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Application of Epoxidized Soybean Oil in Highly Filled Water-Swelling Rubbers

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Abstract

It has been shown by IR spectroscopy that when epoxidized soybean oil (ESO) and swelling polymer are thermostated under conditions close to those of vulcanization, the nature and intensity of the oxirane cycle peak in the range of 900-700 cm^{-1} (C-O-C) changes in the spectrum. A less noticeable effect with the introduction of Sodium carboxymethyl cellulose (NaCMC) compared with cotton powder (CP) is due to the fact that the most chemically active hydroxyl groups in the C_6 position are replaced by carboxyl ones. The TG/DTA method showed the high thermal stability of the swelling filler and the product of its interaction with ESO. It was revealed that upon the introduction of ESO, the composition of rubber compounds filled with powdered cellulose from cotton waste, leads to an increase in tensile strength of the rubbers by 4-7%. Swelling of samples in 10% aqueous solutions of NaCl, KOH, H_2SO_4 and sodium chloride formation water (pH=6.3) were carried out. It has been established that the swelling capacity of rubbers with ESO is increased by 6-15% compared to samples in which the widely used plasticizer oil PN-6 is introduced.

Keywords: Water-swelling rubbers; Nitrile butadiene rubber; Carboxylated cellulose; Plasticizer; Epoxidized soybean oil.
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1. Introduction

An increase in wellbore drilling volumes in the oil and gas industry requires the use of swellable packers of various designs.[1–3] Swellable packers are used to prevent behind-the-casing flows of oil and «oil-water» fluid. Fluid isolation is based on the possibility of swelling of the packer's elastic element, made of special rubber. Swellable rubber technology for offshore and onshore wells is being actively developed by Shell, Easy Well Solutions, Halliburton Energy Services Group, TAM International, Baker Oil Tools, Schlumberger, Tendeka and others. Works of M. Akhtar and others are devoted to the development of swelling rubbers.[3–7]

At the same time, the problem of creating universal elastomeric compositions of such a functional purpose has not been fully resolved to date. To create swelling elastomer compositions, polar nitrile butadiene rubbers (NBR) are widely used.[8–10] One of the significant advantages of NBR-based rubbers in comparison with rubbers based on natural rubber (NR), isoprene rubber, styrene-butadiene rubber is their higher resistance to thermal aging. Rubbers based on NBR have good adhesion to brass-plated metal and in this respect approach rubbers based on NR.

Numerous studies have shown that the properties of swelling rubbers are affected by the nature of the rubber and the special ingredients it contains. The literature presents the results of research on the properties of rubbers, which contain acrylamide copolymers, polyvinyl alcohol, carboxymethyl cellulose and its derivatives, cross-linked starch copolymers and other super absorbents as water-swellable additives.[11–16] The water-absorbing properties of rubbers containing partially cross-linked polyacrylates have been found to be highly dependent on both the salt concentration in the water medium and the crosslink density of the swelling polymer.[5,17]

The use of polyvinyl alcohol (PVA) to create composites provides a high degree of swelling in water and satisfactory mechanical properties.[18] However, the effect is limited in time due to the active dissolution of PVA in water. To reduce this defect, a number of works suggest using the combination of cross-linked polyacrylate and a copolymer of polyvinyl alcohol with polybutyl acrylate in the composition of water-

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swelling rubbers, but the degree of swelling of such rubbers is low.[19]

The use of cellulose and its ethers as a water-swellable additive is of great interest to researchers. This is due to the renewal of the natural resource base and the environmental integrity of the product. The most common cellulose ether is sodium carboxymethyl cellulose (Na-CMC).[20–23]

However, when using Na-CMC, researchers noted an increase in the viscosity of the rubber compound, a decrease in the elastic-strength properties of the rubber. The high viscosity of the rubber compounds makes uniform distribution of ingredients difficult.[13] Replacing carboxylated cellulose with powdered cellulose obtained from non-wood raw materials does not contribute to a decrease in the viscosity of rubber compounds, however, it allows to increase in tensile strength of rubbers.[24,25]

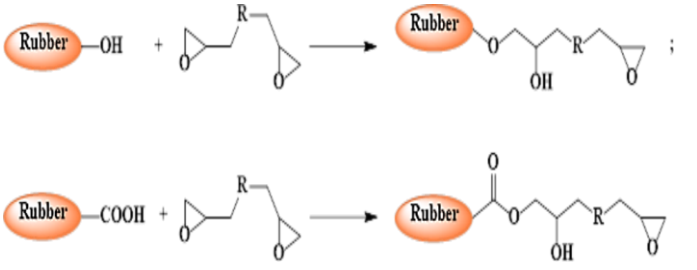
To reduce the viscosity of rigid types of rubbers it is necessary to use plasticizers.[26,27] At present strict environmental and health directives influence the plasticizer market and its applications. Regulation is carried out by the European Council for Plasticizers and Intermediates. Dioctyl phthalate (DOP) occupies the dominant part in the production and use of plasticizers. A number of papers describe the use in the composition of swelling rubbers of oil softener PN-6, which is a concentrate of aromatic hydrocarbons obtained by compounding extracts of selective (phenolic) purification of lube-oil cut.[28] According to research[29,30] the use of DOP and PN-6 has been reduced due to the negative impact on the human body. In addition, traditional plasticizers (DOP, bitumen, rosin, petroleum oil) do not chemically bond with the rubber matrix during vulcanization. This may lead to their migration, extraction upon contact with working liquid media.[31]

