GAS PYROLYSIS RESIN AS A PLASTICIZER FOR COMPOSITE ELASTOMER MATERIALS

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Annotation. The aim of the study is to study the effect of gas pyrolysis resin on the properties of elastomeric composite materials. It has been established that in the presence of it in the thiuram vulcanizing system, the relative rate of vulcanization of styrene-butadiene rubber increases, the time to reach the optimum vulcanization decreases, but the degree of vulcanization decreases, proportional to the maximum torque, and when using a sulfur vulcanizing system, it activates the vulcanization process, which is facilitated by the presence in its composition of active functional groups (-OH, -COOH, etc.). It is shown that the tensile strength and relative elongation of the vulcanizates increase, while the elasticity remains at an average level.

Keywords: rubber, glass transition temperature, plasticizer, thermal aging, structure, vulcanization kinetics, elasticity, composition.

Аннотация. Целью исследования является изучение влияния газопиролизной смолы на свойства эластомерных композиционных материалов. Установлено, что при его присутствии в тиурамовой вулканизирующей системе относительная скорость вулканизации стирольно-бутадиеновой каучуки увеличивается, время достижения оптимума вулканизации уменьшается, но степень вулканизации уменьшается, пропорционально максимальному моменту, а при использовании серной вулканизирующей системы активирует процесс вулканизации, что облегчается наличием в ее составе активных функциональных групп (-OH, -COOH и др.). Показано, что прочность на растяжение и относительное удлинение вулканизатов увеличиваются, в то время как упругость остается на среднем уровне.

Ключевые слова: резина, температура стеклования, пластификатор, термическое старение, структура, кинетика вулканизации, эластичность, состав.

Annotatsiya. Ushbu tadqiqotning maqsadi gaz piroliz smolasining elastomer kompozitsion materiallar xususiyatlariga ta’sirini o‘rganishdan iborat.

ISSN 3030-3907

Aniqlanishicha, tiuram vulkanizatsiyalovchi tizimda uning mavjudligi stirol-butadiyen kauchukning vulkanizatsiya nisbiy tezligini oshiradi, optimal vulkanizatsiyaga erishish vaqtini qisqartiradi, biroq vulkanizatsiya darajasi maksimal burovchi momentga mutanosib ravishda pasayadi. Oltingugurt vulkanizatsiyalovchi tizim qo‘llanilganda esa, u vulkanizatsiya jarayonini faollashtiradi. Bunga uning tarkibidagi faol funksional guruhlar (-OH, -COOH va boshqalar) mavjudligi yordam beradi. Tadqiqot natijalariga ko‘ra, vulkanizatlarning cho‘zilishdagi mustahkamligi va nisbiy uzayishi ortadi, elastikligi esa o‘rtacha darajada saqlanib qoladi.

Kalit so‘zlar: rezina, shishalanish harorati, plastifikator, termik eskirish, tuzilish, vulkanizatsiya kinetikasi, elastiklik, tarkib.

Introduction.

Obtaining composite elastomeric materials with a certain set of properties is associated not only with the development of elastomers of various chemical structures, but also with the creation of appropriate structures. One of the main methods of structural modification of elastomeric materials is plasticization. Plasticization of elastomers leads to an improvement in the elasticity of materials, gives them frost resistance, and also facilitates their processing [1–3].

Currently, dibutyl phthalate (DBP) and dibutyl cebatsionate (DBS) are widely used as plasticizers in the production of composite elastomeric materials. However, due to the lack of their production, much attention is paid to finding new opportunities for obtaining plasticizers with new structures and properties.

The purpose of this work is to study the effect of secondary raw materials, the production of polypropylene, on the properties of composite elastomeric materials based on styrene-butadiene rubbers.

Objects and methods of research. The objects of the study are the gas-pyrolysis resin of secondary raw materials, the production of polypropylene, as a standard rubber mixture based on styrene-butadiene rubber. The properties of the gas-pyrolysis resin were studied by physico-chemical methods, IR spectroscopy, and 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 completion of the viscosity measurement by stopping 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). Technical indicators were determined according to the relevant state standards.

ISSN 3030-3907

Results and its discussion. The creation of ingredients for polymeric materials based on raw materials of non-petroleum origin is an important task of modern chemistry of macromolecular compounds. In this regard, of undoubted interest are secondary raw materials for the production of polypropylene gas pyrolysis resin.

