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FIBROUS MATERIALS AS TECHNOLOGICAL ADDITIVES IN THE PRODUCTION OF BUTADIENE-STYRENE RUBBERS AND ELASTOPLASTICS

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Received: November 26, 2007

Abstract. Prospects of recycling of waste products of fibrous materials (cotton, viscose, kapron) for obtaining of elastic composite materials are shown by creation of fibre-latex composition with subsequent coagulation and vulcanization of the filled rubber. The optimum contents of the fibre and its length is determined.

Key words: composition, rubber, fibre, latex, vulcanizate.

1. Introduction

Preservation of the environment is one of the major problems of mankind. It is connected to increase in extraction and processing of natural resources. Growth of industrial potential is accompanied by formation of a significant amount of waste products. Only 1/3 part of the extracted raw material is used to produce target industrial output; the rest 2/3 make waste products and by-products. An increased technological load on nature has caused a line of ecological problems.

The last years saw the heightened interest to fibres – fillers whose raw materials base is huge. Waste products of fibrous materials manufacturing are in plenty accumulated at textile factories and enterprises of clothing industry: tangled fibres, ends of yarns and strings, rags, offcuts, combings and artificial fur waste, *etc.* [1, 2]. Therefore an actual technical task is the search for the most perspective directions in application of waste products of fibrous materials [1].

Textile waste products are used in various industries. Strongly littered cotton fibrous waste products staunch oil wells at drilling. Rags and scraps can be used in the manufacturing of roofing felt and other roofing materials. Hardly utilizable lining materials are used like cotton wool as fillers in building materials manufacturing, particularly as warm and soundproof basis under linoleum [3].

As it was reported in works [4, 5], fibrous fillers were introduced on rollers during preparation of rubber mixes. Thus rubber mixes got necessary rigidity and durability; the vulcanizates parameters were enhanced.

However such technology of fibrous filler introduction did not allow to achieve uniform distribution of the filler in the rubber mix volume, which affected physicomechanical parameters of the vulcanizates. In addition to this introduction of fibrous filler on rollers required additional energy consumption.

Therefore the following way of obtaining of the fibre-filled rubbers seems more promising:

1. preliminary introduction of a fibre in latex;
2. subsequent coagulation of the latex filled with a fibre to obtain fibre-filled rubber;
3. preparation of a rubber mix from the rubber with its further vulcanization.

The purpose of this work is studying of the influence of cotton, viscose, and kapron fibres entered into latex butadiene-styrene of rubber SKS-30 ARK mark on the process of coagulation, as well as on the properties of rubber, rubber mixes, and their vulcanizates.

2. Experimental

The process of rubber obtaining from latex was studied using coagulator, representing by itself a vessel with stirring device, into which 20 ml of latex SKS-30 ARK (the dry residue ~ 18 %) was loaded. The coagulator was thermostated for 15-20 minutes at 333 K. After that 24 % water solution of coagulant – sodium chloride – was added. The coagulation process was finished by adding of 1–2 % water solution of sulfuric acid up to pH \approx 2.0–2.5. The obtained deposit (coagulum) was separated, washed, dried in a desiccator at 353–358 K and weighed. The weight of formed coagulum was calculated from the dry residue of initial latex. Afterwards possible presence of the small dispersed crumbs of coagulum (or so called in the synthetic rubbers industry “serum”) in the filtrate was visually defined.

Fibrous fillers (cotton, viscose, kapron) were entered into the latex at different stages of the coagulation process:

- in a dry state before adding coagulant to latex;

- moistened with water before adding coagulant to latex;
- in a tall soaps solution;
- simultaneously with the coagulant as water-salt dispersion;
- simultaneously with the sulfuric acid solution as water-acid dispersion.

The length of a fibre (2; 5 and 10 mm) and its amount (0.1–1.0 % calculated from the rubber weight) were changed during experiments.