It is more rational to use compounds capable of chemically bonding with the polymer matrix as plasticizers. Among such compounds, attention is drawn to epoxidized oligomers which can react with the hydroxyl groups of cellulose due to the opening of the epoxy ring as mentioned in the works.[32,33] Authors of the work[34] have shown that the physical and mechanical properties of rubbers based on nitrile butadiene rubber can be better preserved after thermal-oxidative aging when using E-181 epoxy resin (mass fraction of epoxy groups is not less than 25%), which is associated with a change in the structure of the elastomeric matrix. The resin dosage was 10 parts per hundred rubber (phr), which corresponds to the average amount of plasticizer traditionally used in rubbers of this type.

In Refs. [35,36] the possibility of improving the dynamic characteristics and wear resistance of rubbers based on general-purpose rubbers with the introduction of epoxy resins (0.5-1.5 phr) was shown. The achieved effect was explained by the reactions of epoxy resin groups with oxidized rubber groups (Rubber-OH) **(**Scheme 1**)**.

In the case of using cellulose and its derivatives as a filler in the composition of rubbers, it should be taken in to account that the epoxidized resin is able to react with hydroxyl groups[37,38] contained in cellulose and carboxylated cellulose molecules, which can lead to premature structuring and further increasing the viscosity of the rubber compound. Therefore, the use of epoxy resins with a high epoxy number is not appropriate in this case. Apparently, in this case, more rational to consider epoxidized vegetable oils with a low epoxy number (4-6) as an epoxy oligomer.[39–44]

The facts outlined above determined the direction of research: to identify the effect of epoxidized vegetable oil on the strength properties of rubbers based on nitrile butadiene rubber highly filled with a cellulose-containing additive from powdered cotton and carboxylated cellulose.



Scheme 1 The reaction of epoxy resin groups with oxidized rubber groups.

2. Experimental part

2.1 Materials

The choice of base rubber compound (BRC) ingredients was based on the literature data **(**Table 1**)**.[45,46] We used NBR-rubber grade – BNKS-28 AMN, which is most often used in the compositions of swelling rubbers. For vulcanization a sulfur containing vulcanizing system with an accelerator of the thiazole group was used. Zinc oxide (ZnO) and stearic acid ($CH_3(CH_2)_{16}COOH$) were added to activate the vulcanization accelerator. Epoxidized soybean oil (ESO) (50 phr) (TU 0253-061-07510508-2012, epoxy oxygen content 6.2% by weight) and plasticizer PN-6 (TU 38.1011217-89) for comparison were used as a plasticizer.

Table 1. Ingredients of basic rubber compound.

№ n/o	Ingredient	Specifications	Quantity, phr
1	BNKS-28 AMN	TU* 38.30313-2006	100.0
2	Sulfur	GOST** 127.4-93	1.5
3	2-Mercaptobenzothiazole	GOST** 739-74	0.8
4	Zinc oxide	GOST** 202-84	5.0
5	Stearic acid	GOST** 6484-96	1.5
6	Technical carbon P 324	GOST** 7885-86	45.0

* Technical conditions

** State Standard

Cotton powder (CP) obtained by the method of Ref. [47] (degree of polymerization-1120, ash content-0.5%, α–cellulose-95%) and industrial sample Na-CMC – Polycell CMC 9B (TU 2231-017-32957739-09, degree of polymerization not less than 700, degree of substitution 0.8-

0.9) were used as swelling filler (SF). Before the test, the samples were fractionated with a sieve method. A fraction with a particle size of 0.5-1.0 mm was used.

2.2 Preparation of composites

The preparation of composites was carried out in two stages. BRC without SF was prepared beforehand (Table 1). Ingredients (1-5) **(**Table 1**)** of BRC were mixed by laboratory mills. BRC was kept for 1 day at room temperature and then mixed with a water-swelling filler, plasticizer, and sulfur in a closed laboratory rubber mixer of Brabender "Plasti-Corder® Lab-Station" W50 E plasticorder at a temperature of about 60 ℃ and the rotation speed of the rotors 60 rpm. SF was administered in a ratio of 1:1 by weight to BRC.

2.2 Measurements

2.2.1 Fourier-Transform Infrared Spectroscopy Analysis (FTIR)

Functional group analysis of cellulose was performed using IR-Fourier spectrometer "InfraLUM FT-08" (Russia). Measurements were carried out in the range from 600 to 4000 cm^{-1}, with a spectrum resolution – of 2 cm^{-1}.

