Innovative: International Multi-disciplinary Journal of Applied Technology
(ISSN 2995-486X) VOLUME 04 ISSUE 04, 2026

STUDY OF THE INFLUENCE OF GASOPYROLYSIS RESIN ON THE STRUCTURAL FORMATION OF REZINES

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Abstract:
In this work, the possibility of using the tar product of gas-pyrolysis resin - a polymer production waste - in the production of composite elastomeric materials was investigated. The composition and physicochemical properties of gas-pyrolysis resin have been established. It was determined that the boiling and flash point of organic substances used in the production of elastomeric compositions should not be lower than 180°C, therefore, it was heat-treated with gas-pyrolysis resin at 200°C for 4 hours.
It has been established that the cubic residue of gas-pyrolysis resin plays an important role in the formation of the structure and properties of elastomeric composite materials as a result of interaction with donor-acceptor bonds during the inhibition of thermo-photochemical processes, the strength of composites during rupture increases, the relative length during stretching slightly decreases, the hardness and -C-C- bond in the vulcanization grid increase, as a result of which the active substances contained in the cubic residue of gas-pyrolysis resins increase.

Keywords: Structure formation, composite, inhibition, thermo-photochemical, process, gas-pyrolysis resins, elastomer, strength, cubic residue, rupture.

1. Introduction

Today, elastomer-based rubber products and tires are widely used in transportation, aircraft construction, metallurgy, the chemical and food industries, and agriculture, and ingredients derived from organic and inorganic substances are used to improve their structure [1,2,3]. At the same time, it is important to create ingredients that improve the technological properties of rubber products and tires based on elastomers, structurally correcting their physical-mechanical, dynamic, and special properties, taking into account the specified requirements [4,5,6].

Based on the critical analysis of literature and the study of the current state of modification of composite organomineral materials based on plasticizers and elastomers, it has been determined that currently, the most promising direction for creating nano- and similar-structure compositions is the search for and creation of multifunctional ingredients based on local raw materials, and the development of the composition and technology for producing elastomer-based composite materials and products with specified properties and structures using them [7].

Scientific research is being conducted on obtaining organic and inorganic ingredients from the products of the oil and gas processing industry and secondary raw materials and creating methods for their modification, studying their physicochemical properties and structure, substantiating their influence on the properties of compositions in order to bring the structure of rubber products and tires based on elastomers to predetermined requirements, and on their use in the development of the composition and technology for the production of rubber-technical products used in the transport and aviation industry, metallurgical, chemical, and food industries, and agriculture [8].

In this regard, it is relevant to develop methods for obtaining organic and inorganic ingredients based on local and secondary raw materials for the rubber industry, using them to change the structure of composite elastomers of materials and products based on them to the specified requirements, and to create technologies for their production.

The purpose of the research is to create plasticizers for elastomeric compositions based on local and secondary raw materials, as well as to develop compositions and technologies for obtaining products with a given structure, used in various conditions.

2. Materials and Methods

In the work, physicochemical (IRS, MMP, radiography) methods were used to study the properties of gas-pyrrolysis resin - a polymer production waste, and standard compositions based on general (SKI-3, SKMS-30ARKM-15) and special (SKN-18) elastomers were selected to study the influence of the cubic residue of gas-pyrrolysis resin on the properties of compositions, and dibutyl phthalate plasticizer was used for comparison. The technological properties of elastomeric compositions (plastometer, volcometer, deformitometer), physical-mechanical, kinematic, and dynamic indicators (dynamometer) were investigated using standardized methods, including experiment planning and mathematical statistics.

3. Results and Discussion

Main part. As a result of studying the scientific developments carried out in recent years, it has been established that the use of the tar product of gas-pyrolysis resin - a waste product of polymer production - in elastomers has been studied by scientists, but due to the lack of scientific and practical results, it has not been brought to production. Studies have shown that gas-pyrolysis resin is a black, odorless solid substance (Table. In its composition, mainly arenes and olefins, the carbon number reaches 6-12. The olefin content is 23.7%, and the arene content is 67.18%. It also contains alkanes, dienes, and cycloalkanes. Qualitative and quantitative analyses show compatibility of the spectra of the components, their indicator is 90-97%.