Swelling kinetics of vulcanizates filled with different fibres was studied in solvents of various polarities by the following technique. Square-shaped (1δ1 cm) samples were cut out and then weighed. The number of the samples for each series of measurements was 5. The samples were placed in solvents for 8 h. Each hour they were taken out, weighed and their geometrical sizes were measured. The last measurement was in 24 h. Then the obtained data were processed:

- to find the swelling degree a (wt %) the weight of an initial sample was subtracted from weight of swelled sample; the obtained solvent weight was divided by the initial sample weight and multiplied by 100 %; the greatest (equilibrium) value a_{max} was chosen from the five obtained results for each sample;

- a constant of swelling velocity was found by the following formula

$$k = (1/t) \cdot \ln \left[\frac{a_{max}}{a_{max} - a_t} \right]$$

where t – time, h; a_t – current swelling degree in time t .

3. Results and Discussion

3.1. Influence of introduction method, amount and size of filler on latex coagulation process

At the first stage of experiments some kinds of fibrous filler treatment before its mixing with latex of butadiene-styrene rubber SKS-30 ÀÊ were investigated. The size of fibres and their dosages were maintained as 2 mm and 0.5 wt % calculated of rubber weight, respectively. Fibrous filler was introduced into rubber by five various methods:

1. Dry filler without preliminary treatment. The filler was introduced directly into latex and mixed for 15–20 min. Then the latex was coagulated using the above-mentioned technique.

2. Moistened with water filler. The filler was immersed in a small amount of water for 5 min at the temperature of 293 K so that it was only moistened. The damp filler was introduced into latex and mixed for 15–20 min. Then the latex was coagulated.

3. Moistened with a tall soaps solution filler. The filler was immersed in a small amount of 5 % water solution of tall soaps for 5 min at the temperature of 293 K so that it was only moistened. The damp filler was introduced into latex and mixed for 15–20 minutes. Then the latex was coagulated.

4. Filler with a coagulant solution. To prepare such coagulation mix fibrous filler was introduced into a coagulant solution (24 % sodium chloride), which was taken in the volume necessary for coagulation and mixed for 15–20 min. Coagulation of latex was carried out using coagulation mix (fibre + sodium chloride solution).

5. Filler with a solution of an acidifying agent (2 % sulfuric acid). Preliminary fibrous filler was immersed into sulfuric acid solution, which was taken in the quantity necessary for latex coagulation and mixed for 15–20 min. Then the obtained mix (fibre + sulfuric acid) was used as an acidifying agent, and coagulation was carried out by the standard technique.

Uniformity of fibres distribution in polymer was investigated by the following technique. A sample of latex with fibrous filler was placed on glass and dried up in a desiccator until formation of a latex film with fibre inclusions. The sample was examined using an optical microscope; the morphology being fixed with the help of a camera. Moreover, an estimation of the fibre distribution in the matrix was carried out according to shears of coagulum formed after latex coagulation.

In the samples with the fibre introduced without any preliminary treatment, *i.e.* dry, or only moistened with water, no positive effect consisting in fibre uniform distribution in the latex matrix was observed. Dry fibres in latex were tangled. They formed agglomerates which adhere to the stirrer later on. Moistened fibres were also non-uniformly distributed in the matrix, forming lumps.

Introduction of fibre dispersion with tall soaps solution more favorably influenced the distribution uniformity of a fibre in the latex volume. The fibres settled separately from each other in the sample without accumulations.

Introduction of fibrous filler with coagulant resulted in almost uniform distribution of filler, although some accumulations of fibres in the sample were found.

Investigation of the sample in which fibres were introduced simultaneously with sulfuric acid showed uniform distribution of fibres in the volume. Fibres settled separately from each other and no accumulations of fibrous filler in the matrix were observed.

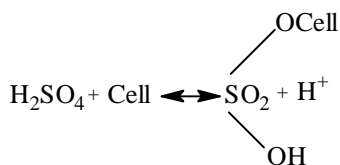
Thus, it is possible to conclude that introduction of dry or moistened with water fibre is not expedient and such methods of composite materials preparation were not used in the further researches. The following most efficient methods of fibrous filler treatment were chosen: filler moistened with 5 % tall soaps solution, filler introduced with coagulant (24 % solution of sodium chloride) and

filler with 2 % solution of sulfuric acid. It should be noted that preliminary treatment of a fibre by tall soaps solution is accompanied by additional expenses.