Studies show that gas pyrolysis resin is a black, odorless, hard substance (Table 1). It consists mainly of arenes and olefins with 6-12 carbons. The amount of olefins is 23.7%, and arenes are 67.18%. Also, it contains alane, diene, cycloalkanes. Qualitative-quantitative analysis showed the correspondence of the components with the spectra, their number is 90-97%.

Table-1.

Chemical composition of hydrolysate resin

Carbon quantity	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

The gas pyrolysis resin was thermally treated at 270°C for one hour, the weight loss was 50% of the total sample weight. Its number average molecular weight according to gel chromatography is ≈700. The resulting mass (Plasticizer P 125) was investigated by the IR method, the results of which are shown in Fig.1.

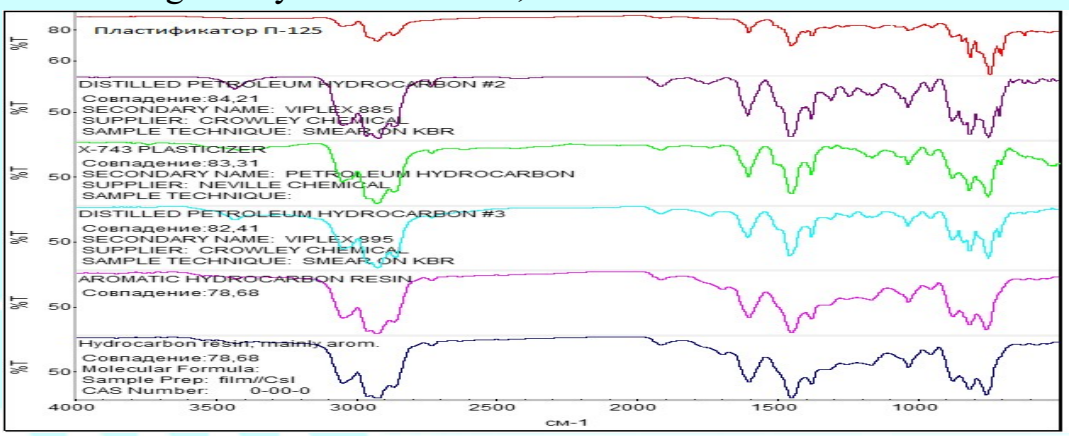


Figure 1. IR spectrum of P 125 plasticizer and plasticizers used in production

ISSN 3030-3907

IR spectroscopic studies show that the structure of P 125 is close to 80-85% of the structures of plasticizers used in the production of composite elastomeric materials. Comparative physical and chemical properties of industrial plasticizers P 125 are given in table 2.

Table-2.

Comparative physical and chemical properties of industrial plasticizers P 125

Manufacturer	**Hansheng**	**Russia**	П 125
Type	**TDAE**	**TDAE**	**TRAE**
Kinematic viscosity at 100 ^{0}C, mm^2/s	17,5-21,5	16,0-23,0	15,3-20,0
Density at 20 ^{0}C, g/sm^3	0,930-0,965	0,927-0,967	0,923-0,934
Refractive index at 50 ^{0}C	1,515-1,545	1,520-1,540	1,5010-1,5110
Aniline point,^{0}C	73±5	68±5	67-72
The content of the PCA extract, % wt.	3,0	3,0	3,0
Sulfur content, % wt.	4.0	3.0	1,72-1,79

The main research methods for determining the plasticizing properties of plasticizers are the determination of the glass transition temperature of polymers and fluidity. Below are data on the effect of P 125 on the glass transition temperature of styrene-butadiene rubber, based on measurements of deformation and elastic modulus (Table 3).

From all the above data, it should be noted that as the content of P 125 increases, the glass transition temperature of styrene-butadiene rubber naturally decreases. This means that in the presence of P 125, styrene-butadiene rubber retains its highly elastic properties at lower temperatures than unplasticized rubber. 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 the glass transition temperature of the plasticized system. The data in the table show that with an increase in the content of P 125, the glass transition temperature of styrene-butadiene rubber can be greatly reduced. In this regard, too much P 125 should not be added to rubber, as this can cause a sharp decrease in the pour point and narrow the temperature range of high elasticity.

Table-3.

Influence of P 125 content on the glass transition temperature of styrene-butadiene rubber.