Table 1. Chemical composition of gas pyrolysis resin

Amount of carbon	Alkanes	Dienes	Olefins	Cycloalkanes	Arenas	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

According to gel chromatography, its average molecular mass is approximately 1000. According to the results of IR spectroscopic studies, the appearance of characteristic absorption spectral lines is 3050 cm-1 (valence vibrations of the C-H bonds of the aromatic ring), 2860, 2930, and 2975 cm-1 (valence vibrations of the C-H bonds of the methylene and methyl groups). Also, absorption bands are observed at 1710 cm-1 of the carbon chain (carbonyl group C=0), at 1730 cm-1 of asphaltene resins, absorption bands at 1500-1600 cm-1 correspond to the valence vibrations of C=C bonds (Figure 1).

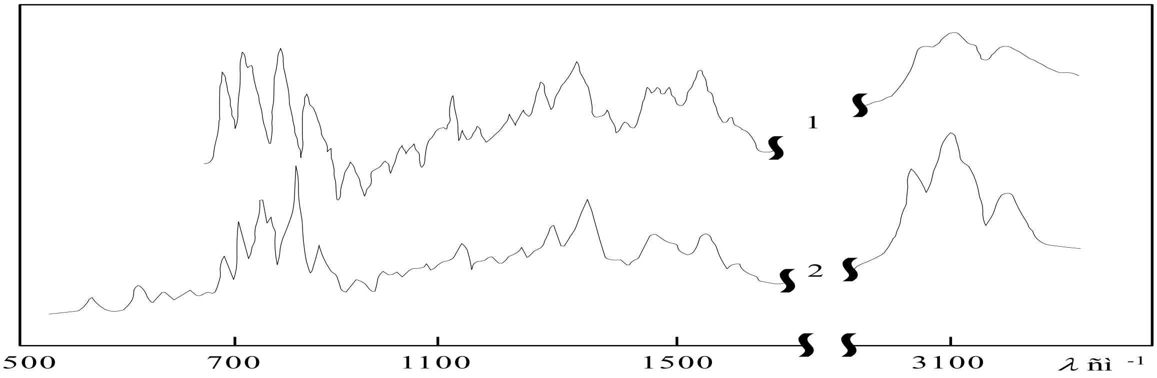


Figure 1. IR spectrum of gas pyrolysis resin.

In turn, the obtained PMR spectra indicate the presence of protons d=6.10 m.u., d=7.12 m.u., d=8.10 m.u., characteristic of aromatic structures and their substituted derivatives. Studies have shown that its softening and melting temperature is around 120-140 °C.

It is known that the boiling and flash point of organic substances used in the production of elastomeric compositions should not be lower than 180°C [1,9,10]. Therefore, we heat-treated the tar-product of gas-pyrolysis resin, which is formed in the technological process of propylene production at 200°C (Fig. 2).

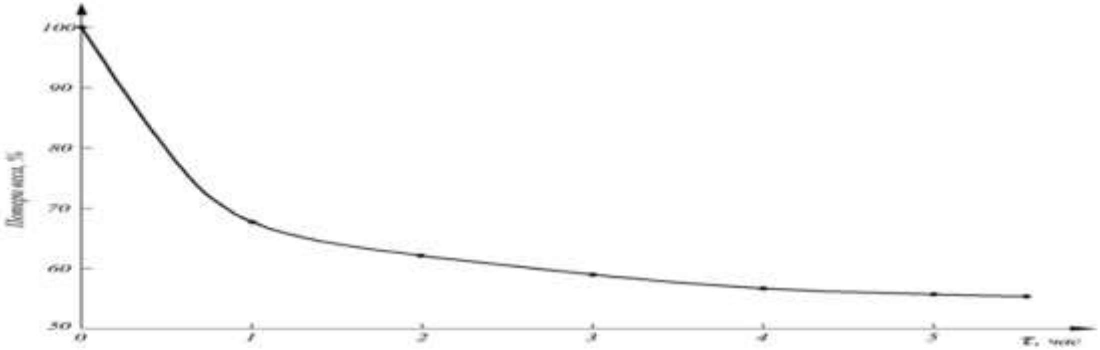


Figure 2. Influence of time on the heat treatment process of the tar-product of gas pyrolysis resin.

