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Sealing Compositions Based on Polysulfide Oligomers Obtained by a Modified Method

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Abstract

The article is devoted to the study of the physical and mechanical properties of composites based on polysulfide oligomers (PSO) filled with carbon black (CB) grade K-354 and multi-walled carbon nanotubes (MWCNTs). The purpose of this work was to study composites obtained by a modified method of thiocol synthesis using sodium sulfide and sodium hydrosulfate. It was revealed that the introduction of nanotubes to the thiocol matrix into the composition leads to a significant change in elastic-strength properties, leading to an increase in tensile strength by 16%. At the same time, the elongation at break decreases by 15%. Thus, in this work, the possibility of obtaining thiocols in a new way with satisfactory physical and mechanical properties was demonstrated. The work also assessed the resistance of composites to the action of aggressive substances after exposure of composites in various media (gasoline, benzene, concentrated acids), it was noted that the introduction of MWCNT increases this indicator.

List of abbreviations

PSO	Polysulfide oligomers
CNT	Carbon nanotubes
MWCNT	Multi-walled carbon nanotubes
CB	Carbon black
PSR	Polysulfide rubbers
LPO-GO/PSR	Liquid polysulfide oligomers-graphene oxide/Polysulfide rubbers

1. Introduction

Industrial production of polysulfide elastomers began in 1929 in the USA by "Thiokol" company. Currently, polysulfide polymers are produced in the USA, Russia, Germany, Japan, and several other countries and are produced in the form of elastomers, liquid rubbers, and aqueous dispersions. After World War II, thiokols were used as a combustible binder for rocket fuels in the United States, however, due to the low enthalpy of formation and tendency to crystallization (leading to deterioration in the physical and mechanical parameters of products during storage), thiokols eventually gave way to other combustible binders for rockets fuels [1].

Currently, polysulfide oligomers (PSO) are most in demand in construction as sealants, sealing compounds, and coatings for various purposes. Consumption of sealing materials in construction today reaches 50% of their total production. The main properties of vulcanizates of polysulfide polymers, which distinguish them favorably from other rubbers, are resistance to various solvents, dilute acids and alkalis, low gas and moisture permeability, high resistance to ozone, ultraviolet light, and fairly high dielectric characteristics [2]. Another rapidly developing area of polysulfide use is the production of lithium-sulfur batteries [3–4].

Polysulfides are produced in the form of solid (high molecular weight) and liquid (low molecular weight) products. Currently, low molecular weight liquid polysulfide oligomers with reactive terminal mercaptan (SH) groups of the general formula are of greatest interest:

$$HS[—R—Sm—]nSH$$

where R is an organic radical.

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By reacting various curing agents with SH end groups, liquid thiokols are cured. The most widely used are low-molecular-weight (liquid) polysulfide oligomers, obtained on the basis of di-β-chloroethylformal.

Thiokol oligomers are of undoubted interest for the development of sealing and protective coatings. Since the middle of the 21st century, quite a number of studies have been carried out on the physicochemical properties of thiokols, and methods for the synthesis of thiokols and disulfides have been searched for [2–12]. However, the only industrial method for producing liquid thiokols at the moment is the reductive cleavage of high-molecular polysulfides with sodium sulfhydrate in the presence of sodium sulfite.

The synthesis scheme for polysulfide oligomers is presented below; it includes several steps:

1) Synthesis of sodium polysulfide:

$$6NaOH + (2n + 1)S \rightarrow \underset{n=4}{2Na_2Sn} + 3H_2O + Na_2SO_3 \quad (1)$$

2) Polycondensation of sodium polysulfides with aliphatic halogen derivatives:

$$Cl\text{-}R\text{-}Cl + Na_2S_4 \rightarrow (\text{-}R\text{-}\ S_4\ \text{-})m + 2NaCl \quad (2)$$

3) Desulfurization of tetrapolysulfide:

$$(\text{-}R\text{-}\ S_4\ \text{-})n \xrightarrow{NaOH} (\text{-}S_2\ \text{-}R\text{-}\ S_2\ \text{-})n \quad (3)$$

4) Cleavage of high molecular weight polymer and production of liquid thiokol:

$$\sim R\text{-}S\text{-}S\text{-}R\text{-}S\text{-}S\sim + NaSH + Na_2SO_3 \rightarrow \sim R\text{-}S\text{-}Na + HS\text{-}R\text{-}S\text{-}S\text{-} + Na_2S_2O_3 \quad (4)$$

But this method has many disadvantages, such as multi-stage synthesis (the complete scheme for the production of thiokol includes about 20 technological stages, including synthesis of di-β-chloroethylformal, preparation of a dispersion, desulfurization, splitting, coagulation, etc.) and large quantities water consumption (washing the polymer from sodium polysulfide), generation of large amounts of wastewater (acidic wastewater formed after coagulation, alkaline wastewater).

Thus, taking into account all the disadvantages of the classical method of producing PSO, various attempts have been made to find new methods for the synthesis of thiols, in particular at the stage of splitting a high-molecular polymer to obtain terminal mercaptan (SH) groups.