2.2.2 Thermogravimetric and Differential Thermal Analysis (TG/DTA)

The thermal behavior of the SF and plasticizer compositions (ESO+Na-CMC and ESO+CP) was evaluated using thermal gravimetric analyzer STA 6000 at a heating rate of 5 °C/min in the temperature range of 30–450 °C.

2.3 Rubber testing methods

2.3.1 Determination of vulcanization characteristics of rubber compounds

The rheometric characteristics of rubber compounds were determined on rheometer "Monsanto 100 S» at 170 °C and a test duration of 30 min. The samples of the rubber compounds (9 g) were placed on an electrically heated oscillating disk cure meter of the device. A kinetic curve was automatically drawn with the recorder.

2.3.2 Vulcanization of rubber compounds

Vulcanization of rubber compounds was carried out in a hydraulic press with electric heating of plates with a lower hydraulic cylinder. Molds are located between steel heated plates in several floors. The press has a minimum pressing force of 1M*N and plates measuring 600×600×36 mm. To vulcanize the rubber compounds in the press, the temperature was set at 170 °C (justified by the type of vulcanizing system and thermal resistance of the rubber), the pressure was 19.6 MPa, the vulcanization time was 10 minutes, and the cooling time was 3 minutes. The thickness of the vulcanized rubber plates was 2+0.2 mm.

2.3.3 Physical and mechanical rubber testing methods

Elastic-strength properties of vulcanizates were determined according to GOST 270-81 on the breaking machine RMI-250 (speed sprains samples 500 mm /min). Rebound elasticity, which is a measure of the elastic-hysteresis properties of rubber, was evaluated on a Shoba pendulum according to GOST 27110-86. Shore A hardness was determined on a TSH-200 hardness tester according to GOST 263-75.

2.3.4 Determination of sorption properties

Swelling was performed in sodium chloride reservoir water (pH=6.3) and aqueous solutions of NaCl, KOH, and H_2SO_4 with a concentration of 10% by weight. The degree of rubber swelling in aqueous media was determined by GOST R ISO 1817-2009 by weight method in relation to the mass of the liquid ($m-m_0$) absorbed by the polymer material sample (vulcanizate) to the mass of the initial vulcanizate sample (m_0):

$$\alpha = \frac{m-m_0}{m_0} * 100\ \% \quad (1)$$

3. Results and discussion

The thermal stability of the swelling fillers was evaluated by thermogravimetry **(**Figs. 1 and 2**)**. It is confirmed that the fillers used are Na-CMC and CP lose adsorbed water when

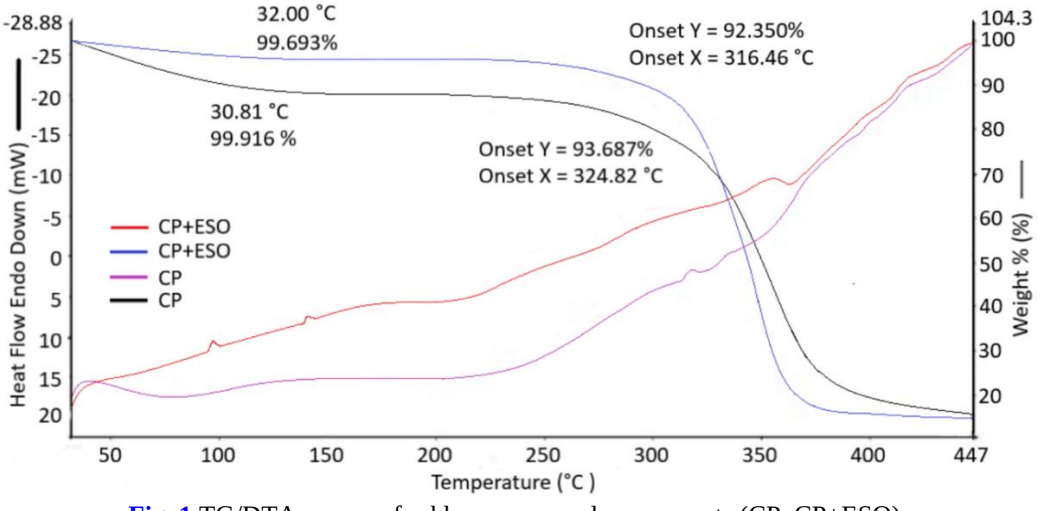


Fig. 1 TG/DTA curves of rubber compound components (CP, CP+ESO).