As a result, a black liquid substance with a molecular mass of approximately 900-1100 was formed. Its quantity decreased by 45%, and the composition was studied as a result of studying the obtained substance in IRS (Fig. 3).

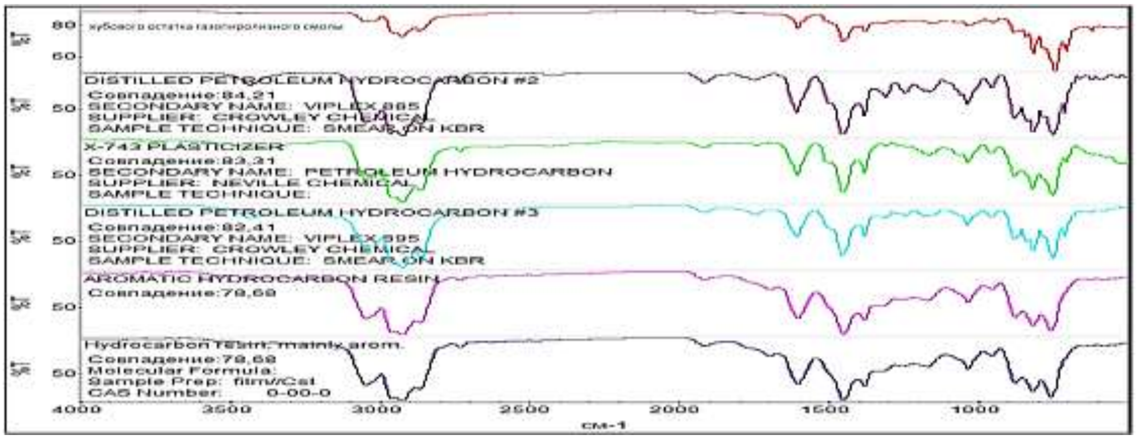


Figure 3. Comparison of the IR spectrum of plasticizers and the cubic residue of gas pyrolysis resin.

The figure shows that the cubic residue of gas-pyrolysis resin is similar in structure to the plasticizer dibutyl phthalate, therefore it can be used as a plasticizer in elastomers and compositions based on them.

To study the influence of the cubic residue of gas-pyrolysis resin on the technological properties of compositions, we selected standard compositions based on elastomers of general - SKI-3, SKMS-30ARKM-15 and special - SKN-18, and for comparison, dibutyl phthalate plasticizer [9,10,11] was used. The main methods for studying the influence of plasticizers on the properties of elastomers are the determination of the glass transition temperature of polymers and their fluidity. Table 2 presents data on the influence of the cubic residue of gas-pyrolysis resin on the glass transition temperature of elastomers, based on deformation measurements and elastic modulus.

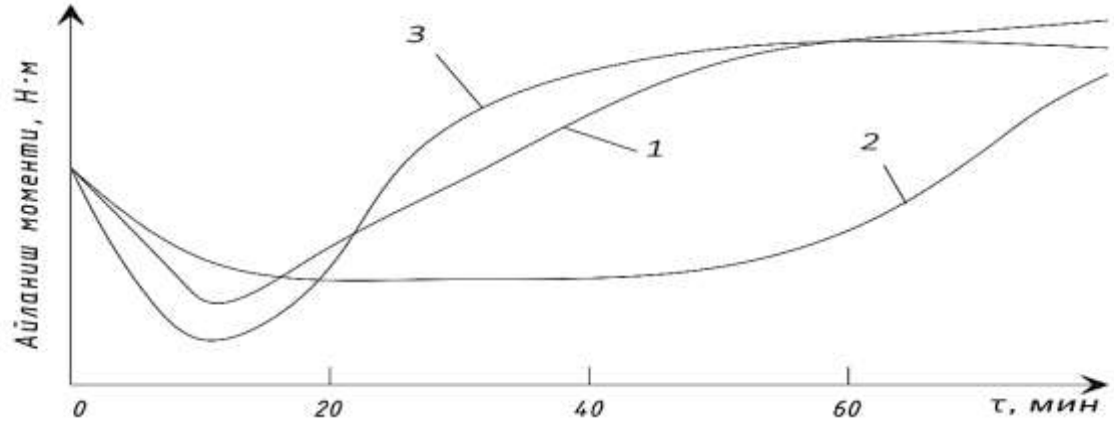
Table 2. Influence of the cubic residue of gas-pyrolysis resin on the glass transition temperature of rubbers.

