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INFLUENCE OF PROCESSING CONDITIONS OF LATEX COAGULUM ON PROPERTIES OF ELASTOMERIC COMPOSITIONS ON THEIR BASE

Properties of the latex coagulum formed during the manufacture of styrene-butadiene latices were investigated. Influence of processing conditions on the properties of coagulum polymer compositions was investigated. Plasticizers for latex coagulum improving its handling on the process equipment were selected. Recommendations for the use of plasticized latex coagulum comprising a polymer base rubber compounds have been proposed.

Introduction. The share of raw materials in the cost of rubber products is 60–90%. Therefore the problem of the rational use of secondary products becomes both ecological and technical economical one. It is solved by the increase in the use of recycled materials by means of involving them in a new production cycle.

Butadiene-styrene (ACS) and butadiene-alpha-methyl-styrene (SKMS) rubbers of emulsion polymerization take a significant place in the volume of production of synthetic rubber. When obtaining them, waste is generated at all stages of the process [1–2]. The number of waste reaches 80% of all polymeric waste in production of SR. Their amount is more than 500 tons at the enterprises annually. This waste i.e. – coagulum – is a product of the spontaneous coagulation of the latex. When producing commodity latex, coagulum is formed by uncontrolled coagulation in the form of polymer deposits on the walls of the apparatus at stopping and starting equipment [3].

The main component of coagulum (co-polymer) is characterized by containing a gel fraction (the amount of cross-linked molecules forming three-dimensional structures), reaching 80%. The molecular weight of the soluble part is 300–500 thousand. Loss of mass at drying is up to 20%, which makes it impossible to be used in the composition of the polymer product.

Research is aimed at the selection of the coagulum processing conditions for further their use in the composition of the polymer base for rubber containing composite materials and rubber compounds.

Main part. Latex coagulum formed in the preparation of commodity styrene-butadiene latexes of the following brands: BS-50, BS-65 and BS-85 was used as the object of our research (Table 1). In appearance latex coagulum is a polymeric crumb with cross-linked rigid inclusions. Average value of the mass loss at drying (volatile content) latex coagulum samples taken for testing from ten lots, amounted to 17.2%, ash content was 3.94%.

Table 1

Physical and chemical parameters of styrene-butadiene latex

Latex brand	NTD	Content of dry residue	Content of bound styrene, %
BS-50	GOST 15080–77	47	48
BS-65	TU 38.103550–84	44	65
BS-85	TU 38.103229–84	47	83

Conventional methods for reducing volatiles by means of heating at a constant temperature above 100°C did not lead to the desired results, since in the process of heating (warm-up) an additional structuring of coagulum took place, which was expressed in increasing rigidity up to its sintering. This is due to the presence in the product of non-polymerized monomers and oligomers residues having different temperatures of boiling and bound moisture.

Comparative analysis of the IR spectra of the starting latex and coagulum has shown the presence of peroxy groups in the latter, which promote rapid oxidation of the samples under these conditions of heat treatment.

In this regard, heating samples was performed by smoothly increasing the temperature for 5 hours in a closed apparatus equipped with a paddle stirrer. It was established that during heating for 5 hours under these conditions, the volatile content decreased from 17.2 to 1.5%, the rigidity of the coagulum increasing slightly. When loading a coagulum in apparatus with an initial temperature of 65°C a decrease in the volatile content up to 1.5% occurred within 2 hours.

Removal of the volatiles by this method involves considerable costs of electricity and time. The use of worm-extractors in the automated line has allowed us to improve productivity and significantly reduce the duration of the process. Coagulum, heat-treated on a line at 70°C for 2–5 min, was characterized by content of 1.5% volatiles in its composition, that being impossible to reduce during further thermo-treatment samples by the selected method. Therefore, we used a heat-treated coagulum with humidity of ~ 1.5% as a starting material in our further studies.