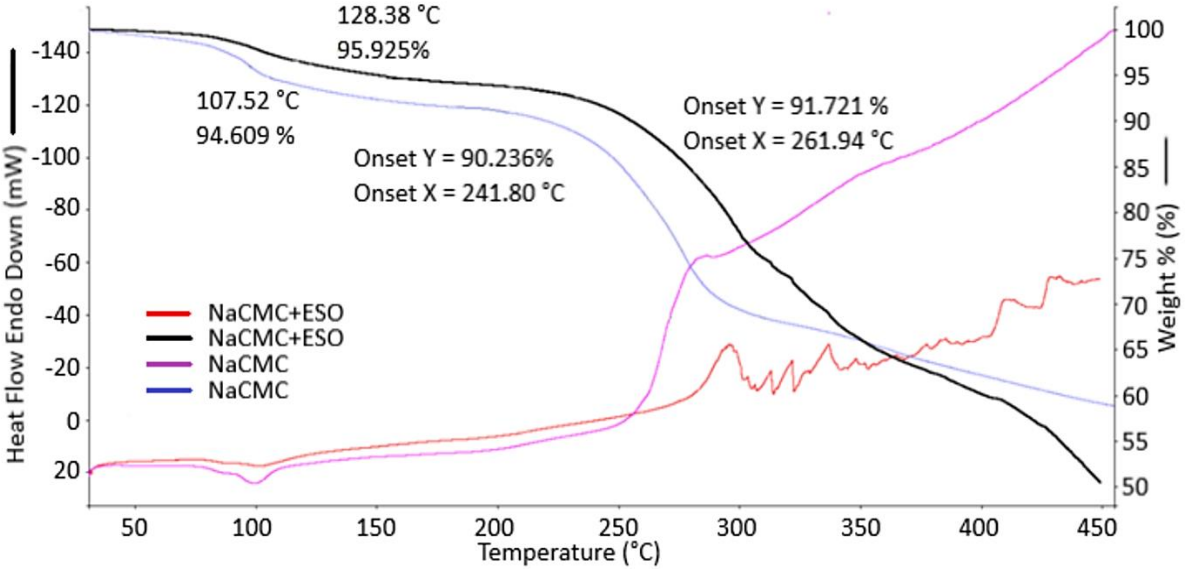


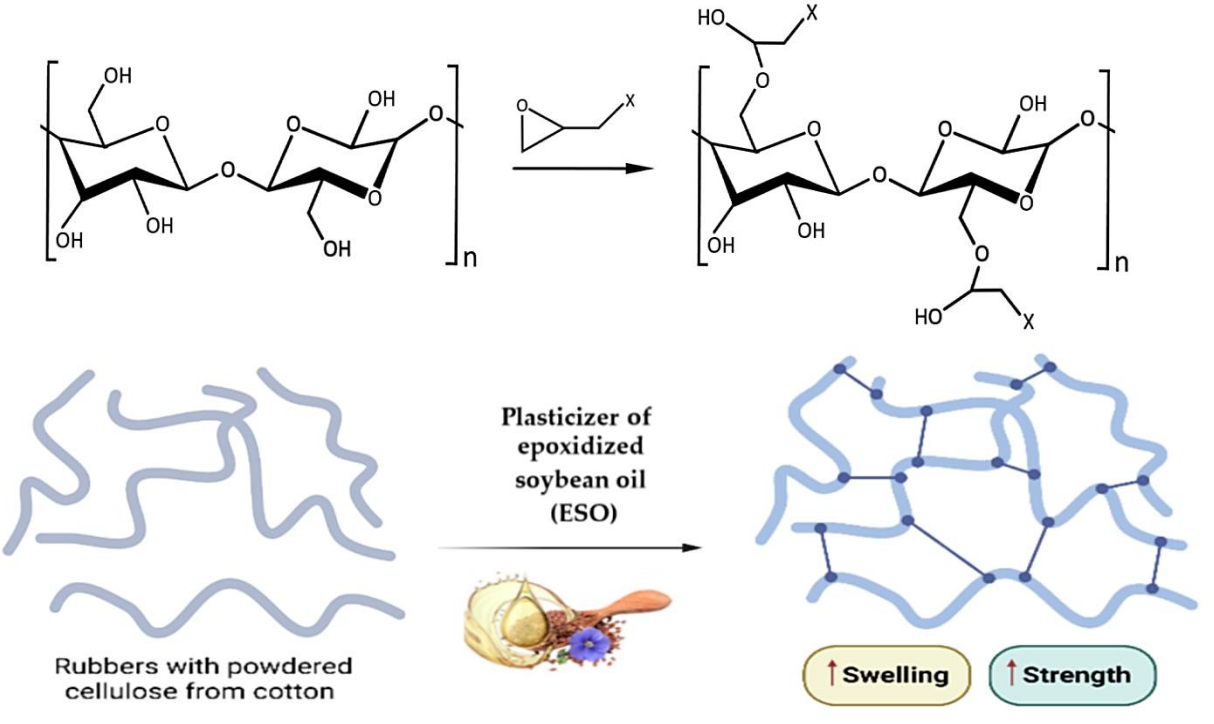
Fig. 2 TG/DTA curves of rubber compound components (NaCMC, NaCMC+ESO).

heated to 120 °C (5.34% wt. and 3,5% wt., respectively), as indicated by the endothermic effect.