One of the most promising, but never found its application in industry, splitting agent is sodium dithionite [5]:

$$R\text{-}S\text{-}S\text{-}R + Na_2S_2O_4 + 2NaOH \rightarrow 2\sim RSH + 2Na_2SO_3 \quad (5)$$

If the polymer contains polysulfide bonds, then when exposed to alkali and dithionite, both desulfurization of the polymer and depolymerization occur simultaneously:

$$R\text{-}\ S\text{-}\ S\text{-}\ S\text{-}\ S\text{-}\ R + 3Na_2S_2O_4 + NaOH \rightarrow 2\sim R\text{-}\ SNa + 6Na_2SO_3 + 2H_2S + 2H_2O \quad (6)$$

Sodium hydroselenide [6] and hydrazine [5] can be used as degrading agents. Depolymerization of di- and polysulfide polymers under the influence of hydrazine occurs in an alkaline medium, and the degree of depolymerization increases with increasing hydrazine and alkali content, increasing reaction duration and decreasing the average degree of sulfidity of the polysulfide polymer.

Polydisulfides can also be cleaved by various organic disulfides, with the low molecular weight disulfide initially forming the RS^- anion, which then attacks the S-S bond in the high molecular weight disulfide [7, 8]. But for the formation of RS^- anions, conditions are necessary, the presence of activators of heterolytic decomposition, for example, sodium disulfide, sodium sulfide, and alkali.

$$RS^- + R'SSR' \leftrightarrow R'S^- + RSSR' \quad (7)$$

In an acidic environment, the active species is the sulfene ion:

$$RS+ + R'SSR' \leftrightarrow R'S+ + RSSR' \quad (8)$$

When cystine reacts with Na_2S, a compound is formed corresponding to the anion $\text{-}S\text{-}S\text{-}CH_2CH(NH_2)COO^-$, upon further interaction of which with Na_2S a cysteine dianion and sodium disulfide or polysulfide are formed. Cysteine enters into an exchange reaction with other disulfides and thiols [9]. The equilibrium of these reactions depends on both the acidity of the thiol and steric factors. Below is the exchange reaction between a thiolate ion and a disulfide:

$$R\text{-}S\text{-}S\text{-}R + R^{35}S \rightarrow R\text{-}S\text{-}^{35}S\text{-}R + RS^- \quad (9)$$

Many researchers have studied the possibility of the cleavage of polysulfide polymers by thiols; the reaction is accompanied by the formation of an intermediate complex as a result of the attack of the undissociated thiol on the disulfide. The rate of the thiol-disulfide exchange reaction at room temperature in the absence of a solvent is low, but it increases with heating or in the presence of catalytic amounts of alkali metal mercaptides, as well as Lewis acids [5].

Under irradiation conditions or at elevated temperatures, if exchange reactions are carried out in a block or non-polar media, they proceed by a radical mechanism:

$$R\text{- }S\text{- }S\text{- }R \rightarrow R_2S\cdot \tag{10}$$

$$RS\cdot + HS\text{- }R' \rightarrow R\text{- }SH + R'S^{\cdot} \tag{11}$$

$$R'S\cdot + RS^{\cdot} \rightarrow R\text{- }S\text{- }S\text{- }R' \tag{12}$$

Cleavage of disulfide bonds in polymers also occurs under the influence of hydrogen in situ, released during the interaction of acids with metals. If the polydisulfide is exposed to lithium aluminum hydride, the resulting complex is hydrolyzed in an acidic environment to form a polymer with terminal mercaptan groups. The mechanism of this process is the attack of sulfur atoms by aluminum hydride or hydride ions [5].

$$2\sim R\text{- }S\text{- }S\text{- }R\sim + LiAlH_4 \rightarrow \sim(RS)_4\text{- }LiAl + 2H_2\uparrow \tag{13}$$

Di- and polysulfide bonds are cleaved by borohydrides, used as individual products or in combination with sodium nitroprusside:

$$\sim R\text{- }S\text{- }Sn\text{- }S\text{- }R'\sim \xrightarrow{NaBH_4} \sim RSH + nH_2S + \sim R'SH \tag{14}$$

If disulfides prone to hydrolysis are used, the first stage of the process is hydrolytic destruction, followed by cleavage of the disulfide bond [9]:

$$R\text{- }S\text{- }S\text{- }CO\ R' \xrightarrow{HO^-} R'CO_2^{\,-} + \sim R\text{- }S\text{- }SH \tag{15}$$

$$\sim R\text{- }S\text{- }SH \xrightarrow{BH_4O^-} \sim RSH + H_2S \tag{16}$$

A very interesting way to obtain PSO is the polycondensation of Bunthe salts with sodium hydrosulfide in an aqueous medium in the presence of toluene [8]. This method is attractive due to the possibility of carrying out processes of synthesis and isolation of liquid thiokol in almost one reactor with the production of liquid thiokols of high purity and with strictly specified properties. The preparation of liquid thiokol through Bunte salts occurs in the following way [10]:

$$ClRCl + 2Na_2S_2O_3 \rightarrow R(S_2O_3Na) + 2NaCl \tag{17}$$

$$(n+1)R(S_2O_3Na) + (1{,}5_n + 2)NaHS \rightarrow HS(RSS)_nRSH + (1{,}75_n + 2)Na_2S_2O_3 + 0{,}75_nH_2O \tag{18}$$

There is a known method for producing liquid thiokols by polycondensation of aqueous solutions of sodium polysulfide with organic halides to obtain a dispersion of a high-molecular-weight polymer, followed by the cleavage of high-molecular-weight thiokol disulfide with sodium sulfite in a toluene medium [11]. This method, like the production of thiokols using Bunte salts, is not applicable in the industry due to the use of a solvent, the use of which significantly increases the cost of the product.

