Application Features of Caprone Fibrous Filler in Production of Emulsion Polymerized Rubbers

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Abstract

It has been demonstrated that introduction of caprone fibre in SKS-30 ARK latex makes it possible to reach its uniform distribution in the polymeric matrix and to increase a yield of coagulum. The availability of interfacial interaction between the surface of the fibre and styrene butadiene rubber matrix has been found. The introduction of caprone fibre makes it possible to enhance the vulcanizate resistance to heat ageing, repeated strains, and tear.

INTRODUCTION

Basic research into application of formed waste and by-products in composite mixtures for various purposes is under way in recent years. However, many waste products have not found a qualified application up to now [1, 2]. Among these are also fibrous wastes that are formed in abundance at textile manufacturers, in sewing workshops, *etc*. In this relation, a search for most promising directions of their application is of great practical value [3, 4].

Fibrous fillers are commercially introduced in large quantities into polymers on rollers during the process of preparation of rubber stocks [3, 5], which imparts the required rigidity to them and enhances their strength indices. However, this introduction of fibrous filler prevents from attaining its uniform distribution in the bulk of the rubber stock, which reflects on physicomechanical indices of the vulcanizate later on.

Consequently, the research in the directions that will allow solving the problem of a uniform distribution of fibrous filler in the bulk of a polymeric composition with minimal technical and economic expenses will be promising. One of these directions is introduction of fibrous filler in the polymer at the latex stage in manufacturing emulsion-polymerised rubbers.

The purpose of this work is to study the influence of admixtures of caprone fibre that is introduced into latex of styrene butadiene rubber (SBR) of an SKS-30 ARK type, on the process of its extraction from latex and also on rheological and vulcanizing characteristics of rubber, rubber stocks, and physicomechanical indices of the vulcanizate.

EXPERIMENTAL

We have found in our works [6–8] that it is advisable to introduce fibrous filler with water solution of sulphuric acid at the final stage of the process of rubber separation from latex.

This process was studied in a laboratory set-up that consisted in a container that was equipped by an agitator and placed in a thermostat to maintain a specified temperature. 20 ml of latex were loaded into a coagulator (the solid residue of ~18 mass %) and held in

TABLE 1

Influence of the content and the length of caprone fibre on the completeness of SKS-30 ARK latex coagulation with the various consumption of sodium chloride

Consumption	Fibre content, mass parts per 100 mass parts of rubber															
of NaCl,	0	0.1			0.3			0.5			0.7			1.0		
kg/t of rubber	Fibre length, mm															
	0	2	5	10	2	5	10	2	5	10	2	5	10	2	5	10
25	8.9	10.6	9.5	11.4	10.5	10.1	12.9	9.9	9.8	10.7	11.4	9.72	9.8	10.5	9.2	11.4
50	21.4	21.1	19.8	23.0	21.4	22.1	20.5	20.6	20.1	21.0	22.5	20.7	22.7	24.1	21.4	22.4
75	32.8	31.0	28.8	32.4	31.3	30.0	34.0	32.7	33.0	28.2	28.2	29.1	36.0	31.6	29.4	31.1
100	62.7	40.1	38.4	42.2	40.0	41.2	41.9	38.8	35.7	41.8	43.6	39.4	40.8	44.6	42.4	39.9
125	80.6	82.2	85.8	85.3	82.6	88.5	87.0	86.0	90.1	89.6	85.2	86.2	90.2	84.8	83.6	88.3
150	93.4	94.0	93.4	93.6	94.7	97.0	94.5	99.6	99.4	99.8	95.0	96.6	98.3	94.2	94.1	95.8

thermostatically controlled unit at a required temperature over the course of 10–15 min. Fibrous filler was introduced into the latex at the final stage of the extraction process with sulphuric acid solution. Coagulation was conducted with 24 % water solution of sodium chloride; the coagulation pH was kept a constant (≈2.0) in all cases by way of 1–2 % water solution of sulphuric acid introduced.

The experiment was conducted in two stages.

At the first stage, we studied the influence of the caprone fibre content and length on the process of rubber separation during its combined addition with sulphuric acid solution into the latex, as well as on the properties of rubber stocks and the vulcanizate. The length of the introduced caprone fibre was 2, 5, and 10 mm, and the content was 0.1, 0.3, 0.5, 0.7, 1.0 mass parts per 100 mass parts of rubber.

At the second stage, we investigated kinetics of vulcanizate swelling in heteropolar solvents with the aim to confirm interfacial interaction of the caprone fibre with the rubber matrix.

Interfacial interactions for vulcanizates with caprone filler were evaluated based on equilibrium swelling degree α_{max} and on kinetic constant k of swelling of samples in solvents.