The degradation of CP starts at a noticeable rate at 270 °C and ends at about 380 °C. About 80% of the mass of the initial material is lost during intensive decay. The carbonized residue at 450 °C is 15%. According to literature in this area, there is a rupture of interlink glycoside bonds and depolymerization.[48] The decay of CP begins at a noticeable rate at 270 °C and ends at approximately 380 °C. During the period of intense decay, about 80% of the mass of the original substance is lost; the carbonized residue at 450 °C is 15%. According to the literature data, interlink glycosidic bonds are broken and depolymerization occurs in this region.[48]

In contrast to CP, the Na-CMC sample lost mass in steps. Within a temperature range of 120-220 °C, the sample lost up to 10% of its mass. This may be due to the start of the decarboxylation process because of the break of the weakest acetal bond observed by a number of researchers. The weight loss of the Na-CMC sample in the range of 220–350 °C is apparently related to the process of breaking the interlink glycosidic bonds and depolymerization, which proceed more slowly than in CP due to screening of the glycosidic bond by the carboxyl group.[49–51] The carbonized residue at 450 °C is about 40%.

The TG/DTA curves of the mixture of Na-CMC with ESO differ from the curves of the initial products. This may indicate



Scheme 2 The interaction reaction of epoxy groups with hydroxyl groups of cellulose.

a chemical interaction between them (Scheme 2).

Such a process is very likely to occur during vulcanization, since, according to literature data, the interaction of cellulose with epoxy compounds occurs under rather mild conditions.[52,53]

To prove the statement about the interaction between ESO and SF, the IR spectra of their mixtures were taken. The band of vibrations of bonds of the epoxy (oxirane) C–O–C cycle in the region of 910-821 cm^{-1} was used as an analytical band (Figs. 3 and 4).[54] The samples were thermostated at 170 °C. The choice of temperature is determined by the conditions of vulcanization. The change in the nature and intensity of the peak of the oxirane ring in the region 900-700 cm^{-1} when thermostating the mixture of ESM and SF at 170 °C indicates the interaction between the compounds (Fig. 3).

Less noticeable effect of the influence of SF when administered Na-CMC in comparison with CP is due to the fact that hydroxyl groups in position C_6 are the mostly chemically active, which are partially replaced by carboxylic ones in Na-CMC.

At then extstage of the work an analysis of the vulcanization rheograms of rubber compounds was carried out. It was found that with the introduction of a SF in rubber compounds without plasticizer and with ESO plasticizer, the minimum torqueM_{min}, which characterizes the viscosity of rubber compounds, and the maximum torque M_{max} increase. M_{min} is inversely proportional to plasticity. With the introduction of a plasticizer induction period increased. Based on the analysis (Table 2) of vulcanization rheograms, the optimal vulcanization time was determined. Vulcanization of rubber compounds was carriedoutat a temperature of 170 °C for 10 minutes.

Table 2. Parameters of rheometric vulcanization curves of rubber compounds ("Monsanto 100S", 170°C, ratio BRC:SF=1:1 by mass).

Composition of rubber compounds (ratio, wt%)	t_s, min	M_{min}, dN·m	M_{max}, dN·m	t_{90}, min
Without plasticizer				
Control sample (BRC)	1.0	15	41	9.4
BRC:Na-CMC (50: 50)	0.8	20	53	9.8
BRC:Na-CMC:CP (50:30:20)	1.2	20	50	10.0
BRC: CP (50:50)	2.0	28	57	9.6
Plasticizer ESO				
Control sample (BRC)	2.2	15	47	9.5
BRC:Na-CMC (50: 50)	1.2	18	65	9.8
BRC:Na-CMC:CP (50:30:20)	2.0	26	88	10.0
BRC: CP (50:50)	1.5	38	80	9.7