Also interesting is the work [12], which describes the reaction between sodium sulfide and cystine. The experiment consisted of reacting sodium sulfide with cystine, followed by passing ammonia through the solution and adding hydrochloric acid. As a result of the reaction, cysteine was obtained; the work demonstrated the dependence of the conversion of cystine to cysteine on the amount of sodium sulfide used; ammonia, in this case, was presumably a reducing agent:

$$RSS^- + H+ \rightarrow [RSSH] \rightarrow RSH + S\downarrow \tag{19}$$

Thus, attempts to find new methods for obtaining polysulfide oligomers, to improve certain stages of synthesis in the classical method of obtaining PSO, were not successful, and the presented methods of splitting did not find application in industry. In the current work, a method for splitting polysulfides using sodium sulfide was considered by analogy with work [12], however, instead of ammonia, sodium hydrogen sulfate was used as a hydrogen donor H+, and the properties of polysulfide polymers obtained by this method were studied.

2. Experimental

2.1. Preparation

Preparation of 2,2-dichlorodiethylformal. 2,2-Dichlorodiethylformal was synthesized using paraform and chloroethanol. The reaction proceeds according to the following scheme:

$$2CH_2OH\text{-}CH_2Cl + CH_2O \leftrightarrow ClCH_2\text{-}CH\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2Cl + H_2O \tag{20}$$

The synthesis of 2,2-dichlorodiethylformal took place at T = 65–70 ^{o}C. Sulfuric acid was added as a dehydrating agent. The remaining ethylene chlorohydrin was neutralized with alkali in an amount of 0.05 g per 1 ml of 2,2-Dichlorodiethylformal. The alkali was loaded into the reactor for 1.5–2 h at T = 65–70 ^{o}C, with stirring.

Preparation of sodium tetrasulfide. Sodium polysulfide was synthesized using sodium hydroxide and sulfur in a ratio of 2:3. Sodium hydroxide was dissolved in distilled water, then heated to 85–90 °C, and sulfur was added in excess with constant stirring. Gradually the sulfur dissolved and a brown solution of sodium tetrasulfide was formed. The reaction equation follows (1).

Preparation of thiokol emulsion. Freshly prepared magnesium hydroxide was used as a dispersant: obtained by reacting magnesium chloride and sodium hydroxide. The dispersant solution was added to the reactor.

With constant stirring, then the resulting suspension was heated to 60 °C and di-β-chloroethylformal was added dropwise with constant stirring, gradually increasing the temperature to 85–90 °C, the reaction was carried out for 1.5–2 hours. As the dispersion of liquid thiokol was formed, the color of the solution changed, from dark brown to lighter brown, and a polymer was formed. The reaction equation follows (2).

Desulfurization of polysulfide. Desulfurization was carried out, and the molecular weight of the dispersion was reduced: sodium hydroxide was added to the resulting liquid thiokol dispersion, and the reaction lasted 1.5–2 h at a temperature of 85–90 °C. The reaction equation follows (3).

When alkali was added, the color of the solution changed sharply and became bright orange, indicating desulfurization. The resulting dispersion settled at the bottom, and the top layer containing unreacted polysulfide was drained. The emulsion was not washed.

Thiokol cleavage. To split the thiokol dispersion, sodium sulfide Na_2S was prepared according to the reaction equation:

$$6NaOH + (2n+1)\,S \rightarrow 2Na_2Sn + 3H_2O + Na_2SO_4 \qquad (21)$$

where n=1 for sodium sulfide.

The digestion was carried out with sodium sulfide at a temperature of 70–80 °C, with constant stirring for 20–30 minutes. After the calculated amount of sodium hydrogen sulfate and sodium sulfite has been added, excessive addition of hydrogen sulfate can increase the acidity of the medium and break the emulsion.

Emulsion destruction. The last stage of obtaining PSO was the addition of a 30% solution of hydrochloric acid to destroy the emulsion. Figure 1 demonstrates the main stages of obtaining PSO: preparation of sodium tetrasulfide (a); obtaining a thiokol emulsion (b); desulfurization of polysulfide (c); decantation of thiokol emulsion (d); emulsion destruction (f).

After the destruction of the emulsion, viscous solutions of resin were obtained, which were washed with distilled water, which was then separated on a centrifuge. Thiokol compositions were then prepared.

2.2. Characterization

The main physicochemical properties of thiokol matrix fillers according to their passport data are given below:

Carbon black K354: specific geometric surface – 92 m^2/g; pH – 3.7–4.5; ash content, % – no more than 0.05;

Commercial AlLDRICH MWCNTs >90% – dimensions D × L 110-170 nm × 5–9 µm.

Sealing compositions were prepared in a laboratory mixer Pl-2000.