RESULTS AND DISCUSSION

The examination of the experimental data has demonstrated that the introduction of fibrous caprone filler in a sulphuric acid solution with the consumption of sodium chloride being from 25 up to 150 kg/t of rubber (Table 1) exerts no negative effect on the process of rubber separation from latex. It should be remarked that the content and the length of fibrous filler in the studied intervals have no effect on technical and economic indices of this process. However, the introduction of a fibre at a ratio of more than 1 mass part per 100 mass parts of rubber involved difficulties because of an increase in the viscosity of the system (sulphuric acid solution + fibre). Gain in the yield of coagulum is caused, apparently, by a decrease of the losses that are related to the entrainment of a fine-dispersed rubber chip with serum, with washing waters [9], as well as owing to fibrous filler that is present in the formed coagulum.

Later on, rubber stocks and vulcanizates around them have been prepared on the basis of the produced coagulum with a various content of caprone fibre.

Tests were conducted according to the All-Union State Standard GOST 15627–79 requirements for SKS-30 ARK rubber with reference to a standard sample.

It is evident from the data given in Tables 2 and 3 that the presence of caprone fibre in amounts of 0.3–0.7 mass parts per 100 mass parts of rubber and 2–10 mm in length produces an insignificant increase in the Mooney plasticity (from 55 to 55–58 for rubber, and from 57 to 58–60 units for rubber stock) and to an increase of minimal rotation torque from 4.8 (in the standard sample) to 7.0–8.5 N · m.

TABLE 2

Properties of raw rubber and rubbers on the basis of SKS-30 ARK that is filled by caprone fibre

Index	Reference sample (without admixtures)	Fibre length, mm					
		2		5		10	
		Content, mass parts per 100 mass parts of the rubber					
		0.3	0.7	0.3	0.7	0.3	07
Mooney plasticity ML (1 + 4) (100 °C), arb. units:							
of the raw rubber	55	57	56	55	57	57	57
of the rubber stock	57	59	58	59	58	58	60
Karrer plasticity of the rubber stock, arb. units	0.34	0.33	0.34	0.33	0.36	0.34	0.34
Reducibility, mm	1.4	1.3	1.2	1.4	1.2	1.3	1.3
Conventional stress at 300 % elongation, MPa	9.4	5.6	7.1	6.1	6.6	5.9	6.0
Conventional tensile strength, MPa	26.3	29.0	23.0	23.1	23.0	23.0	20.5
Breaking elongation, %	618	680	610	670	640	670	650
Relative permanent deformation, %	12	16	14	14	14	14	14
Rebound resilience (in %) at a temperature of, °C:							
20	40	38	42	40	42	40	43
100	53	50	52	52	50	50	50
Shore hardness *A*, arb. units	57	57	57	54	55	56	57
Tear resistance, kN/m	53	89	90	81	85	66	73
Resistance to multiple stretching (thousand cycles)	70	78	82	93	73	76	78
Ageing coefficient (100 °C, 72 h):							
with respect to strength	0.44	0.65	0.67	0.72	0.69	0.80	0.96
with respect to relative elongation	0.33	0.46	0.40	0.40	0.41	0.45	0.54

Note. Vulcanization temperature 143 °C, optimum time for vulcanization 60 min.

The decrease in the reducibility of the rubber stock from 1.4 (without fibre) to 1.2 mm (with the fibre) (see Table 2) is caused by the fact that caprone fibres that are more compatible with SBR are oriented within the rubber stock matrix in the direction perpendicular to the direction of the applied load (calender effect). Presence of admixtures of fibrous filler limits the scatter of magnitude of the rubber stock plasticity within the range of 0.33–0.36 units.

It appears that owing to adsorption of some part of the components of a vulcanizing group by the surface of fibres for the vulcanizates with caprone fibre, a decrease of the optimum time for vulcanization from 27.5 (for a standard sample) to 15–21 min, as well as loss in strength and stress at 300 % elongation has been noted as compared to vulcanizates without a fibre owing to a smaller crosslinking degree (see Table 3).

TABLE 3

Vulcanization rheogram for rubber stocks on the basis of SKS-30 ARK rubber that is filled by caprone fibre

Index	Reference sample (without admixtures)	Fibre length, mm					
		2		5		10	
		Content, mass parts per 100 mass parts of the rubber					
		0.3	0.7	0.3	0.7	0.3	0.7
Minimal rotation torque, N · m	4.8	8.5	7.5	7.0	7.5	7.5	7.0
Maximum rotation torque, N · m	36.5	31	34	32	34	32	32
Time of the vulcanization beginning, min	3.5	5	5	4	5	4	5
Time of an optimum vulcanization, min	27.5	21	20	21	19	15	21

Essential increase in tear resistance from 53 to 66–90 kN/m and in resistance to multiple cyclic deformations with 5–10 mm long fibres to 93 thousand cycles (up to 15 %) is attributable to the manifestation of reinforcing effect that has been revealed before for the vulcanizates that were filled by fibres at a stage of rubber mixing [10].