Introduction of a fibre simultaneously with coagulant or acidifying agent is the most technologically promising direction. Thus, experiments with addition of sulfuric acid on the one hand showed increase of the coagulum yield and on the other hand – uniform distribution of a fibre in the volume of formed crumb as compared with the experiment when fibre was introduced simultaneously with coagulant.

Dependences of coagulation completeness of SKS-30 ARK latex upon the various methods of fibres introduction with various amounts of sodium chloride are presented in Table 1.

Positive effect observed at introduction of cotton fibre simultaneously with sulfuric acid can be explained by the fact that the basic component of the given fibre – cellulose (Cell) is capable to form sour ethers of the following structure with sulfuric acid:



The mentioned reaction is reversible because ethers of sulfuric acid and cellulose are easily hydrolyzed. Thus in a water solution there will be a balance between sulfuric acid and cotton fibre containing up to 98 % of cellulose. This phenomenon, most likely, also promotes more uniform distribution of the given fibrous filler in a volume of acidifying agent. Based on the above-mentioned facts it is possible to assume that the coagulation mechanism at additional introduction of cotton fibre into the acidifying agent is more complex and requires deeper additional studies.

The similar positive effect can be explained in the case of viscose fibre with sulfuric acid introduction. Indeed, during obtaining of viscose fibre from cellulose xanthate the decomposition of xanthate takes place with

–OH groups release and reduction of significant number of cellulose cyclic parts up to glucopyranose, which is typical for cotton fibres also.

Taking into account obtained results, the dependence of the coagulation process upon the amount of cotton, viscose or kapron fibre treated with sulfuric acid and introduced into latex at coagulation final stage was investigated. The fibre contents in rubber were 0.1; 0.3; 0.5; 0.7; 1.0 wt %. The obtained data are presented in Tables 2-4.

The the experimental data analysis has shown that application of fibrous filler during obtaining of rubber from latex slightly increases coagulum yield. Apparently, it is connected with two reasons: (i) reduction of coagulum losses, connected with rubber crumb carry-over together with serum; (ii) introduction of fibrous filler into coagulum.

Serum was investigated by the filtration method. The results showed the absence of fibrous filler in it, which proves that the fibre was fully captured by the formed crumb of rubber.

The best results were obtained for the fibre volumes within the range from 0.3 to 0.7 % calculated of the rubber weight.

The results showed the optimum length of cotton, viscose and kapron fibre is 2–5 mm. The change of fibre length within this interval insignificantly affects the weight change of the selected coagulum.

It is visually noted that separated from rubber serum contains rubber fine crumb in less amount than rubber in control tests without application of fibrous fillers. This allows:

- to reduce the rubber losses with sewage and thereby to increase the productivity of the technological process;
- to reduce the ecological loading of treatment facilities.

However the final conclusion about the size of fine crumb losses can be made after manufacturing application because industrial technological process can not be exactly reproduced under laboratory conditions.

Table 1

Influence of various method of fibres (2 mm) introduction on coagulation completeness (wt %) of SKS-30 ARK latex with various amounts of sodium chloride

The amount of sodium chloride, kg/t of rubber	The content of the formed coagulum at various introduction methods, wt %									
	Without a fibre (control)	Preliminary treated by a tall soaps solution			With coagulant			With acidifying agent		
		cotton	viscose	kapron	cotton	viscose	kapron	cotton	viscose	kapron
25	8.93	13.58	11.77	9.22	8.73	9.97	9.01	11.51	10.63	10.89
50	21.37	19.64	19.58	22.13	15.53	22.87	18.94	19.72	21.77	22.63
75	32.78	28.86	34.02	31.25	25.87	22.97	24.47	29.37	31.47	32.65
100	62.71	40.29	47.67	41.11	40.33	43.20	38.11	45.90	46.62	46.81
125	80.63	79.61	77.83	78.75	68.85	82.84	75.45	79.82	79.61	84.91
150	93.41	94.05	94.62	90.52	92.53	90.21	88.21	97.54	95.76	99.60

Note: fibres content is 0.5 wt % of rubber; tall soaps solution (5 %); coagulant – sodium chloride solution (24 %); acidifying agent – sulfuric acid (2 %).