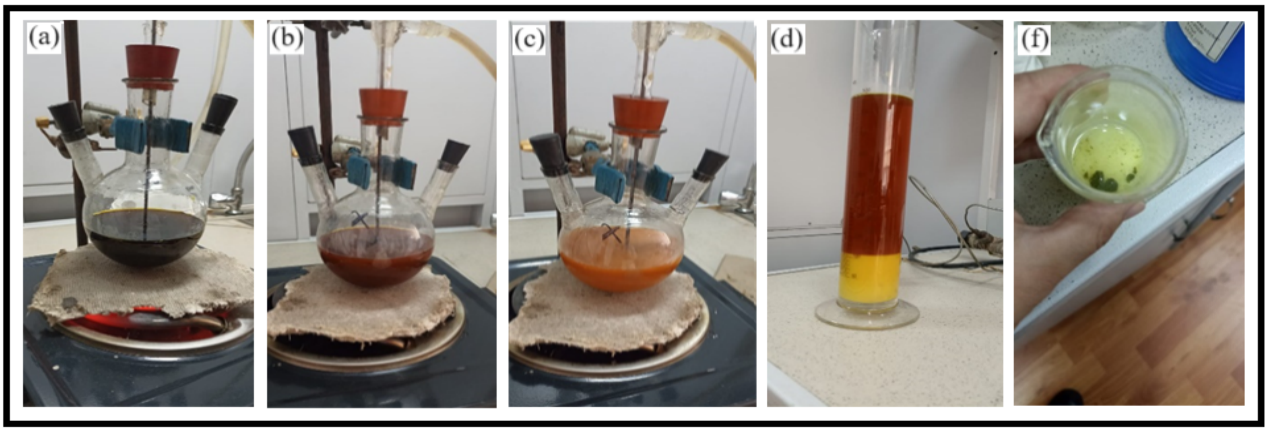

Fig. 1. Preparation of polysulfide oligomer: (a) – preparation of sodium tetrasulfide; (b) – obtaining a thiokol emulsion; (c) – desulfurization of polysulfide; (d) – decantation of thiokol emulsion; (f) – emulsion destruction.

The physical and mechanical properties of sealing materials were studied as follows: mixture compositions for vulcanization were prepared from liquid thiokols; the resulting vulcanizates were molded using a template according to GOST 21751-76; cured at room temperature for 2 days, then cured at a temperature of (60±3) ^{o}C for another day. The test specimens were clamped in the clamping device of a tensile testing machine HT 400 Pneumatic Grip Controller (Tinius Olsen) and stretched. At the moment of sample rupture, the force and length of the working zone were recorded.

To study carbon black by IR analysis, the tablet pressing method (dry method) was used. The filler powder was mixed and ground in a mortar with dried potassium bromide in a mass ratio of 1:50. Next, the crushed mixture was placed in a hand press and molded under pressure. A translucent tablet was obtained, which was subsequently used for measurements on a Spektrum 65 Perkin & Elmer IR spectrometer. The structure of electrically conductive composites was analyzed using a Quanta 3D 200i Dual scanning electron microscope.

Resistance to liquid aggressive media was determined according to GOST 9.030-74. The essence of the method was that samples in an unstressed state were exposed to the environment at a given temperature and duration, and their resistance to the specified exposure was determined by the mass of substances extracted from the samples by the environment.

The determination of the mass fraction of SH-groups was carried out according to GOST "Thiokol liquid technical conditions" 12812-80. A sample of thiokol weighing from 0.2 to 0.3 g was weighed and dissolved in 75 cm^3 of toluene, 35–40 cm^3 of iodine solution was added from a burette while stirring, the flask was immediately capped, stirred, and kept in the dark for 10 min, after which the excess iodine was titrated at high shaking with sodium thiosulfate solution. In parallel, a control titration of a solution containing the same amounts of iodine and toluene was carried out.

3. Results and discussion

3.1 Cleavage of thiokols

The process by which the molecular weight of thiokol decreases is called cleavage. Cleavage occurs using a cleavage agent capable of separating the thiokol molecules. This process determines the viscosity of the thiokol. In industry, sodium hydrosulfide is used as a decomposition agent. One molecule of sodium hydrosulfide is capable of splitting a thiokol molecule into two molecules. The viscosity of the resulting thiokol depends on the amount of hydrosulfide supplied. Previously [5], the process of cleavage of thiokols by labeled $Na\acute{S}H$ in the presence of Na_2SO_3 was studied. It was demonstrated that thiosulfene derivatives are first formed, which, when heated, release sulfur, which is then bound by sodium sulfite.

$$\sim R\text{-}S\text{-}S\text{-}R\sim + Na\acute{S}H \rightarrow \sim R\text{-}SH + \sim R\text{-}S\text{-}\acute{S}\text{-}Na \tag{22}$$

$$\sim R\text{-}S\text{-}\acute{S}\text{-}Na \rightarrow \sim R\text{-}SNa + \acute{S} \tag{23}$$

$$\acute{S} + Na_2SO_3 \rightarrow O_2S(ONa)\acute{S}Na \leftrightarrow O_2\acute{S}\,(ONa)_2 \tag{24}$$

The cleavage of bonds in a polymer by sodium sulfide or disulfide is described by the following equations [5]:

$$\sim R\text{-}S\text{-}S\text{-}R\sim + 2NaSNa \leftrightarrow 2\sim R\text{-}SNa + Na\text{-}S\text{-}S\text{-}Na \tag{25}$$

$$\sim R\text{-}S\text{-}S\text{-}R\sim + NaSSNa \leftrightarrow \sim R\text{-}S\text{-}SNa + NaS\text{-}S\text{-}R\sim \tag{26}$$

In current work, the mechanism of cleavage is assumed to be the following: initially, sodium disulfide breaks down the polymer; then the hydrogen sulfate interacts with the split polymer:

$$\sim S_2\text{-}R\text{-}S_2\sim + Na_2S + NaHSO_4 + 3Na_2SO_3 \rightarrow NaS\text{-}R\text{-}SH + Na_2SO_4 + 3Na_2S_2O_3 \tag{27}$$

This method of splitting thiokols is new, it is also another way to obtain mercaptans, but it may become more widespread in the production of thiokols. In contrast to the previously proposed methods for splitting thiokols using aluminum hydride, borohydride, hydrazine, and Bunthe salts [7, 9–11], this method is the simplest and most commercially viable.