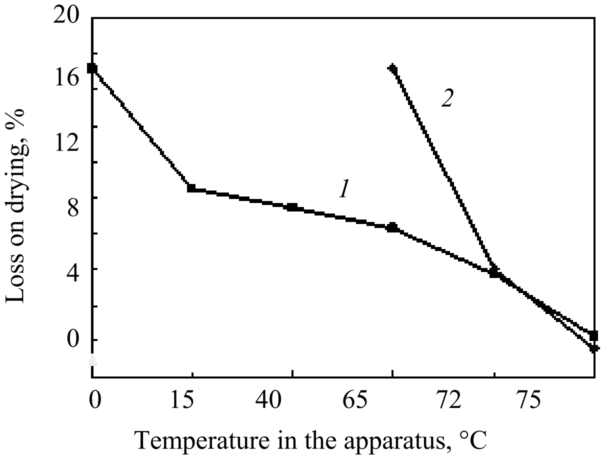

Fig. 1. Dependences of volatiles content in coagulum on treatment temperature: *1* – coagulum loading in cold apparatus, time treatment-5hours; *2* – coagulum loading in heated apparatus, time treatment 2 hours

One method for polymers modifying is plasticization [3] associated with the introduction of these low molecular substances, that improving the elastic and plastic properties. It is well known [3–4] that the condition defining the possibility of practical application of the low molecular weight substance as a plasticizer is its compatibility with the polymer.

Considering conditions of coagulum formation, one can assume the presence of a block of polystyrene, copolymer sites and polybutadiene fractions. Assuming selective effect of plasticizers in relation to different units, we have used petroleum oil PN-6, the industrial oil-1-2A, dibutyl phthalate (DBP) and low molecular polybutadiene (PBN) individually and in combinations as plasticizers [5–7].

Analysis of the spectra of the initial and plasticized coagulum during machining coagulum has shown that the copolymer chains microstructure changes, it being indicated by the change in positions and intensities of the peaks belonging to the groups $–CH_2$ and $–CH_3$ in the wavenumber range 2800–3200 cm^{-1}. During plasticization we observed a change in the structure of the entire area of wave numbers associated with a decrease in the absorption intensity in separate groups of atoms. The efficiency of the plasticizer was evaluated on the behavior of plasticized coagulum during milling (the ability to form a polymeric film on rolls in accordance with scale and the presence of cross-linked inclusions (table 2).

$$\eta \approx \varphi^4 f\left(V_{\text{св}}\right);$$

$$\frac{\eta}{\eta_0} = \varphi^{3,4}\left(\frac{\mu}{\mu_0}\right)\left(\frac{\langle S^2\rangle}{\langle S_0^2\rangle}\right), \qquad (1)$$

where η and η_0 – viscosity of plasticized and unplasticized polymers at a given temperature; φ – the volume fraction of polymer; μ and μ_0 – segmental friction coefficients; $\langle S\rangle$ and $\langle S_0\rangle$ – the rms radii of inertia of plasticized and unplasticized polymers, respectively.

It follows from equation (1) that the bad plasticizer will reduce viscosity more strongly than the good one, since in the latter the size of the macromolecular coil will be larger.

Table 2

Indicators of workability of plasticized coagulum

Sample number	Plasticizer		Workability rating	
	Type	Content	Points	Inclisions
No 1			5	fine
No 2	И-12А	18	4	coarse
No 3	PBN	12	1	coarse
No 4	PBN	18	2	fine
No 5	И-12А : 1PBN = 1 : 1	12	2	Fine
No 6	И-12А : PBN = 1 : 2	18	5	very fine
No 7	И-12А : PBN = 2 : 1	18	3	very fine
No 8	И-12А : PN-6 = 1 : 1	12	4	absent

* 1, doesn't form a film, crumb; 2 – doesn't form a film, loose flakes; 3 – forms a film, adheres, 4 – forms a film, quickly destroys; 5 – forms a film

This approach was adopted by us in the analysis of the influence of plasticizers on the change in viscosity of the samples according to Mooney. It has been established that plasticizers, which improve the processing of coagulum on the rollers, provide higher values of Mooney viscosity (Table 3).