Table 2
Influence of content (wt %) and length (mm) of the cotton fibre introduced with acidifying agent on coagulation completeness (wt %) of SKS-30 ARK rubber from latex with various amount of sodium chloride

The amount of sodium chloride, kg/t of rubber	Fibre content, wt %																	
	0 %			0.1 %			0.3 %			0.5 %			0.7 %			1.0 %		
	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm
25	8.93	11.14	12.65	12.14	12.15	12.56	12.29	11.51	13.39	11.89	13.20	12.78	13.26	12.64	11.75			
50	21.37	20.36	21.02	19.73	20.50	20.78	19.91	19.72	21.40	20.99	20.85	23.68	20.31	23.11	21.02			
75	32.78	31.37	30.21	29.44	29.30	31.49	28.74	29.37	31.56	28.78	29.66	32.05	29.17	31.93	30.14			
100	62.71	42.49	40.97	40.80	45.70	43.45	40.16	45.90	41.69	42.26	45.48	41.67	45.12	41.26	39.53			
125	80.63	88.12	80.16	75.12	87.50	76.51	75.50	79.82	73.85	76.12	88.13	75.92	78.11	80.32	76.48			
150	93.41	96.00	95.24	93.85	95.60	97.78	94.30	97.54	97.13	95.92	95.12	97.98	95.94	95.09	95.43			

Table 3
Influence of content (wt %) and length (mm) of the viscose fibre introduced with acidifying agent on coagulation completeness (wt %) of SKS-30 ARK rubber from latex with various amount of sodium chloride

The amount of sodium chloride, kg/t of rubber	Fibre content, wt %																	
	0 %			0.1 %			0.3 %			0.5 %			0.7 %			1.0 %		
	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm
25	8.93	12.60	11.02	9.26	12.60	9.94	7.68	10.63	10.01	8.08	9.44	10.03	9.76	11.70	11.58	10.69		
50	21.37	23.08	22.79	20.38	29.50	20.93	20.65	21.77	20.97	19.87	21.52	23.33	20.89	20.34	22.33	17.77		
75	32.78	31.57	28.29	32.14	29.76	30.96	30.42	31.47	31.61	30.42	33.71	30.22	34.16	29.07	28.82	26.91		
100	62.71	44.31	43.65	42.40	46.67	46.13	39.50	46.62	39.67	37.89	45.29	46.89	42.28	44.38	41.30	37.68		
125	80.63	83.55	84.93	89.18	92.59	92.67	81.63	79.61	84.82	83.94	86.34	85.67	82.99	70.11	75.39	88.59		
150	93.41	97.66	98.70	96.46	95.41	99.03	96.11	95.76	97.67	95.09	94.38	96.93	94.83	93.28	93.51	94.08		

Table 4
Influence of content (wt %) and length (mm) of the kapron fibre introduced with acidifying agent on coagulation completeness (wt %) of SKS-30 ARK rubber from latex with various amount of sodium chloride

The amount of sodium chloride, kg/t of rubber	Fibre content, wt %																	
	0 %			0.1 %			0.3 %			0.5 %			0.7 %			1.0 %		
	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm	2 mm	5 mm	10 mm
25	8.93	10.64	9.49	11.42	10.49	10.11	12.92	10.89	9.77	10.67	11.38	9.72	10.54	9.21	11.36			
50	21.37	21.13	19.84	22.96	21.35	22.05	20.46	22.63	20.13	20.92	22.51	20.67	24.07	21.35	22.41			
75	32.78	30.94	28.78	32.38	31.32	29.51	33.97	32.65	32.99	28.23	28.16	29.10	31.62	29.37	31.10			
100	62.71	40.12	38.35	42.15	39.55	41.21	41.85	46.81	35.71	41.81	43.55	39.41	44.55	42.38	39.91			
125	80.63	82.20	85.79	85.33	82.56	88.47	87.04	84.90	90.10	89.59	85.19	86.16	84.80	83.63	88.31			
150	93.41	94.00	93.42	93.55	94.67	96.95	94.52	99.60	99.36	99.79	95.04	96.61	94.15	94.14	95.75			

3.2. Influence of cotton, viscose and kapron fibre on the properties of rubber mixes and vulcanizates

In all experiments fibrous filler was introduced into latex simultaneously with an acidifying agent at the final

stage of the coagulation process. Researches of the obtained rubbers properties were carried out according to the requirements of GOST 15627-79 using SKS-30 ARK rubber (Tables 5-7). The obtained results were compared with the properties of standard samples – the samples without fibres.