The cleavage of the polymer depends on the molecular weight of the initial thiocol, the higher the molecular weight, the more cleavage agents are required for this process. It was found that the ratio at which liquid resins can be obtained corresponds to the ratio of hydrosulfate to sulfite, by varying these components, liquid resins can be obtained. Table 1 shows the results of determining the mass fraction of the SH groups.

Table 1. Determination of the mass fraction of SH groups

#	Ratio of $NaHSO_4$:Na_2SO_3	The mass fraction of SH groups, %
1	1:1	0.4
2	1:2	1.6
3	1:3	2.1

It was revealed that the ratio of acid salt and sodium sulfite affects the content of the mass fraction of SH groups in the resulting thiocol resin, the best results were obtained when these components were added in a ratio of 1:3 ($NaHSO_4$:Na_2SO_3). The product yield was 70–75%.

3.2 Physico-chemical parameters of the initial components

Researches demonstrate that the generally accepted strategy for obtaining mechanically durable materials is the direct addition of appropriate fillers to an insulating polymer matrix, for example graphene [13–14], carbon nanotubes [15–16], nanoscale aluminum oxide [17], nanoclays [18]. The introduction of reinforcing fillers makes it possible to obtain polymers with satisfactory properties.

Filler also has a great influence on mechanical and technological properties. In [13], a polysulfide composite filled with modified graphene oxide was investigated. Compared with a pure polysulfide polymer, the elongation at break and the tensile strength of 0.5% LPO-GO/PSR composites were significantly increased by 70% and 43%, respectively. The modulus of elasticity of the PSR increased by 206% with the addition of 0.5% LPO-GO. In addition, the addition of LPO-GO also improved the thermal conductivity of the composite.

In the present study, CB and CB+MUNT were used as fillers. These fillers were examined using Raman spectroscopy.

Figure 2 shows the Raman spectrum of MWCNT used in sealing compositions. Two main typical graphite bands are present in the Raman spectrum of MWCNT beams: the 1579 cm^{-1} band (G band), attributed to the C–C bond oscillation plane, typical for defective graphite-like materials, and the 1360 cm^{-1} band (D band), activated by the presence of disorder in carbon systems. The Raman spectrum also contains a band of 2728 cm^{-1}, named referring to the overtone of the D band, this is the first overtone of the main D oscillation at 1360 cm^{-1} and already belongs to the second-order Raman spectrum [19].

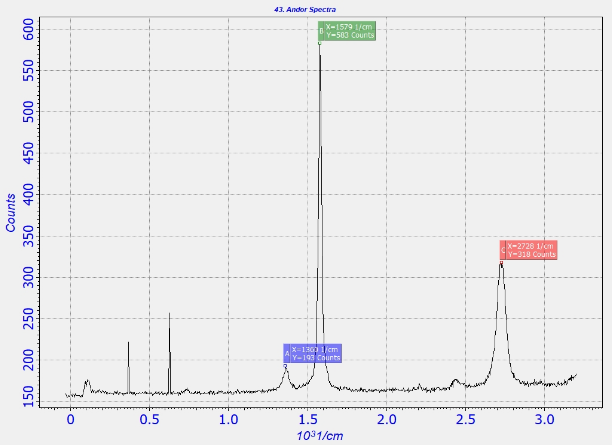

Fig. 2. Raman spectrum of multi-walled carbon nanotubes.

Figures 3–4 show SEM images of CB and MWCNT. CB particles are an accumulation of small and large agglomerates, with a very wide range in size. Small CB agglomerates merge to form large, densely packed

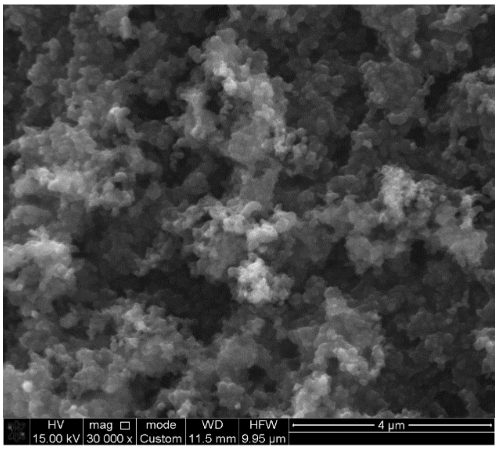

Fig. 3. SEM image of carbon black.

