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Studying the Influence of Gas Pyrolysis Resin Still Bottoms on The Vulcanization Kinetics of Rubbers

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Abstract

This study examined the influence of gas pyrolysis resin bottoms, a by-product of the joint venture Uz-Kor Gas Chemical LLC, on the vulcanization kinetics of rubber compounds based on SKI-3, SKMS-30ARKM-15, and Nairit KR-50 rubbers in thiuram and sulfur vulcanizing systems. It was shown that in the thiuram system, the distillate residue accelerates the achievement of the vulcanization optimum with a slight decrease in the degree of crosslinking, whereas in the sulfur system, it exhibits a pronounced activating effect due to the presence of hydroxyl and carboxyl functional groups. IR spectroscopy confirmed the chemical interaction of the distillate residue with thiuram during the formation of the vulcanization network. The kinetic parameters of the thermo-oxidative degradation of plasticized composites were determined – the duration of the induction period, critical inhibition concentrations, and effective modifier consumption constants. The optimal ratio of the distillate residue to the traditional plasticizers dibutyl phthalate and dibutyl sebacate was determined. The results suggest that the distillate residue of gas pyrolysis resin can be considered a multifunctional modifier for vulcanizing systems of elastomeric composites.

Keywords: Still residue, gas pyrolysis resin, vulcanization kinetics, thiuram system, sulfur vulcanizing system, plasticizer, thermal oxidation, elastomer compositions.

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1. Introduction

Rubber products and tires based on elastomers are widely used in transport engineering, aircraft manufacturing, metallurgy, the chemical and food industries, and agriculture. The operational reliability of these products is largely determined by the structure of the vulcanization network formed during the cross-linking of rubber macromolecules. Controlling the kinetics of this process - the rate at which optimum vulcanization is achieved, the degree of cross-linking, and the type of cross-links formed - remains a key challenge in the chemistry and

technology of elastomeric materials [1, 2].

Traditionally, various plasticizers and modifiers, including petroleum derivatives, are used to regulate vulcanization kinetics [3]. However, the use of scarce petroleum feedstocks limits the economic feasibility of such solutions, making the search for alternative multifunctional ingredients based on local and recycled raw materials relevant [4, 5].

Similar problems of involving secondary petrochemical products in vulcanizing systems are also being solved in foreign research: the fundamental possibility of using oils from the pyrolysis of worn tires as plasticizers for rubber mixtures based on styrene-butadiene rubber has been demonstrated [6], and it was further established that the cure rheokinetics and the resulting vulcanizate structure depend significantly on the chemical nature of the plasticizer used [7].

The only polymer production facility in Central Asia, the joint venture Uz-Kor Gas Chemical LLC, annually produces approximately 387,000 tons of polyethylene and 83,000 tons of polypropylene, simultaneously producing approximately 10,000 tons of pyrolysis resin tar product, which has not yet found qualified industrial application. We previously studied the physicochemical nature of this product and its heat-treated distillate residue, demonstrating their structural similarity to the plasticizer dibutyl phthalate, and establishing the role of the distillate residue in shaping the vulcanization network structure of elastomer composites [8]. However, the kinetic principles of the vulcanization process in the presence of this modifier - the rate of crosslinking in various vulcanizing systems, the mechanism of activating action, and resistance to thermal oxidation - have not previously been separately examined and require further study.

The aim of this work is to study the influence of the still residue of gas pyrolysis resin on the kinetics of vulcanization of rubber mixtures based on general-purpose (SKI-3, SKMS-30ARKM-15) and special-purpose (nairit KR-50) rubbers in thiuram and sulfur vulcanizing systems, as well as to establish the kinetic parameters of thermo-oxidative destruction of the compositions plasticized by it.

2. Methods

The modified sample was a pyrolysis resin product - a waste product from the polyolefin production process at the Uz-Kor Gas Chemical joint venture - heat-treated at 200°C to produce a distillate residue (a black liquid substance with an average molecular weight of 900 - 1100). The industrial plasticizer dibutyl phthalate (DBP) was used as a reference standard, as was dibutyl sebacate (DBS) when studying the modified systems.

The studies were conducted on standard rubber compounds based on general-purpose rubbers SKI-3 and SKMS-30ARKM-15, special-purpose rubber Nairit KR-50, and nitrile butadiene rubber SKN-18, vulcanized using the thiuram and sulfur methods. Vulcanization kinetics were recorded as the change in torque over time at the vulcanization temperature (rheometric method). The chemical structure of the original and modified products, as well as the nature of their interaction with the components of the vulcanizing systems, were monitored using IR spectroscopy. The thermo-oxidation kinetics of the plasticized compounds were studied by the manometric method based on oxygen absorption at 160°C, for both technical-grade and purified (reprecipitated with isopropyl alcohol) SKMS-30ARKM-15 and Nairit KR-50 rubbers. Thermal aging of the vulcanizates was assessed by changes in relative elongation and tensile strength after thermostatting the samples. The experimental data were processed using mathematical statistics methods and experimental design.