Table 5

Properties of rubbers, rubber mixes and rubbers on the basis of SKS-30 ARK, filled with cotton fibre of various length (mm) and various contents (wt%)

Parameter	Without a fibre	2 mm		5 mm		10 mm	
		0.3 %	0.7 %	0.3 %	0.7 %	0.3 %	0.7 %
Mooney viscosity MV 1+4 (373 K):							
- rubber	55	57	56	52	56	52	55
- rubber mix	57	58	57	56	57	55	58
Karrer plasticity, r/m, rel.units	0.34	0.34	0.36	0.36	0.35	0.39	0.37
Capacity for restoration, mm	1.4	1.4	1.4	1.4	1.4	1.2	1.2
Engineering stress at 300 % elongation, MPa	9.4	9.0	8.6	8.6	8.1	8.3	7.8
Conditional tensile strength, MPa	26.3	25.3	24.1	23.4	21.6	25.5	20.7
Relative elongation at rupture, %	618	605	615	570	486	616	582
Relative residual deformation, %	12	14	12	10	10	14	12
Rebound elasticity, %:							
- 293 K	40	39	39	39	34	34	34
- 373 K	53	52	55	54	57	52	60
Shore hardness, rel. units	57	56	57	56	61	58	57
Tear resistance, kN/m	53	52	61	56	59	52	55
Multifold tensile resistance, thousand cycles	70	69	77	57	62	49	53
Ageing factor (373 K, 72 h):							
- by strength	0.44	0.51	0.48	0.53	0.51	0.46	0.60
- by relative elongation	0.33	0.37	0.33	0.39	0.41	0.33	0.41

Note: vulcanization temperature is 416 K; duration 60 min.

Table 6

Properties of rubbers, rubber mixes and rubbers on the basis of SKS-30 ARK, filled with viscose fibre of various length (mm) and various contents (wt%)

Parameter	Without a fibre	2 mm		5 mm		10 mm
		0.3 %	0.7 %	0.3 %	0.7 %	0.3 %
Mooney viscosity MV 1+4 (373 K):						
- rubber	55	53	53	53	52	51
- rubber mix	57	55	56	55	56	55
Karrer plasticity, r/m, rel.units	0.34	0.38	0.31	0.32	0.35	0.36
Capacity for restoration, mm	1.4	1.4	1.7	1.8	1.5	1.4
Engineering stress at 300 % elongation, MPa	9.4	3.9	4.9	6.3	5.8	6.0
Conditional tensile strength, MPa	26.3	24.3	20.0	23.0	22.0	23.0
Relative elongation at rupture, %	618	698	690	680	675	688
Relative residual deformation, %	12	18	18	16	14	14
Rebound elasticity, %:						
- 293 K	40	43	43	46	44	44
- 373 K	53	49	50	53	50	51
Shore hardness, rel. units	57	55	56	55	59	57
Tear resistance, kN/m	53	71	75	81	96	95
Multifold tensile resistance, thousand cycles	70	70	72	76	96	85
Ageing factor (373 K, 72 h):						
- by strength	0.44	0.63	0.77	0.53	0.56	0.60
- by relative elongation	0.33	0.45	0.43	0.33	0.33	0.41

Note: vulcanization temperature is 416 K; duration 60 min.

Table 7

Properties of rubbers, rubber mixes and rubbers on the basis of SKS-30 ARK, filled with kapron fibre of various length (mm) and various contents (wt%)

