

# Multifunctional ingredients for composite elastomer materials

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**Abstract.** The purpose of this work is to study the effect of multifunctional ingredients on the complex of properties of composite elastomeric materials. New multifunctional ingredients with stabilizing properties are proposed, and their optimal content in the composition is determined. It is shown that thermal aging of composites stabilized by furan oligomers, with an increase in the duration of aging time, a decrease in the relative elongation of the composites is observed, which, in the process of thermal exposure under the action of furan units, additional structuring occurs. The expediency of using furan oligomers as effective multifunctional ingredients for elastomer compositions has been established, which made it possible to purposefully regulate the structural and physico-mechanical characteristics of the compositions without changing the technology and instrumentation of the existing production.

## 1 Introduction

In the process of formation of a spatial structure, with an increase in the degree of cross-linking, a decrease in the number average ( $M_c$ ) segments of polymer chains occurs and, accordingly, an increase in the number of cross-links per unit volume of the vulcanizate ( $v$ ). With a change in the degree of cross-linking, a gradual change in the properties of the vulcanizates occurs. The equilibrium modulus with increasing density of the vulcanization network and in accordance with the molecular kinetic theory of elasticity increases in direct proportion to the number of cross-links or inversely proportional to the average molecular weight of the chain segments between the nodes of the spatial network of the vulcanizate [1, 2]. The change in hardness and strength characteristics of vulcanizates depends on many factors. With an increase in the density of the vulcanization network, the relative and residual elongations decrease to very small values, which are characteristic of brittle materials. In this case, the elasticity changes according to a complex relationship: the maximum elastic properties appear at such a density of the vulcanization network, at which the maximum strength for soft rubbers is observed. In addition, swelling in solvents decreases in proportion to the increase in the degree of crosslinking [3, 4].

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To obtain rubbers with a given set of properties, it is necessary to provide a certain degree of cross-linking of elastomers by introducing a certain amount of vulcanizing agents into the composition. In this case, the number of cross-links formed will depend on the nature of the rubber, the nature and content of the vulcanizing agent, the vulcanization conditions, as well as other ingredients [1,2].

The purpose of this study is to study the possibility of using furan oligomers as a multifunctional ingredient in elastomeric compositions, which allows targeted control of the structure of the vulcanization network of furan oligomers.

The objects of the study are furan oligomers, as a standard rubber compound used on the basis of rubbers for general and special purposes (butadiene-styrene, isoprene and chloroprene rubbers). The physicochemical properties of the starting materials were studied by GOST 25699-93, IR spectroscopy, viscometry. The production of rubber compounds was carried out on laboratory mixing rollers RC-WW 150/330 (Rubicon, Germany). The determination of the Mooney viscosity of rubber compounds was carried out on a Mooney viscometer MV 2000 (Alpha Technologies, England). The stress relaxation test is carried out on the same specimens as the Mooney viscosity immediately after the completion of the viscosity measurement by stopping the rotation of the rotor very quickly and measuring the drop in the final Mooney viscosity over time. The vulcanization kinetics of rubber compounds was determined on an ODR 2000 rheometer (Alpha Technologies, UK). Physical and mechanical parameters were determined by the relevant state standards.

2 Results and discussion

One of the main methods of structural modification of composite elastomeric materials is the introduction into their composition of various ingredients that differ in structure and influence on the properties of the composition.

Research was carried out to create more effective polyfunctional ingredients for elastomeric composite materials based on furan oligomers obtained from furan, furfuryl and terafurfuryl alcohol of catalytic polymerization [3, 4]. Furan monomers are obtained from pentosan-containing raw materials and their oligomers (Table 1) have high chemo-thermal and radiation resistance.