Growth of ageing resistance (100 °C, 72 h) is related apparently to the completion of the vulcanization process as a result of desorption of the components of vulcanizing group from the surface of the fibres.

Hence, the influence of the caprone fibre content on rheological and curing behaviour of rubber, rubber stock, and on service properties of rubbers has been revealed. Based on the above, an assumption is possible about the manifestation of interfacial interaction of the raw rubber (filled rubber) matrix with the surface of caprone fibre that is introduced at the stage of rubber separation from latex.

To provide support to this hypothesis, kinetics of vulcanizate swelling in heteropolar solvents has been examined at the second stage, and interfacial interactions has been estimated from the equilibrium swelling degree α_{max} and kinetic constant k of swelling of samples in solvents (Table 4).

It has been found that irrespective of the fibre content, α_{max} increases from 120–140 to 243–276 and 514–550 mass % respectively with increasing polarity of solvents: octane, toluene, and chloroform with the respective solubility parameters δ 15.4, 18.2, 18.8 $MJ^{0.5}/m^{1.5}$ [11]. The maximum value α_{max} of the vulcanizate with the fibrous filler in chloroform is suggestive of an increase in the polarity of the vulcanizate and of its solubility parameter approaching to that for chloroform (18.8 *vs.* 17.4 $MJ^{0.5}/m^{1.5}$ for the initial rubber) owing to added fibre and to the cross-linking grid.

The apparent motive power that is determined by the magnitude α_{max} exerts no effect on the swelling rate.

Distinction in thermodynamic compatibility of solvents and of SBR vulcanizate with the fibre has defined its swelling rate.

The vulcanizate–octane system with a greater magnitude of the compatibility parameter $\beta = (\delta_{vulc} - \delta_{solv})^2$ [12, 13] that is equal to 4–12 MJ/m^3 features a smaller swelling rate (k = 0.97–1.54 h^{-1}). For the systems vulcanizate–toluene (or chloroform) with β = 0.4–2.0 MJ/m^3, the swelling rate shows an increase (k = 0.84–2.25 h^{-1}).

It appears that the increasing swelling rate in chloroform with an increase in the content of caprone fibre from 0.3 to 0.7 mass parts per 100 mass parts of rubber is controlled by "the conductivity effect" that creates "vulcanizate–caprone" boundary layer. This layer is made up of products of the interaction of the modified surface of polyamide (δ_{PA} = 27.8 $MJ^{0.5}/m^{1.5}$) with polar low-molecular-weight compounds that are inherent in rubber (for example, fat and abietic acids) by the onium mechanism [13] owing to a high contribution of hydrogen bonds in the presence of chloroform [11].

TABLE 4

Influence of solvent nature, of sizes and content of caprone fibre admixtures on the equilibrium degree (α_{max}, %) and the swelling rate (k, h^{-1}) of vulcanizates based on SKS-30 ARK

Fibre length, mm/ content, mass parts per 100 mass parts of the rubber	*n*-Octane		Toluene		Chloroform	
	α_{max}	k	α_{max}	k	α_{max}	k
2/0.3	140	−1.38	272	−1.73	550	−1.38
5/0.3	142	−0.97	276	−1.73	525	−1.38
10/0.3	134	−1.19	252	−1.20	520	−1.66
2/0.7	128	−1.73	270	−1.73	540	−2.14
5/0.7	120	−1.43	243	−0.84	514	−2.25
10/0.7	122	−1.54	262	−0.93	524	−1.96

For toluene, with a small contribution of hydrogen bonds, a decrease of magnitude k with an increase in the content of caprone fibres has been revealed because of the manifestation of barrier characteristics by the boundary layers with high polarity.

CONCLUSIONS

Thus, the following results have been obtained during the performed research:

– It has been found that additional introduction of caprone fibre provides the enhanced yield of coagulum in the investigated intervals of the content and length.

– It has been demonstrated that caprone fibre that is introduced at the stage of latex coagulation makes it possible to reach its uniform distribution over the bulk of rubber, which reflects on certain properties of the obtained vulcanizates.

– Deviations of rheological, curing behaviour and of physicomechanical indices of vulcanizates that incorporate caprone fibres with a modified surface have been explained.

– The availability of interfacial interaction between the surface of caprone fibre and the matrix of styrene butadiene rubber and vulcanizate on its basis has been revealed.

– The influence of the fibre length and its content in the interval of 2–10 mm and 0.3–0.7 mass parts per 100 mass parts of rubber on the viscosity of rubber and of rubber stock has been found.

– It has been noted that the introduction of caprone fibre allows certain indices of vulcanizates to be enhanced, such as the resistance to heat ageing, to repeated strains, and to tear resistance.

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