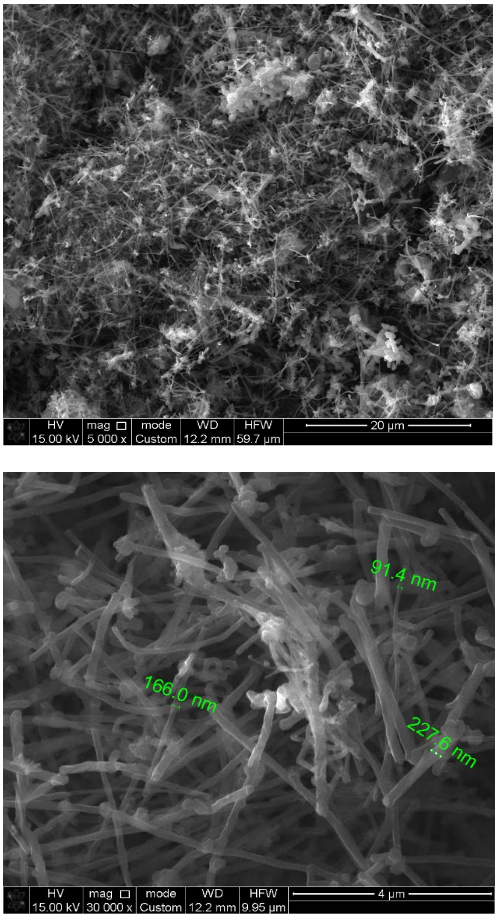

Fig. 4. SEM image of multi-walled carbon nanotubes.

clusters. For a uniform distribution of particles in the matrix, large agglomerates must be broken down by mechanical action. In this work, the prepared mixtures were thoroughly mixed in a laboratory mixer. The diameters of MWCNTs generally correspond to their passport data, ranging from 110–170; in some places, you can see MWCNTs larger in diameter.

3.3 Physical and mechanical properties of composites

To study the physical and mechanical properties, resins were obtained with a ratio of hydrosulfate to sulfite of 1:3, using carbon black and MWCNTs. As is known, carbon black is most often used as a filler, sometimes in a mixture of MWCNTs and graphene [20–21]. To test thiokol resins, mixtures were prepared, the composition of which is given in Table 2.

Table 2. Composition of the mixture for vulcanization

#	Component	Content, mass parts	Content, mass parts
1	Thiokol	100	100
2	Carbon black K 354	0; 5; 10; 20; 30	0; 5; 10; 20; 30
3	MWCNT	-	0.1
4	Diphenylguanidine	0.15	0.15
5	Lead peroxide	10	10

Samples were prepared containing CB in the amount of 0; 5; 10; 20; 30 parts by weight and samples containing CB 0; 5; 10; 20; 30 parts by weight and MWCNTs in the amount of 0.1 parts by weight. Lead peroxide PbO_2 was chosen as a hardener. Curing occurs easily in the presence of alkaline activators, so diphenylguanidine was added to the mixture. Liquid thiokols are cured by the oxidation of terminal mercaptan groups to disulfide groups at low temperatures with virtually no shrinkage [23].

The effect of organic and inorganic solvents on filled thiokol compositions containing MWCNTs in an amount of 0.1 parts by weight was studied with CB content 0; 5; 10; 20; 30 parts by weight and compositions with a CB content of 0; 5; 10; 20; 30 parts by weight that do not contain MWCNTs. Data on the resistance of compositions to liquid aggressive media are given in Table 3. High thermodynamic flexibility and the presence of chemically bound sulfur in the main chain give composites based on polysulfide oligomers resistance to fuels and aggressive environments. It was found that thiokols containing MWCNTs are superior in solvent resistance to composites containing only CB. This can be especially observed in the example of CB 30 and CB 30+MWCNT 0.1 in a gasoline environment, where the mass of substances extracted by gasoline from the sample was 1.4%, thereby the resistance of CB 30 increased by 18% with the addition of MWCNT. In general, it can be noted that with increasing filler content, the resistance of composites increases, for example, between CB 20 and CB 30, resistance to gasoline increased by 10% with an increase in CB content. Tests in a benzene environment demonstrated significant softening of the composites; both types of samples are not resistant to benzene. The composites were not tested for resistance in concentrated environments.

The nominal tensile strength increased with increasing CB concentration, and at a concentration of 30 parts by weight was 2.10 MPa (Fig. 5a). The amount of introduced CB generally had a positive effect on the improvement of physical and mechanical properties. With the addition of MWCNTs in an amount of 0.1 parts by weight in the sample containing 30 parts by weight of CB, the tensile strength increased and amounted to 2.43 MPa (Fig. 5b). Elongation at break decreases significantly with increasing filler content. With a CB content of 30 parts by weight, the elongation at break was 168%. With the addition of MWCNTs, this figure decreased further and amounted to 148%.

Thus, as can be seen from Fig. 5, the introduction of nanotubes into thiokol-based compositions leads to an increase in tensile strength by 16%. At the same time, the relative elongation at break of composites containing CB 30 mass parts + MWCNT decreases by 15% compared to composites containing CB 30.

Using IR spectroscopy, the spectrum of carbon black was obtained and studied. The structure of carbon black is a conjugated system of carbon bonds, which is characterized by wide and low-intensity absorption bands.

Figure 6 shows the IR spectrum of carbon black having the following absorption bands: fluctuations –C=C–bonds in the region of 1560–1600 cm^{-1}, causing polyaromatic layers of carbon black; at 1000–800 cm^{-1}, wide and low-intensity bands of the C-C group can be observed; wide low-intensity bands in the region of 3200-3600^{-1} can also be seen see, which indicate the presence of OH groups [22–23].

The infrared spectrum of thiokol CB 30+MWCNT 0.1 is shown in Fig. 7. Narrow and low–intensity bands in the region of 490 cm^{-1} and 608–657 cm^{-1} are classified as sulfur-containing compounds, correspond to fluctuations of S-S and C-S, respectively [14].