Table 1. Physicochemical properties of furan oligomers.

| Name of indicator                           | Furanoligomers                                                                    |                       |                                  |
|---------------------------------------------|-----------------------------------------------------------------------------------|-----------------------|----------------------------------|
|                                             | From furfural                                                                     | From furfuryl alcohol | From tetrahydro-furfuryl alcohol |
| Appearance                                  | viscous homogeneous liquid from dark brown to black without mechanical impurities |                       |                                  |
| Mass fraction of volatile substances, % n/b | 7                                                                                 | 10                    | 10                               |
| pH                                          | 6.5                                                                               | 6.5                   | 6.5                              |
| Boiling point, K                            | 401                                                                               | 393                   | 398                              |
| Flash point, K                              | 453                                                                               | 453                   | 453                              |
| Self-ignition temperature, K                | 725                                                                               | 725                   | 725                              |
| Pour point, K                               | 243                                                                               | 243                   | 243                              |
| Molecular mass                              | 1000-1200                                                                         | 1000-1200             | 1000-1200                        |

The main methods for studying the effect of plasticizers on the properties of elastomers is the determination of the glass transition temperature of polymers and their fluidity. Table 2 shows data regarding the effect of furan oligomers on the glass transition temperature of elastomers based on strain and modulus measurements. The data obtained indicate that as the content of furan oligomers increases, the glass transition temperature of elastomers

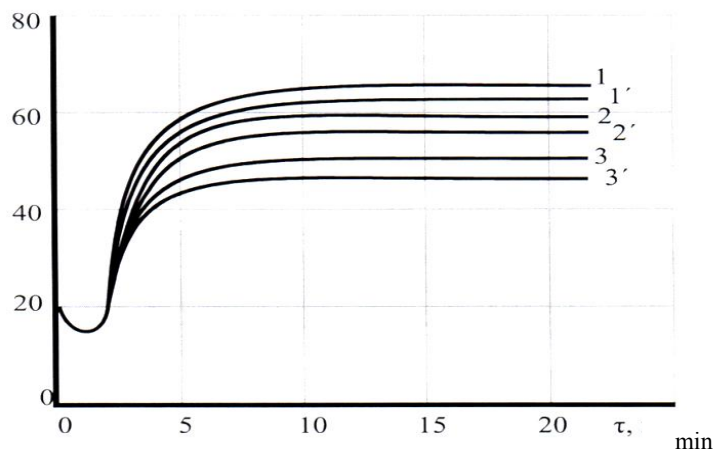
proportionally decreases. This means that in their presence, elastomers retain their highly elastic properties at lower temperatures than non-plasticized elastomers. In this case, a frequency dependence of the deformation and the value of the glass transition temperature is observed. The higher the frequency, i.e. the shorter the exposure time, the higher will be the glass transition temperature of the plasticized system [1–13].

**Table 2.** Influence of the content of furan oligomers on the glass transition temperature of elastomers\*).

| Name and content of ingredients, wt.h. per 100 wt.h. rubber | Glass transition temperature of elastomers, K |              |                 |
|-------------------------------------------------------------|-----------------------------------------------|--------------|-----------------|
|                                                             | SKI-3                                         | Nairit KR-50 | SKMS-30 ARKM-15 |
| 0                                                           | 203-205                                       | 263          | 221             |
| OFF 5                                                       | 201                                           | 260          | 219             |
| 10                                                          | 198                                           | 256          | 215             |
| 15                                                          | 190                                           | 254          | 112             |
| OTHFS 5                                                     | 200                                           | 259          | 218             |
| 10                                                          | 197                                           | 254          | 214             |
| 15                                                          | 189                                           | 253          | 211             |
| OFFS 5                                                      | 199                                           | 260          | 217             |
| 10                                                          | 197                                           | 257          | 213             |
| 15                                                          | 196                                           | 256          | 210             |

\* OFF-oligomer from furfural, OTHFS-oligomer of tetrahydrofurfuryl alcohol, OFFS-oligomer from furfuryl alcohol.