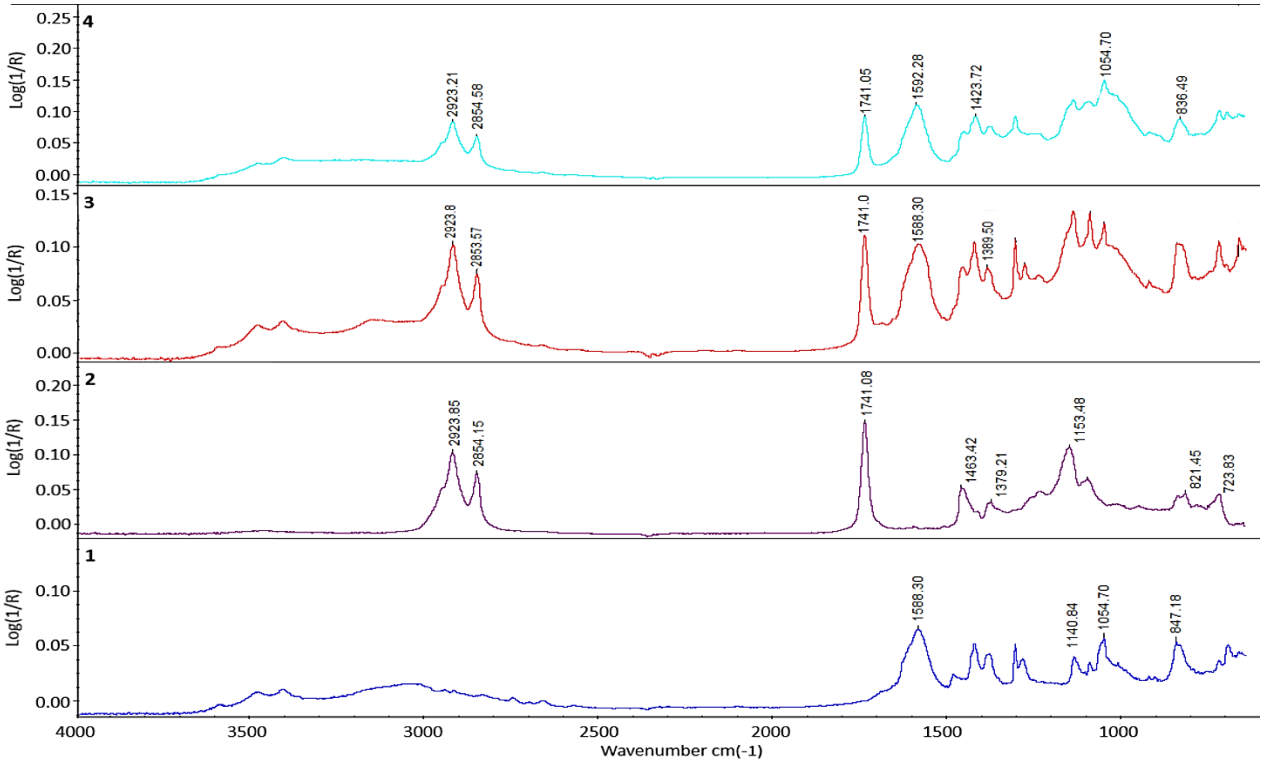


Fig. 3 IR-spectra of the change in the nature and intensity of the peaks before and after thermostating the mixture ESO with Na-CMC at 170 °C (1-Na-CMC, 2-ESO, 3-NaCMC+ESO, 4-NaCMC+ESO thermostated).

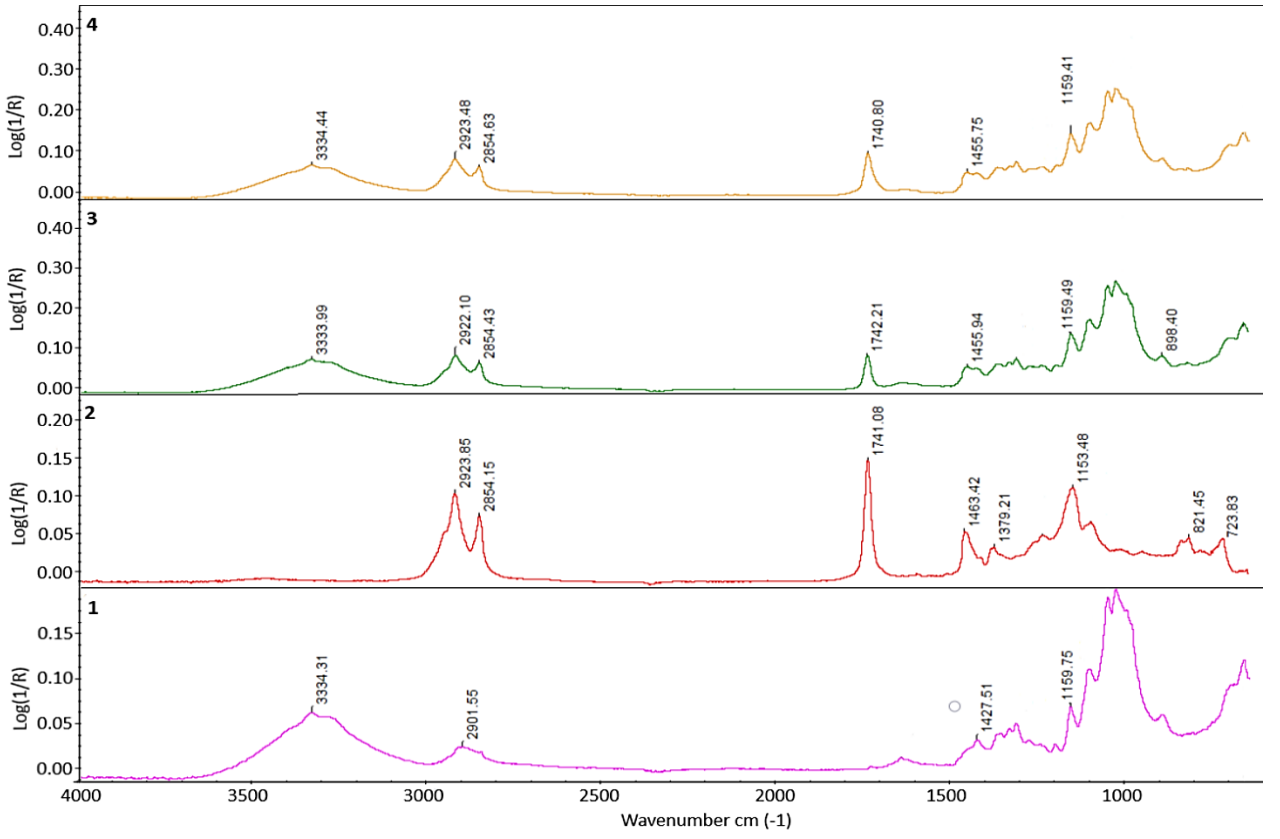


Fig. 4 IR-spectra of the change in the nature and intensity of the peaks before and after thermostating the mixture ESO with PC at 170 °C (1 - CP, 2 - ESO, 3 - CP+ESO, 4 - CP+ESO thermostated).

