18 KCl – 80 PPG_3 – 0.5 PGO-4 – 2	SCDN-N – 18 KCl_m – 82* PPG_3 – 0.5
293–303	23.8	92.7	58.3	39.0	35.1
303–313	17.7	78.2	44.0	32.2	30.6
313–323	11.3	63.5	24.4	21.4	19.2

Note: * – KCl_m – potassium chloride modified by PGO-4 (2 wt.%).

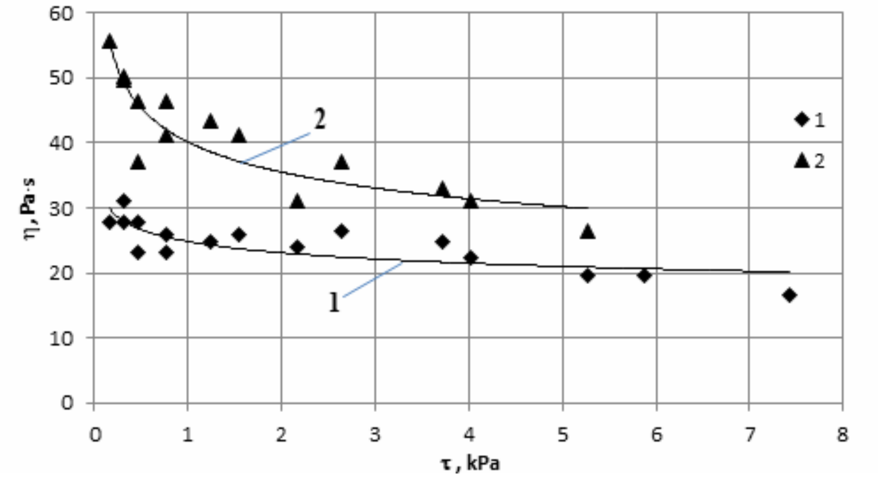

Fig. 6. Comparative characteristics of the viscosity of the paste composition on the basis of the SCDN-N rubber and 0.5 wt.% of the surfactant (PPG_3) at a degree of filling of 80 wt.% of KCl from the method of the addition of the PGO-4 recycling additive (2 wt.%). 1 – surface modification of KCl, 2 – introduction to the phase of rubber. Temperature 323 K

When solving equations (1) and (2) for two values of temperature, one can obtain the following expression for the activation energy of the viscous flow of a given polymer system:

$$E = \frac{RT_1T_2 \ln\left(\frac{\eta_1}{\eta_2}\right)}{T_2 - T_1}. \qquad (3)$$

The higher the value of E, the greater is the effect of T on η, i.e. there is a sharp change in viscosity in a narrower temperature range. The values of the calculated activation energy of a viscous flow for the studied systems are given in Table 2 (the error in calculating is no more than 1%). They indicate the possibility of obtaining highly filled compositions characterized by a viscosity that is comparable with the viscosity of the original unfilled oligomeric rubber.

Regarding the need to strive for an optimal degree of filling (the value of about 90 wt.% that ensures the oxygen balance of the system close to zero [1]), it was interesting to estimate the effect of the presence of highly disperse powdered aluminum [1] on the rheological properties of the composition with the aim of increasing fuel energy. In this connection, a partial replacement of KCl filler by Al has been tested in the work with a simultaneous increase in the total degree of filling up to 85 wt.%, since the volume degree of filling is reduced due to a higher density of aluminum. The obtained results

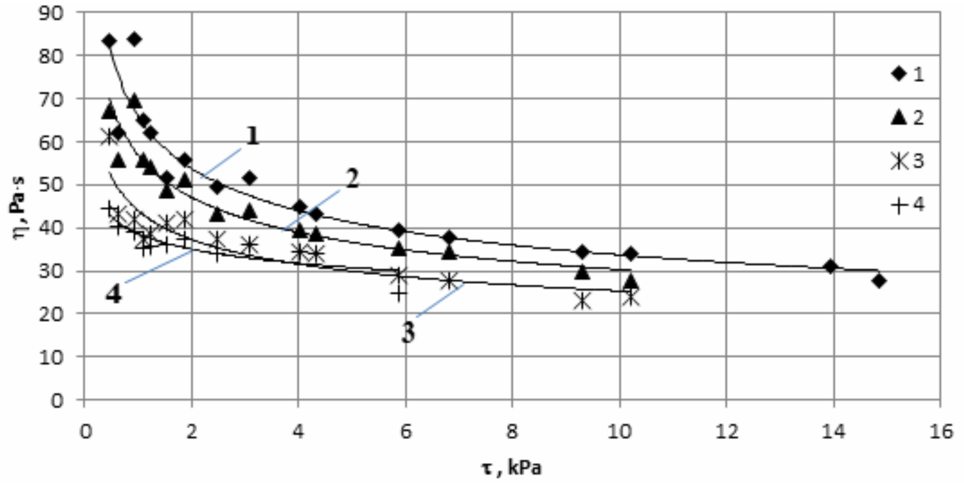

Fig. 7. The effect of the content of plasticizer DOP on the viscosity of a pasty composition based on SCDN-N rubber and 0.5 wt.% of surfactant (PPG_3) with a degree of filling of 85 wt.% (70 wt.% of KCl modified by 2 wt.% of additive PGO-4, Al – 15 wt.%). The content of plasticizer DOP (wt.%): 1 – 0, 2 – 3, 3 – 6, 4 – 9. Temperature 323 K

are shown in Fig. 7.