It is shown that the introduction of elastomeric compositions of furan oligomers significantly change the kinetic parameters of the vulcanization of rubber compounds (Fig. 1) and the mechanical properties of the composition, regardless of the polarity of the rubbers, while increasing the plasticity of rubber compounds by 12%, and stickiness by 62% compared to similar dosages plasticizer dibutyl phthalate.



**Fig. 1.** Kinetics of vulcanization of rubber mixtures based on SKI-3 at a temperature of 428K. The contents of PO and DBP 5 (1.11), 10 (2.21) and 15 (3.31) wt.h. per 100 wt.h. rubber.

The study of the effect of furan oligomers on the kinetics of vulcanization of rubber compounds based on SKI-3 made it possible to establish that in its presence in the thiuram vulcanizing system, the vulcanization rate of cis-1,4-polysoprene increases, and the time to reach the optimum vulcanization decreases. However, the degree of vulcanization is markedly reduced. And the use of a sulfur vulcanizing system activates the vulcanization

process, which is facilitated by the presence of active functional groups (-OH, -COOH, etc.) in its composition [8–10].

**Table 3.** Technological and operational properties of industrial rubber \*).

| Indicators                          | DBP  | FO   |
|-------------------------------------|------|------|
| Plasticity, arb. unit               | 0.49 | 0.48 |
| Mooney viscosity (MI 4-373 K)       | 30.0 | 34.0 |
| Scorch at 394 K, min                |      |      |
| τ <sub>5</sub>                      | 10.0 | 13.0 |
| τ <sub>35</sub>                     | 20.0 | 15.0 |
| Vulcanizability at 416 K, min       |      |      |
| τ <sub>nach.v.</sub>                | 4.0  | 4.0  |
| τ <sub>opt.v.</sub>                 | 8.0  | 8.0  |
| Density, kg/m3                      | 1220 | 1220 |
| Ring module,3/2                     | 4.0  | 5.0  |
| Physical and mechanical properties: |      |      |
| f <sub>p</sub> , MPa                | 5.48 | 9.48 |
| E <sub>otn</sub> , %                | 195  | 210  |
| E <sub>ost</sub> , %                | 2    | 10   |
| Coef. heat resistance, strength     | 0.42 | 0.86 |
| Brittleness temperature, K          | 239  | 233  |
| Shore-A hardness                    | 54   | 61   |
| Abrasion, pm3 / J                   | 77   | 70   |

\*) the content of DBP and FO 10 wt.h. per 100 wt.h. rubber

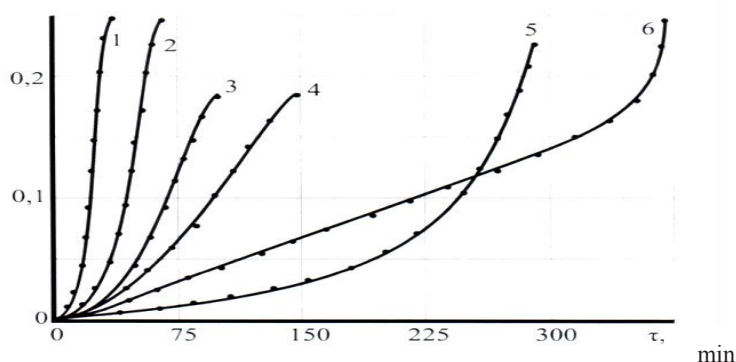
The observed effect is confirmed by IR studies of the reaction products of furan oligomers and thiuram at elevated temperature. A sharp decrease in intensity at 1720 cm<sup>-1</sup>, related to the C=O group of the carboxyl group, and a slight decrease in its intensity in the region of 360-300 cm<sup>-1</sup> (OH group) indicate that when furan oligomers are combined with thiuram, new compounds are formed with the participation these groups. By studying the effect of the amount of furan oligomers on the properties of rubber based on rubbers SKMS-30 ARKM-15, SKI-3, nairit KR-50, it was found that its optimal content is 10 wt. h per 100 wt. h rubber. Such samples have high tensile strength and relative elongation, and elasticity is maintained at an average level. Hardness and stress at 300% elongation and tear resistance in all tested rubbers increase compared to dibutyl phthalate (Table 3).