3. Results and Discussion

The studies showed that gas pyrolysis resin is a black, odorless solid (Table 1). The gas pyrolysis resin is composed primarily of arenes and olefins, with a carbon number of up to 6-12. Olefins account for 23.7%, and arenes for 67.18%. It also contains alkanes, dienes, and cycloalkanes. Qualitative and quantitative analyses show that the spectra of the components are consistent, with a 90-97% agreement.

Chemical composition of gas pyrolysis resin

Table 1

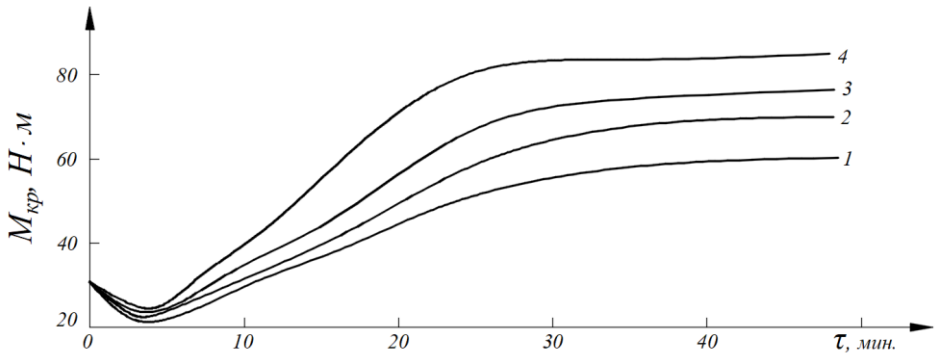
Number of carbons	Alkanes	Dienes	Olefins	Cycloalkanes	Arenes	Σ
5	0,8	0,89	4,91	0,19	0	6,79
6	0,22	0,41	3,87	0,41	32,94	37,85
7	0,25	0,14	0,84	0,45	11,23	12,91
8	0,12	0,08	0,18	0,48	9,75	10,61
9	0,04	0,1	0,04	0,15	7,56	7,89
10	0,03	0,11	9,07	0,4	5,23	14,84
11	0,18	0,69	2,95	0	0,47	4,29
12	0	0,15	1,84	0	0	1,99
Σ	1,64	2,57	23,7	2,08	67,18	97,17

The physicochemical properties and structure of the gas pyrolysis resin still residue have been characterized in detail previously [8]: according to IR and ^{1}H NMR spectroscopy data, the product contains predominantly aromatic fragments as well as active functional groups (–OH, –COOH), and in terms of compatibility with the elastomer matrix it is close to dibutyl phthalate. It is the presence of these functional groups that determines the specific behavior of the still residue in various types of vulcanizing systems, which was the subject of further kinetic analysis.

A study of the vulcanization kinetics of rubber compounds based on SKI-3 and SKMS-30ARKM-15 showed that the introduction of the still residue into the thiuram vulcanizing system significantly accelerates the crosslinking process: the relative vulcanization rate increases, and the time to reach the optimum is reduced, compared to both the unmodified mixture and the composition containing DBP. In this case, the degree of vulcanization, proportional to the maximum torque, turns out to be somewhat lower than in the absence of a modifier, which indicates a change not only in the speed, but also in the maximum density of the resulting vulcanization network (Fig. 1).

As the dosage of still residue increases from 5 to 15 parts by weight per 100 parts by weight of rubber, the observed effects increase almost monotonically. However, at the highest dosage studied (15 parts by weight), the increase in vulcanization rate slows somewhat, which can be attributed to the saturation of the reactive thiuram sites with the active groups of the modifier.

Unlike the thiuram system, in the sulfur vulcanization system, still residue of gas-pyrolysis resin exhibits a pronounced activating effect: the vulcanization process is more intense already at the initial stage, due to the participation of its hydroxyl and carboxyl groups in the reactions that form intermediate sulfiding complexes. Chemical interaction is confirmed by IR spectroscopy data on the products of combining the distillation residue with thiuram at elevated temperatures: a sharp decrease in the intensity of the absorption band at 1720 cm^{-1}, corresponding to the carbonyl group, and a noticeable weakening of the band in the region of 3600–3300 cm^{-1}, attributed to hydroxyl groups, is observed. This indicates their consumption during the formation of new chemical bonds.



The content of DBP is 10 parts by weight (1), the still bottoms of gas pyrolysis resin are 5 parts by weight (2), 10 parts by weight (3), 15 parts by weight (4) per 100 parts by weight of rubber.

Figure 1. Vulcanization kinetics of an elastomeric compound based on SKI-3 rubber.

A study of the kinetics of oxygen absorption during oxidation of technical-grade and purified SKMS-30ARKM-15 rubber, as well as Nairit KR-50, plasticized with gas-pyrolysis resin still bottoms, showed that as the modifier content increases, the duration of the oxidation induction period regularly increases, whereas the rate of oxygen absorption at the deep stages of the process, after the end of the induction period, remains practically unchanged. The efficiency of the same concentration of distillation residue is higher in technical rubber than in purified rubber, which is explained by the presence of residual amounts of the antioxidant VS-1 in the former, which acts synergistically with the studied modifier.