Determination of tensile strength of the rubber (fp) showed that the introduction of SF in an amount of 1:1 in relation to the BRC leads to a significant decrease in tensile strength (fp) (Fig. 5). Thus, rubber without SF had tensile strength of 14.8 MPa, while rubber filled with Na-CMC – 2.7 MPa; and filled CP – 8.9 MPa. Note that tensile strength of the rubber filled with CP is almost 3 times higher than when using Na-CMC. This can be explained by the poor compatibility of the two polymers with each other, the formation of defects. The complex of properties of such systems is determined by the size and shape of the particles of the dispersed phase, as well as the size of the interfacial layer formed on the interface as a result of the mutual diffusion of the components.[55]

According to the literature data, the introduction of a

Table 3. Physical and mechanical properties of rubbers.

BRC:NaCMC:CP, %wt.	Elasticity, %	Hardness, Shore A
Without plasticizer		
Control (without SF)	27	67
BRC:Na-CMC=50: 50	25	82
BRC:Na-CMC:CP=50: 30: 20	25	87
BRC:Na-CMC:CP=50: 20: 30	26	86
BRC:CP=50: 50	27	92
Plasticizer PN-6		
BRC:Na-CMC=50: 50	17	79
BRC:Na-CMC:CP=50: 30: 20	18	81
BRC:Na-CMC:CP=50: 20: 30	19	82
BRC:CP=50: 50	20	87
Plasticizer ESO		
BRC:Na-CMC=50: 50	14	79
BRC:Na-CMC:CP=50: 30: 20	13	85
BRC:Na-CMC:CP=50: 20: 30	14	84
BRC:CP=50: 50	17	91