Parameter	Without a fibre	2 mm		5 mm		10 mm	
		0.3 %	0.7 %	0.3 %	0.7 %	0.3 %	0.7 %
Mooney viscosity MV 1+4 (373 K):							
- rubber	55	57	56	55	57	57	58
- rubber mix	57	59	58	59	58	58	60
Karrer plasticity, τ/m , rel.units	0.34	0.33	0.34	0.33	0.36	0.34	0.34
Capacity for restoration, mm	1.4	1.3	1.2	1.4	1.2	1.3	1.3
Engineering stress at 300 % elongation, MPa	9.4	5.6	7.1	6.1	6.6	5.9	6.0
Conditional tensile strength, MPa	26.3	29.0	23.0	23.1	23.0	23.0	20.5
Relative elongation at rupture, %	618	680	610	670	640	670	650
Relative residual deformation, %	12	16	14	14	14	14	14
Rebound elasticity, %:							
- 293 K	40	38	42	40	42	40	43
- 373 K	53	50	52	52	50	50	50
Shore hardness, rel. units	57	57	57	54	55	56	57
Tear resistance, kN/m	53	89	90	81	85	66	73
Multifold tensile resistance, thousand cycles	70	78	82	93	73	76	78
Aging resistance (373 K, 72 h):							
- by strength	0.44	0.65	0.67	0.72	0.69	0.80	0.96
- by relative elongation	0.33	0.46	0.40	0.40	0.41	0.45	0.54

Note: vulcanization temperature is 416 K; duration 60 min.

According to the data given in Table 5 introduction of cotton fibre into polymer increases the viscosity disorder parameter of rubber and rubber mix as well as plasticity of rubber mix.

Adsorption of crosslinking agents (sulfur, accelerators, activators) on fibres surface decreases crosslinking degree of vulcanizate. This leads to the retrogression of strength, engineering stress at 300 % elongation and relative elongation at rupture. The value of tear resistance increases from 53 to 56–61 kN/m and multifold tensile resistance decreases at 0.7 wt % of fibre.

The increase of aging resistance (373 K, 72 h) can be explained by completion of the vulcanization process as a result of any part of crosslinking agents desorption from a fibres surface.

One can see from Table 6 that the presence of viscose fibre results in insignificant decrease of rubber viscosity from 55 to 51–53 units and rubber mix viscosity – from 57 to 55–56 units. The minimum torsion torque increases from 4.8 (in a standard sample) up to 5.5–6.5 N·m (Table 8). Orientation of badly moistened viscose fibres in a rubber mix matrix does not appear in the direction perpendicular to the loading direction (calender effect). This fact explains the increase of samples restorability from 1.4 to 1.5–1.8 mm mainly at fibres length of 5 mm and content of 0.7 wt % (Table 6). The reduction of rubber mixes creep is connected with this fact as well. The presence of fibre additives increases disorder of rubber mix plasticity within the limits of 0.31–0.38 units (Table 6).

For vulcanizates with viscose fibre adsorption of a part of sewing agents on fibrous filler also takes place. Owing

to pauperization of rubber by sulfur and accelerators the crosslinking degree of vulcanizates decreases. In comparison with vulcanizates without fibrous filler it results in:

- increase of optimum time of composites vulcanization from 27.5 (for standard sample) up to 28–30 min;
- decrease of strength and strain at 300 % elongation;
- increase of relative elongation and residual rupture strain.

However, the essential increase of values of tear resistance from 53 to 71–96 kN/m and multifold tensile resistance from 70 to 72–96 thousand cycles (Table 6) proportional to the content and length of viscose fibres in composites is observed. It is explained by reinforcing effect of fibres, determined before for vulcanizates filled with fibres at mixing stage [8].

Growth of aging resistance (373 K, 72 h) can be explained by vulcanization completion as a result of gradual desorption of any part of crosslinking agents (sulfur, accelerators, activators) from the surface of these fibres.

Anisotropy of elastic-strength properties of the vulcanizates with fibres increases hardness disorder and decreases rebound elasticity from 53 (a comparative sample) to 49–51 % for viscose and to 50–52 % for kapron (Tables 6 and 7) at 373 K.

One can see from Table 7 that the presence of kapron fibre at amount of 0.3–0.7 wt % and length of 2–10 mm results in insignificant increase of Mooney viscosity: from 55 to 56–58 units for rubbers and from 57 to 58–60 units for rubber mix. The introduction of kapron fibre compared with viscose fibre significantly increases the

minimum torsion torque from 4.8 (for standard sample) to 7.0–8.5 (kapron) against 5.5–6.5 N·m (viscose) (Table 8). It indirectly indicates high compatibility of butadiene-styrene rubber matrix with a surface of kapron introduced into rubber with acidifying agent at the final stage of the coagulation process as compared with viscose.