Table 3. Resistance of compositions containing CB and compositions containing CB+MWCNTs to the effects of liquid aggressive media

Solvents	Content of filler, mass parts	Swelling, weight.%	The condition of the sample after testing
Gasoline AI-92	-	2.2	Good
	CB 5	2.1	Good
	CB 5+MWCNT 0,1	2.0	Good
	CB 10	2.0	Good
	CB 10+MWCNT 0,1	1.8	Good
	CB 20	1.9	Good
	CB 20+MWCNT 0,1	1.6	Good
	CB 30	1.7	Good
	CB 30+MWCNT 0,1	1.4	Good
Benzene	-	195	Softened
	CB 5	194	Softened
	CB 5+MWCNT 0,1	192	Softened
	CB 10	190	Softened
	CB 10+MWCNT 0,1	188	Softened
	CB 20	187	Softened
	CB 20+MWCNT 0,1	184	Softened
	CB 30	182	Softened
	CB 30+MWCNT 0,1	177	Softened
Concentrated nitric acid	-	Collapsed within a day	Collapsed within a day
	CB 5	Collapsed within a day	Collapsed within a day
	CB 5+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 10	Collapsed within a day	Collapsed within a day
	CB 10+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 20	Collapsed within a day	Collapsed within a day
	CB 20+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 30	Collapsed within a day	Collapsed within a day
	CB 30+MWCNT 0,1	Collapsed within a day	Collapsed within a day
Concentrated hydrochloric acid	-	Collapsed within a day	Collapsed within a day
	CB 5	Collapsed within a day	Collapsed within a day
	CB 5+ MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 10	Collapsed within a day	Collapsed within a day
	CB 10+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 20	Collapsed within a day	Collapsed within a day
	CB 20+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 30	Collapsed within a day	Collapsed within a day
	CB 30+MWCNT 0,1	Collapsed within a day	Collapsed within a day
Concentrated sulfuric acid	-	Collapsed within a day	Collapsed within a day
	CB 5	Collapsed within a day	Collapsed within a day
	CB 5+ MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 10	Collapsed within a day	Collapsed within a day
	CB 10+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 20	Collapsed within a day	Collapsed within a day
	CB 20+MWCNT 0,1	Collapsed within a day	Collapsed within a day
	CB 30	Collapsed within a day	Collapsed within a day
	CB 30+MWCNT 0,1	Collapsed within a day	Collapsed within a day