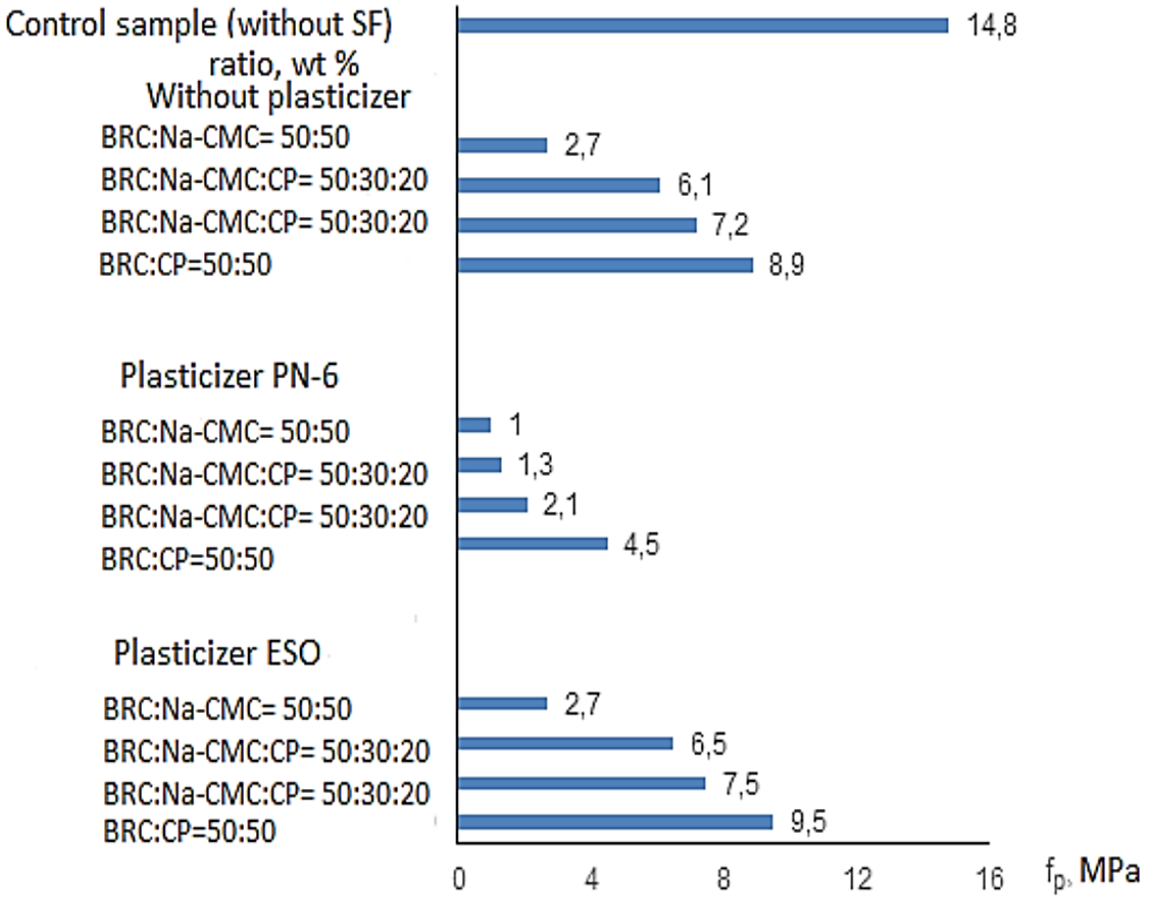


Fig. 5 Influence of swelling filler and plasticizers (PN-6 and ESO) on tensile strength of the vulcanizates.

plasticizer into the composition of rubber should be accompanied by a decrease in tensile strength.[56] However, when using the plasticizer ESO, tensile strength changed in significantly in comparison with the chemically inactive plasticizer PN-6. Moreover, increasing the amount of CP led to the increase of strength characteristics. This is due to the fact that, in the structure of cellulose, there are both intramolecular and intermolecular hydrogen bonds between oxygen atoms and hydroxyl groups of d-anhydroglucopyranose units. These types of hydrogen bonding interactions can make a vital contribution to the crystalline characteristics of cellulose. This allows to increase tensile strength.[57]

According to the data shown in Table 3, it can be seen that the introduction of SF does not lead to a significant decrease in rebound elasticity, which, apparently, is due to the structure of the filler itself. The introduction of both PN-6 and ESO plasticizers is expected to reduce this parameter.

A consequence of the high filling of SF is an increase in the Shore A hardness of composites compared to the control sample without SF.

Since the operating conditions of sealing elements assume their operation at elevated temperatures, it was important to find out the effect of temperature control on tensile strength.

Tensile strength of the rubbers tested samples with ESO aged for 72 hours at a temperature of 100 °C increased. This fact is a positive moment, because indicates that the product will be thermally stable under operating conditions at elevated temperatures. Aging results are shown in Table 4.

The swelling capacity of cellulose, according to literature data,[58] occurs due to the coordination of the metal with oxygen atoms of the hydroxyl groups O(2)H and O(3)H and depends on the pH of the medium and the properties of the coordination sphere of cations, which often affect each other. Table 5 shows the effect of the composite composition on the degree of vulcanizate swelling in aqueous media of different

Table 4. Physical and mechanical properties of rubbers after aging (plasticizer ESO).

BRC:NaCMC:CP, % wt.	Tensile strength, MPa		Elasticity, %		Hardness,Shore A	
	After aging	Δ	After aging	Δ	After aging	Δ
BRC (without SF and plasticizer)	18,2	3,4	30	3	68	1
BRC:Na-CMC =50:50	4,1	1,4	17	3	77	-2
BRC:Na-CMC:CP=50:20:30	9,1	1,5	19	5	83	1

Table 5. Effect of composite composition and plasticizer type on the degree of vulcanizates welling in aqueous media (vulcanization at 170 °C for 10 min).

Composition of the rubber compound	Ratio, % wt.	Water media for swelling			
		H_2SO_4	KOH	NaCl	Reservoir water
Maximum degree of swelling, %					
Without plasticizer					
BRC:Na-CMC	50:50	56	102	95	49
BRC:CP	50:50	19	37	15	13
Plasticizer PN-6					
BRC:Na-CMC	50:50	62	108	76	54
BRC:Na-CMC:CP	50:30:20	41	74	46	30
BRC:Na-CMC:CP	50:20:30	34	59	35	25
BRC:CP	50:50	24	39	17	10
Plasticizer ESO					
BRC:Na-CMC	50:50	64	105	87	51
BRC:Na- CMC:CP	50:30:20	30	69	47	33
BRC:Na- CMC:CP	50:20:30	25	53	36	25
BRC:CP	50:50	20	38	14	11

mineralization. According to the data obtained, the degree of swelling of rubber, including SF, does not depend much on the presence of a plasticizer. The degree of swelling is largely influenced by the pH of the medium and mineral composition.

4. Conclusions

It is revealed that the use of a chemically active plasticizer of epoxidized vegetable oil can improve the strength characteristics of rubbers filled with powdered cellulose from cotton waste, (from 4.5 MPa to 9.5 MPa), a composition of powdered cellulose and as well as with carboxylated cellulose from 2.1 to 7.5 MPa in comparison with rubber, where PN-6 oil is used as a plasticizer, which is associated with the formation of new spatial structures due to the interaction of NO-groups of cellulose and the oxirane ring of epoxidized vegetable oil.

At the same time, tensile strength of the rubbers filled with powdered cellulose is higher than when filling Na-CMC. This is due to the formation in the latter case of a rarer additional network formed by the hydroxyl groups of cellulose and ESO. For the same reason, when replacing Na-CMC for powdered cellulose from cotton waste in aqueous media of different mineralization, the degree of swelling decreases regardless of the presence of a plasticizer.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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