Table 3

Mooney viscosity (conv. units.) Plasticized coagulum

Number of tests	Time of rest, hours			
	0	24	48	120
No 1	4	10	6	8
No 2	6	12	10	9
№ 3	2	3	3	5
No 4	2	2	2	2
No 5	2	10	12	16
No 6	6	12	12	15
No 7	4	4	6	9
No 8	2	16	22	24

Polymer compositions with rubber SCS 30ARKM-15 in ratio of 30 : 70 were manufactured on the basis of plasticized coagulum (8 samples) [8]. Analysis of test results of obtained compositions (Table 4) has shown that the introduction of plasticizers causes an increase in the volatile content in compositions with 1.5% in the initial coagulum and to 2.3–5.2% in plasticized ones.

Mooney viscosity of the compositions is determined by the viscosity of the plasticized coagulum (Table 3).

During the rest process under normal conditions an increase in the Mooney viscosity of plasticized coagulum number 5 and 8 was noted which was connected, apparently, with the prevalence of molecular plasticization over structural one in the course of time.

Table 4

The properties of the polymeric compositions of plasticized coagulum with the rubber SCS 30ARK (30 : 70)

Test numbers	Δ*, %	Ashes, %	Mooney viscosity conv, units
No 1	3.94	3.17	31
No 2	2.31	5.49	30
No 3	4.92	5.51	16
No 4	5.19	5.15	14
No 5	4.91	3.26	31
No 6	2.61	5.82	27
No 7	2.62	5.84	28
No 8	3.67	4.78	35

* Losses of mass at drying at 105°C.

Rubber mixtures filled according to the standard recipe of rubber of SCS 30ARKM-15 on the basis of the obtained polymer compositions were made. Analysis of vulcanized plast-elastic properties of the rubber mixes and physical-mechanical indexes of vulcanizates has shown (Table 5) that the use of experimental compositions as polymer base determines sufficiently high Mooney viscosity and torque at rheometer test, a short time (about 2 minutes) curing start, which may lead to a deterioration in the processing of rubber compounds and require adjustments to the formulation of rubber mixtures.

Table 5

Results of tests of rubber compounds and rubber based on plasticized coagulum with rubber SCS 30ARK (30 : 70)

Names of indexes	Sample numbers							
	No 1	No 2	No 3	No 4	No 5	No 6	No 7	No 8
Mooney viscosity, conv. units	84	68	76	72	72	74	70	70
Monsanto rheometry, 155°C								
Minimum torque	38	30	36	35	34	30	34	36
Maximum torque, dH ·m	146	191	130	172	149	114	158	148
The starting time of vulcanization, min.	1.8	1.5	1.7	2.0	1.7	2.0	2.0	1.7
Optimum of vulcanization, min	19.5	12.2	19.5	20.6	19.2	10.0	18.0	18.7
Rate of vulcanization, dH · m/min	5.7	7.2	5.6	5.9	5.7	12.5	6.2	6.1
Physical mechanical indexes, , 155°C × 20 min								
The conventional stress at elongation at 100% MPa	3.6	6.6	2.9	4.8	4.0	5.1	4.8	4.6
The conventional stress at elongation at 200% MPa	8.0	–	7.7	10.8	8.4	–	10.2	8.8
Conventional tensile strength, MPa	9.3	6.8	9.5	11.3	11.0	9.0	11.5	11.2
Relative elongation, %	231	105	224	206	249	166	233	248

It is noted that the use of the plasticized coagulum in the composition of the polymer base provides conventional tensile strength at 11 MPa and relative elongation of 250%, which complies with the control of some rubber products. Polymeric compositions can be used in the formulations of such products to reduce their prime cost.

Conclusion. Thus, the possibility of producing polymer compositions based on the treated latex coagulum and their use in the composition of the polymer base of industrial rubber products has been shown. It is noted that samples based on polymer compositions with coagulum, plasticized by combination of petroleum oils "paraffin-naphthenic aromatic" have the best combination of properties of rubber compounds and rubbers.

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