In butadiene-styrene rubber matrix (SKS-30 ARK) an orientation of more compatible kapron fibres in a direction, perpendicular to a loading (calender effect), explains the decrease of rubber mix restorability from 1.4 (without a fibre) to 1.2–1.3 mm (with a fibre) (Table 7). Presence of kapron fibre limits disorder of plasticity of rubber mix within the limits of 0.33–0.36 units.

Adsorption of some crosslinking agents on kapron fibre surface results in reduction of vulcanizates crosslinking degree, reduction of strength and tension at 300 % elongation, as well as in growth of relative residual deformation and elongation at rupture in comparison with the vulcanizates without fibre. A decrease of optimum vulcanization time from 27.5 (for a standard sample) to 15–21 min due to the presence of fibrous filler of the basic character (polymer with amide groups) having properties of vulcanization accelerator is observed (Table 8) [10].

The essential increase (Table 7) of tear resistance from 53 to 66–90 kN/m and multifold tensile resistance from 70 to 73–93 thousand cycles is explained by

reinforcing effect of kapron fibres with the length of 5–10 mm. The same effect was before revealed for vulcanizates filled with fibres at mixing stage [9].

Growth of aging resistance (373 K, 72 h) is explained by vulcanization completion as a result of desorption of some crosslinking agents from fibres surface.

3.3. Study of swelling kinetics of vulcanizates filled with fibres

An important estimation parameter of the obtained composites properties is the presence or absence of interphase interaction between rubber (vulcanizate) matrix and surface of fibrous filler (viscose or kapron), introduced at a separation stage of rubber from latex.

Swelling kinetics of filled vulcanizates on the basis of butadiene-styrene rubber in solvents of various polarity has been investigated with the purpose of estimation of interphase interaction of fibre additives with rubber matrix. Interphase interaction was estimated by an equilibrium degree of swelling (a_{max}) and constant of swelling velocity (k, h^{-1}) of vulcanizates containing viscose or kapron filler. *n*-Octane, toluene and chloroform with solubility parameters 15.4, 18.2 and 18.8 $kJ^{0.5} \cdot (m^{-1.5})$ respectively [9], were used as solvents (Table 9).

Viscose fibre. Irrespective of solvent nature there is not unequivocal dependence of size and amount of viscose

Table 8

Rheogram of rubber mixes curing based on SKS-30 ARK rubber filled with viscose and kapron fibre

Parameter	Standard sample (without additives)	Fibres size (mm) and amount (wt %)											
		Viscose fibre						Kapron fibre					
		2 mm		5 mm		10 mm	2 mm		5 mm		10 mm		
		0.3 %	0.7 %	0.3 %	0.7 %	0.3 %	0.3 %	0.7 %	0.3 %	0.7 %	0.3 %	0.7 %	
The minimum torsion torque, N·m	4.8	6.3	6.0	5.5	5.5	6.5	8.5	7.5	7.0	7.5	7.5	7.0	
The maximum torsion torque, N·m	36.5	30	32	34	33	36	31	34	32	34	32	32	
The beginning of curing, min	3.5	5	4	4	5	4	5	5	4	5	4	5	
Optimum time of curing, min	27.5	30	29	28	29	29	21	20	21	19	15	21	

Table 9

Effect of solvent nature, size and amount of viscose and capron fibre on equilibrium swelling degree (a_{max} , wt %) and constant of swelling velocity (k, h^{-1}) of vulcanizates based on SKS-30 ARK rubber

Fibres size/amount in rubber, mm/wt %	Viscose fibre						Capron fibre					
	<i>n</i> -octane		toluene		chloroform		<i>n</i> -octane		toluene		chloroform	
	a_{max}	k	a_{max}	k	a_{max}	k	a_{max}	k	a_{max}	k	a_{max}	k
2/0.3	168	-0.93	360	-1.43	675	-1.07	140	-1.38	272	-1.73	550	-1.38
5/0.3	162	-0.93	316	-1.43	600	-1.07	142	-0.97	276	-1.73	525	-1.38
10/0.3	145	-0.93	294	-1.43	582	-1.43	134	-1.19	252	-1.20	520	-1.66
2/0.7	150	-1.19	302	-1.33	590	-1.33	128	-1.73	270	-1.73	540	-2.14
5/0.7	154	-1.19	312	-1.33	614	-1.43	120	-1.43	243	-0.84	514	-2.25
10/0.7	-	-	-	-	-	-	122	-1.54	262	-0.93	524	-1.96

fibre within the range of 0.3–0.7 wt % on a_{max} value for vulcanizates.