Initially, positive results were not obtained, because only 13 to 15 wt.% of the binder in composition lost integrity and fluidity. In order to increase the degree of filling (up to 85 wt.%), while maintaining its ability to flow, the introduction of a plasticizer DOP was considered. The weight fraction of the binder phase was maintained at the same level of 15%. In this binder phase, the additive PGO-4 made up 2 wt.%, and the weight fraction of the rubber was 13%. The rubber was partially replaced with the plasticizer DOP in the following ratios of these components: 10:3; 7:6 and 4:9 (wt.%).

From the point of view of the reduction of the viscosity in the system with these compositions at 323 K, an optimum content is 6–9 wt.% of DOP (Fig. 6, curves 3 and 4). However, it turned out that these compositions lose their plasticity and homogeneity at lower temperatures (293 K): they become friable in the case of mechanical action. Therefore, a lower content of the plasticizer (3 wt.% in the binder phase) is preferable. This allows preparing a stable, plastic and highly filled (up to 85 wt.%) composition having a lower viscosity than a composition with a filling of 80 wt.% based on a rubber alone.

Summarizing the results of the research, it should be noted that the effect of pre-encapsulating a dispersed filler by covering the surface of its particles with an oligomeric component can significantly reduce the viscosity of the paste-like compositions based on oligomeric rubber and thereby significantly increase their filling.

Conclusions

The dependence of viscosity on shear stress in the temperature range of 293–323 K was determined for highly filled pasty systems based on non-functionalized oligomeric rubber SCDN-N and highly disperse fillers (potassium chloride and aluminum) as a model system of pasty fuel.

The surface modification of the filler with the products of glycerolysis of the degraded PET in an amount of 2 wt.% was considered to prepare plastic pasty compositions with a high degree of filling.

In order to increase the degree of filling, the effect of the plasticizer dioctylphthalate on the rheological properties was examined and the allowable amount thereof in the composition was estimated.

The joint use of the surface modification of the filler with oligomer products of glycerolysis of the degraded PET and the introduction of a binder surfactant and a plasticizer into the composition of the phase allows increasing the degree of filling of paste-like fuel compositions to 85 wt.%.

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ВПЛИВ ПОПЕРЕДНЬОГО ІНКАПСУЛЮВАННЯ ДИСПЕРСНОГО НАПОВНЮВАЧА НА РЕОЛОГІЧНІ ВЛАСТИВОСТІ ВИСОКОНАПОВНЕНИХ ПАСТОПОДІБНИХ КОМПОЗИЦІЙ НА ОСНОВІ ОЛІГОМЕРНОГО КАУЧУКУ

О.Б. Суровцев, Г.Г. Пайос, М.Р. Дяченко, І.А. Мандзюк

У статті надані результати вивчення пастоподібних високонаповнених композицій і оцінки їх реологічних властивостей з використанням ротаційного віскозиметра на системі конус-площина. Дисперсний наповнювач хлорид калію в початковому вигляді або його поверхнево-модифікована форма (внаслідок осадження олігомерних продуктів гліцероліза поліетилентерефталату на поверхні частинок) вводився в пастоподібну композицію в якості основного компонента. Також до неї входили: додатковий наповнювач (високодисперсний порошок алюмінію), олігомерний каучук СКДН-Н разом з пластифікатором в якості зв'язуючого та поверхнево-активна речовина. В діапазоні зсувних напружень 1–30 кПа і температур від 293 до 323 К оцінено вплив на в'язкість композицій технології їх приготування, складу та природи компонентів. Поряд з використанням поверхнево-активної речовини і додаванням діоктилфталату в якості пластифікатора запропонований варіант модифікації поверхні наповнювача (шляхом попереднього інкапсулювання його частинок олігомерними продуктами гліцеролізу поліетилентерефталату) дозволяє значно збільшити ступінь наповнення пастоподібної композиції та при цьому зберегти динамічну в'язкість, близькою до рівня в'язкості вихідного олігомерного каучуку.

Ключові слова: високонаповнені пастоподібні композиції, олігомерний каучук, поверхнева модифікація, олігомерні продукти, гліцероліз, поліетилентерефталат, реологія.

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The article presents the results of the study on the past-like highly filled compositions and the assessment of their rheological properties using a rotational viscometer of a cone-plane system. Dispersed filler in the initial form of potassium chloride or in its surface-modified form (prepared by the precipitation of the oligomeric products of glycerolysis of polyethylene terephthalate on the surface of the particles) was introduced into the paste-like composition as a main component. The composition also included an additional filler (fine aluminum powder), oligomeric rubber SCDN-N together with a plasticizer as a binder and a surfactant. The effects of the preparation technology, composition and nature of the components on the viscosity of the compositions were evaluated in the range of the shear stresses of 1 to 30 kPa and the temperatures of 293 to 323 K. Along with the use of a surfactant and the addition of dioctylphthalate as a plasticizer, the developed modification of the filler surface (by means of pre-encapsulating its particles with oligomeric glycerolysis products of polyethylene terephthalate) allows significantly increasing the degree of filling of the paste-like composition, the dynamic viscosity close to the viscosity of the original oligomeric rubber being maintained.

Keywords: highly filled pasty compositions; oligomeric rubber; surface modification; oligomeric products; glycerolysis; polyethylene terephthalate; rheology.

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