This circumstance can be explained by an increase in the degree of crosslinking due to the cyclization of furan units under the influence of temperature. The equilibrium swelling of vulcanizates with respect to machine oil, gasoline, kerosene, etc. has been studied. and found a significant improvement in oil - and gasoline resistance of the obtained elastomeric compositions. Thus, the use of furan oligomers as plasticizers for elastomer compositions has shown that, being a product of a multifunctional action, they exhibit high plasticizing properties, while increasing the stickiness of rubber compounds and the strength properties of rubber. It has also been established that they significantly activate the process of both sulfuric and thiuramic vulcanization [12-14].

There is no information in the literature about the stabilizing properties of furan oligomers. It must be assumed that furan oligomers, due to such properties as the ability to donor-acceptor interactions, inhibition, thermal, photochemical processes, can play an important role in the formation of the structure of composite elastomeric materials. In the light of the foregoing, we have developed for the first time effective stabilizing additives for elastomeric compositions based on furan oligomers. The stabilizing effect of furan oligomers was studied during the oxidation of technical and purified chloroform with subsequent

threefold reprecipitation of synthetic rubbers SKS-30 ARCM-15 and nairit KR-50 with isopropyl alcohol. It follows from the obtained results that with an increase in the content of furan oligomers in SKS-30 ARCM-15 rubber, the duration of the stage of the induction period of the oxidation reaction increases. In this case, the rate of oxygen uptake remains virtually unchanged even after the end of the induction period. It has been established that the efficiency of the same concentration of furan oligomers in crude rubber is higher than in purified rubber. Apparently, this is due to the presence of the antioxidant BC-1 in the latter. It should also be noted that at high concentrations of furan oligomers, an increase in the induction period is accompanied by an increase in the rate of oxygen uptake during the induction period (Fig. 2).

The amounts of the critical concentration of furan oligomers corresponding to the inflection points on the curve "induction period-antioxidant concentration" were determined as 0.07 and 0.014% ( $1.4 \cdot 10^{-3}$  and  $2.4 \cdot 10^{-3}$  mol/kg), respectively, for crude and refined rubber. The critical concentrations of furan oligomers during the oxidation of technical and purified rubber SKS-30 ARKM-15 correspond to 0.24 and 0.5%, which is significantly higher than for dibutyl phthalate. The effective consumption constants of furan oligomers in SKS-30 ARKM-15 rubber are  $3.2 \cdot 10^{-4}$  s<sup>-1</sup> for purified and  $1.9 \cdot 10^{-4}$  s<sup>-1</sup> for technical rubber, which indicates its great influence on side reactions to inhibit the oxidation of elastomers.



**Fig. 2.** The kinetics of oxygen uptake during the oxidation of purified (1.2.5) and crude (3.4.6) SKS-30RP in the absence of additives (1.4) and in the presence of 10% OPN (5.6) and MOPN (2.3);  $T=1600$ .

Studies of the thermal aging of composites stabilized with furan oligomers have shown that with an increase in the duration of aging time, a decrease in the relative elongation of the composites is observed, compared with samples stabilized with neazone D. Apparently, in the process of thermal exposure under the action of furan units, additional structuring occurs due to which leads to an increase in rigidity and a decrease in the values of relative elongation of composites [9–15].

### 3 Conclusion

The expediency of using furan oligomers as effective modifying additives for elastomer compositions has been established, which made it possible to carry out purposeful regulation of the structural and physico-mechanical characteristics of the compositions without changing the technology and instrumentation of the existing production. The significant role of furan oligomers as an important component in the formation of three-dimensional structures of elastomer compositions has been elucidated.

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