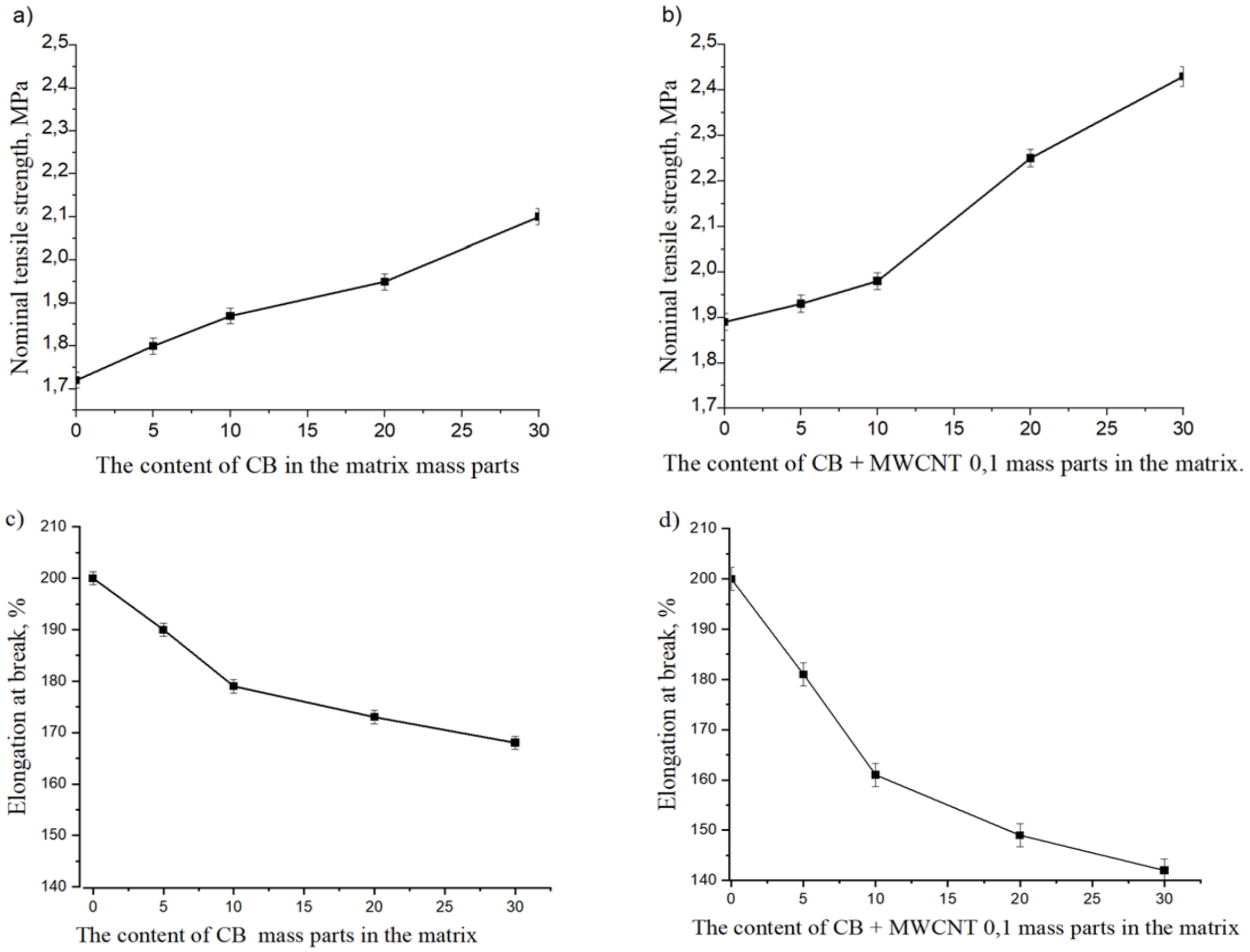

Fig. 5. Physical and mechanical properties of composites: (a) – conditional tensile strength (MPa) of composites containing CB; (b) – conditional tensile strength (MPa) of composites containing CB+MWCNT 0.1; (c) – elongation at break of composites containing CB; (d) – elongation at break of composites containing CB+MWCNT 0.1.

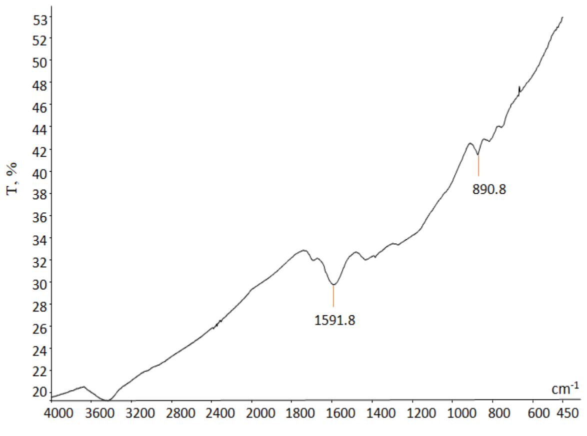

Fig. 6. IR spectrum of carbon black.

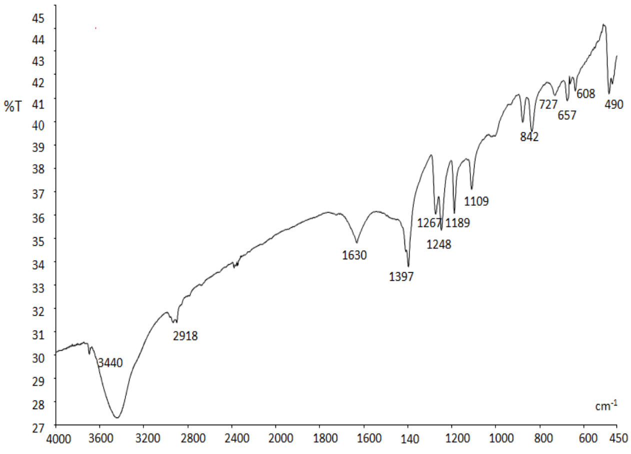

Fig. 7. IR spectrum of polysulfide polymer containing CB 30+MWCNT 0.1.

In addition, peaks 727–842, 1109, 1189, 1248–1267, 1397, and 2918 cm^{-1} correspond to in-plane C–H vibrations, C–C,–CH_2– stretching vibrations, C–H fan vibrations, and bending torsional vibrations of ethylene segments, in-plane scissor C–H vibrations, symmetric C–H stretching vibrations and asymmetric C–H stretching vibrations, respectively [18–19]. In addition, the peaks around 1630 and 3440 cm^{-1} are attributed to scissor vibrations and symmetrical vibrations of –OH units of absorbed moisture with KBr [14, 20, 24–25].

Thus, despite numerous studies devoted to polysulfide oligomers, the unique set of properties of materials based on them and the wide application possibilities determine the growing interest in this class of compounds. The structural features of PSO determine the widespread use of materials based on them in aircraft, machine and shipbuilding, electrical engineering and construction industries. The production of sealing compositions based on polysulfide oligomers using elemental sulfur, millions of tons of which accumulate in oil fields, helps to improve the environmental situation in these regions and leads to a more rational use of resources.

4. Conclusion

The physical and mechanical properties of composites based on PSO and various thiokol contents from 5 to 30 parts by weight were studied, with the addition of multi-walled carbon nanotubes in the amount of 0.1 parts by weight. The introduction of carbon nanotubes into the composition led to an increase in tensile strength by 16%, but the relative elongation at break decreased by 15%.

The work also assessed the durability in terms of maintaining strength properties after aging the composites in aggressive environments (gasoline, benzene, concentrated acids). It was found that the resistance to solvents of filled thiokols is influenced by the amount of filler content; the more filled the polymer, the more its resistance to aggressive environments increases, this is especially observed in composites containing CB 30 and CB 30 + MWCNT 0.1, the resistance of which with the addition of MWCNT increased by 18%.

The method of obtaining PSO proposed in this work is able to replace the existing classical method of producing liquid thiocols using sodium hydrosulfide, due to the fact that inexpensive available reagents are used; the operation of washing the thiocol emulsion after reaction with sodium tetrasulfide is reduced when using sodium sulfide as a splitting agent, it may not be used; also, this method can be used to obtain liquid thiocols from other chlorinated hydrocarbons.

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