Name and content of plasticizers, wt.		**Glassing temperature, K**		
		SKI-3	**SKMS-30ARKM-15**	**SKN-18**
0		204	221	218
Dibutyl phthalate	5	201	219	216
	10	198	215	214
	15	190	213	211

Name and content of plasticizers, wt.		Glassing temperature, K		
		SKI-3	SKMS-30ARKM-15	SKN-18
Cubic residue of gas pyrolysis resin	5	199	219	215
	10	197	215	213
	15	189	210	209

The obtained data indicate that as the content of the cubic residue of gas-pyrolysis resin increases, the glass transition temperature of elastomers decreases proportionally. This means that in their presence, rubbers retain their highly elastic properties at lower temperatures compared to non-plasticized rubbers. In this case, a frequency dependence of deformation and the glass transition temperature is observed. The higher the frequency, i.e., the shorter the exposure time, the higher the glass transition temperature of the plasticized system [13].

During the vulcanization process of organomineral compositions based on elastomers plasticized with a cubic residue of gas-pyrolysis resin, the kinetics of sulfur bonding with macromolecules (Figure 4) shows that the formation of the vulcanization grid occurs quite intensively.



Standard prescription-1, 5 mass parts-2 and 10 mass parts cubic residue of gas pyrolysis resin-3.
Figure 4. Kinetics of vulcanization of organomineral compositions based on SKMS-30ARKM-15.

It has been established [14], that the cubic residue of gas-pyrolysis resin contributes to the maximum absorption of sulfur atoms on the surface of the filler particles and thereby affects the formation of stronger vulcanization structures[15]. This effect shows that the cubic residue of gas-pyrolysis resin not only activates but also accelerates the process of vulcanization structure formation in elastomers. The advantage of the cubic residue of gas-pyrolysis resin over dibutyl phthalate is that it has a good effect on the kinetics of mixture vulcanization when the vulcanization process is carried out at high temperatures (Table 3).

Table 3. Influence of plasticizers on the structure of the vulcanization grid and the properties of vulcanizers of the organomineral composition based on SKMS-30ARKM-15 (content of 10 wt. parts per 100 wt. parts of rubber)

Name of plasticizers	Established connections, %				Fp, MPa	CT, 373K, 72 hours
	$-C-S_x-C-$	-C-S-S-C-	-C-S-C-	-C-C-		
The vulcanization temperature of the SKMS-30ARKM-15 composition is 433K, the time is 40 minutes						
Dibutylphthalate	33	32	22	13	10,6	0,75
Cubic residue of gas pyrolysis resin	**20**	**26**	**22**	**32**	**14,8**	**0,94**

As a result, it was established that elastomeric compositions plasticized with the cubic residue of gas-pyrolysis resin have a greater influence on the type, nature, and number of transverse bonds formed during vulcanization, and vulcanizers with higher strength and thermal wear coefficient were obtained compared to the composition plasticized with dibutyl phthalate plasticizer.

4. Conclusion

Based on the obtained results, it can be assumed that the cubic residue of gas-pyrolysis resin plays an important role in the formation of the structure and properties of elastomeric composite materials as a result of interaction with donor-acceptor bonds during the inhibition of thermo-photochemical processes. When studying the aging of composites under the influence of heat during plasticization of the composite with the cubic residue of gas-pyrolysis resin, it was observed that with increasing aging time, compared to the samples stabilized with the stabilizer "Neozon-D," the tensile strength of the composites increases, the relative length during stretching slightly decreases, and the hardness and -C-C- bond in the vulcanization grid increase. As a result of the analysis, it can be confirmed that the active substances contained in the cubic residue of gas pyrolysis resin, under the influence of heat and time, lead to the formation of an additional structure in the composite.

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