At elevated distillation residue concentrations, an increase in the induction period is accompanied by an increase in the rate of oxygen absorption directly during the induction period-an effect similar to that observed during the inhibited oxidation of polyolefins [8]. Critical distillation residue concentrations corresponding to the inflection point on the "induction period duration - inhibitor concentration" dependence were determined: 0.07 and 0.014% (1.4 x 10^{-3} and 2.4 x 10^{-3} mol/kg) for technical and purified rubber, respectively; for the oxidation of composites based on SKMS-30ARKM-15, these values are 0.24 and 0.50%, which significantly exceeds the corresponding values for dibutyl phthalate. The effective constants for the consumption of the distillate residue are 3.2 x 10^{-4} s^{-1} for purified rubber and 1.9 x 10^{-4} s^{-1} for technical rubber, which indicates its significant participation in side reactions that inhibit the oxidative destruction of elastomers.

Indirect confirmation of the change in the kinetics of structure formation is the consistent decrease in the glass transition temperature of elastomers with increasing vat residue content (Table 2): in its presence, elastomers maintain a highly elastic state at lower temperatures compared to unplasticized samples. A frequency dependence of deformation is also observed: the higher the frequency of loading (shorter the loading time), the higher the apparent glass transition temperature of the plasticized system, which is typical of relaxation processes in cross-linked polymers. However, excessive vat residue content is inadvisable, as it leads to a sharp decrease in the flow temperature and a narrowing of the temperature range for high elasticity.

Effect of gas-pyrolysis resin still bottoms on the glass transition temperature of elastomers, K

Table 2

Plasticizer/modifier	Content, phr	SKI-3	Nairit KR-50	SKMS-30ARKM-15
Plasticizer-free	0	203–205	263	221
DBF	5	201	261	219

Plasticizer/modifier	Content, phr	SKI-3	Nairit KR-50	SKMS-30ARKM-15
DBF	10	199	258	215
DBF	15	192	255	213
Gas-pyrolysis resin stillage	5	201	260	219
Gas-pyrolysis resin stillage	10	198	256	215
Gas-pyrolysis resin stillage	15	190	254	212

Combining the distillate residue of gas pyrolysis resin with traditional plasticizers DBP and DBS in various ratios allows for targeted control of the structure formation kinetics of the composites (Table 3). The optimal ratio of distillate residue to DBP (or DBS) was found to be 1:3; exceeding this ratio leads to a decrease in the pour point and a narrowing of the high-elasticity temperature range, as well as to an increase in the strength of the vulcanizates compared to the unmodified plasticizer. The introduction of modified systems into Nairit KR-50-based composites is accompanied by an increase in the viscosity of the mixture, which is associated with the interaction of the functional groups of the distillate residue with polychloroprene.

A study of the thermal aging of vulcanizates plasticized with distillation residue revealed that with increasing aging time, the relative elongation of the composites decreases more rapidly than that of samples stabilized with NeoZone D, while strength properties change to a significantly lesser extent. This is due to additional structuring under the influence of the remaining active centers of the distillation residue, leading to an increase in vulcanizate rigidity during aging.

Effect of modified DBP/DBS plasticizers with pyrolysis resin residue on the glass transition temperature of elastomers, K

Table 3

Plasticizer composition	Ratio, phr	SKI-3, K	Nairit KR-50, K	SKMS-30RP, K
Without plasticizer	0	203-205	263	221
DBF	10	199	258	215
Pyrolysis resin stillage	10	197	254	214
DBF + stillage	5+5	190	250	208
DBF + stillage	10+5	192	252	210
DBF + stillage	15+5	194	253	212

4. Conclusion

It was established that the distillation residue of gas pyrolysis resin- a by-product of polyolefin production at

the Uz-Kor Gas Chemical LLC joint venture-has a pronounced and multidirectional effect on the vulcanization kinetics of elastomer composites depending on the type of vulcanization system: in a thiuram system, it accelerates the achievement of the vulcanization optimum with a slight decrease in the degree of crosslinking, while in a sulfur system, it acts as a process activator due to the participation of hydroxyl and carboxyl functional groups. IR spectroscopy confirmed the chemical interaction of the functional groups of the distillate residue with thiuram during the formation of the vulcanization network. The kinetic parameters of the thermal oxidation of plasticized composites-induction period duration, critical inhibition concentrations, and effective modifier consumption constants-were determined, indicating its significant contribution to inhibiting the oxidative degradation of elastomers. It has been shown that the optimal ratio of distillate residue to traditional plasticizers DBP and DBS is 1:3, allowing for targeted control of the structure formation kinetics and the range of technological properties of the compositions without changing the existing production process.

These results, taken together, allow us to consider distillate residue of gas pyrolysis resin as an effective multifunctional modifier of vulcanization systems-simultaneously accelerator/activator of the vulcanization process, plasticizer, and stabilizer of elastomer compositions-suitable for practical use in the rubber industry.

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