Name and content of plasticizers, wt.h. per 100 wt.h. rubber.	Styrene butadiene rubber
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DBS	5	219
	10	215
	15	213
P 125	5	219
	10	215
	15	112

It is known [4-6] that plasticizers slow down the formation of vulcanization structures (networks) with various types of cross-links. The effect of P 125 on the kinetics of vulcanization of rubber compounds based on styrene-butadiene rubber was studied (table 4).

Table-4.

Influence of P 125 on the properties of bonds formed in rubber based on styrene-butadiene rubber. (Vulcanization time 40 minutes 416 K, aging 373 K 72 hours).

Name	Formed connections, %				F_p, MPa	C_T, conventional units.
	$-C-S_x-C-$	-C-S-S-C-	-C-S-C-	-C-C-		
Standard Recipe	32	34	24	10	11,2	0,66
DBS	36	29	25	10	8,6	0,61
P 125	29	25	24	22	13,1	0,78

Studies show that the introduction of P 125 into the elastomer composition significantly affects the structuring kinetics. The increase in the rate of structuring may be due to the participation of P 125 in the process of structuring due to functional groups [7-9], which is also evidenced by an increase in the number of cross-links and an increase in the elastic-strength properties of the composites (Fig. 2).

ISSN 3030-3907

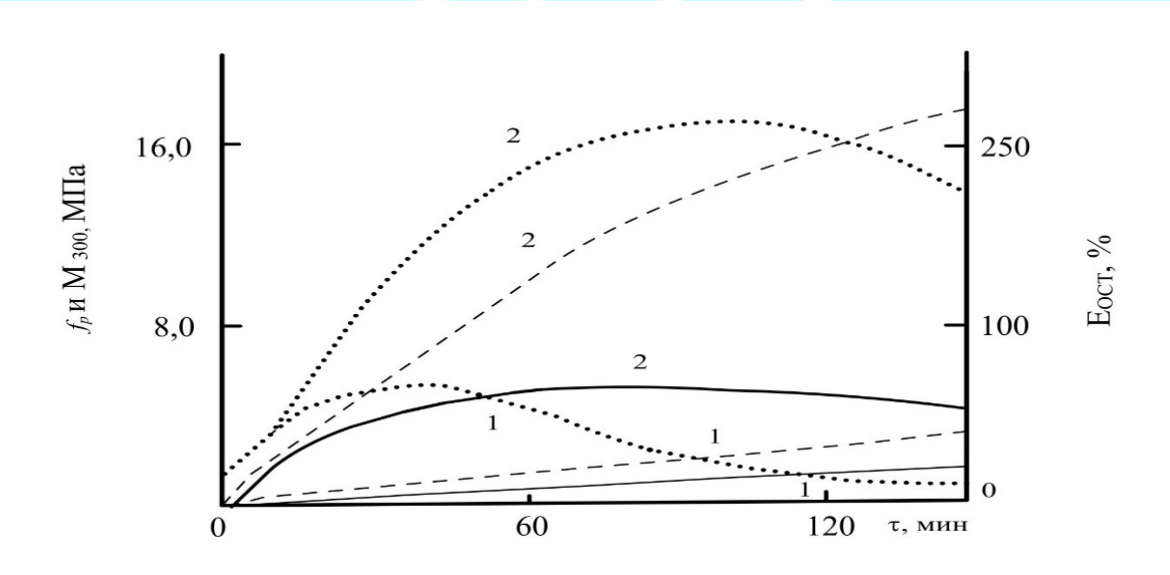


Figure 2. Dependence of the structuring action of rubber plasticizers based on methylstyrene rubber on the duration of vulcanization at a temperature of 428K. Modulus at 300% elongation (M300) (−), ultimate tensile strength (*f*p) (- - -), residual elongation (Erest) (●●●), 10 wt.h. DBS (1) and P 125 (2) per 100 wt.h. rubber.

Simultaneously with an increase in the strength of composites (by 13-17%), there is a decrease in elasticity, residual elongation, and an increase in rigidity. This circumstance can be explained by an increase in the degree of crosslinking and the introduction of P 125 into the composition, which lead to a deterioration in the flexibility of elastomer macromolecules [10, 11]. The equilibrium swelling of vulcanizates with respect to machine oil, gasoline, kerosene, etc. has been studied. and clarified the relative oil and petrol resistance of the compositions.

Conclusion Thus, the study of the behavior of P 125 in rubber compounds and vulcanizates showed that, being a product of a multifunctional action, they exhibit the properties of a plasticizer, at the same time the stickiness of rubber compounds increases, and the strength characteristics of rubbers improve.

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