With increase of solvents polarity in the row octane < toluene < chloroform irrespective of the viscose fibre amount, growth of values a_{max} for these solvents is observed: 145–168, 294–360 and 582–675 wt % respectively. Maximum values a_{max} obtained in chloroform for vulcanizate with viscose filler denote its polarity increase, as well as approximation of its average solubility parameter $r_{vulc/viscose}$ to solubility parameter of chloroform $r_{ch} = 18.8$ in comparison with $r_{rubber} = 17.4$ (mJ)^{0.5} · (m^{-1.5}) for initial unfilled and uncured rubber SKS-30 ARK [10]. The reason is the presence of more polar viscose fibre ($\rho_{viscose} = 31.9$ (mJ)^{0.5} · (m^{-1.5})) in a vulcanizate matrix and occurrence of additional curing network. [11].

Apparent driving force – value a_{max} – did not affect the swelling velocity of the filled vulcanizate.

Difference between thermodynamic compatibility of various solvents and vulcanizate with viscose fibre defines the swelling velocity of the latter. For “vulcanizate – octane” system with greater value of squared difference of solubility parameters $b = (r_{rubber} - r_{octane})^2 = 4$ (mJ) · (m⁻³) [9, 10] the swelling velocity is smaller ($k = 0.93$ – 1.19 h⁻¹). For “vulcanizate – toluene” (or “vulcanizate – chloroform”) system with smaller values $b = 0.64$ or 1.96 (mJ) · (m⁻³) the swelling velocities were higher: $k = 1.33$ – 1.43 or 1.07 – 1.43 h⁻¹, respectively.

Value b defined swelling kinetics of vulcanizates in various solvents. For “vulcanizate – chloroform” system the influence of amount and size of the viscose fibre on the swelling velocity is observed. Thereby doubling of the fibre amount from 0.3 to 0.7 wt % with the length of 2 and 5 mm resulted in increase of value k from 1.07 to 1.33–1.43 h⁻¹.

Thus, no essential influence of viscose fibres size and its amount in vulcanizate on the swelling velocity of *n*-octane and toluene was established. Apparently, the reason is weak interphase interaction of rubber matrix with fibres and presence of boundary layers because of the significant differences between r_{rubber} and $r_{viscose}$, for which $b = (r_{rubber} - r_{viscose})^2 = 210$ (mJ) · (m⁻³).

Kapron fibre. For vulcanizates with kapron fibre the value a_{max} increases with the increase of solvents polarity in the row octane < toluene < chloroform, irrespective of fibre content. The corresponding values of a_{max} are within following intervals: 120–140, 243–276 and 514–550 wt %. The greatest value α_{max} , obtained in chloroform, denotes the increase of vulcanizate polarity and approximation of its solubility parameter $r_{vulc/kapron}$ to the value $r_{ch} = 18.8$ (mJ)^{0.5} · (m^{-1.5}) in comparison with value r for initial unfilled and nonvulcanized rubber. The reason is the presence of polar fibre additives in vulcanizate matrix, for which $r = 27.8$ (mJ)^{0.5} · (m^{-1.5}) [11].

Apparent driving force – value a_{max} – did not affect the swelling velocity of vulcanizate filled with kapron fibre.

Difference between thermodynamic compatibility of various solvents and vulcanizate with kapron fibre defines its swelling velocity. For “vulcanizate – octane” system with greater value $b = (r_{rubber} - r_{octane})^2 = 4$ (mJ) · (m⁻³) the interval of swelling velocity $k = 0.97$ – 1.54 h⁻¹ is typical. For “vulcanizate – toluene” system with smaller value $b = 0.64$ (mJ) · (m⁻³) the swelling velocity interval is wider ($k = 0.84$ – 1.73 h⁻¹). For “vulcanizate – chloroform” system with $b = 1.96$ (mJ) · (m⁻³) the interval of swelling velocity shifts to values $k = 1.38$ – 2.25 h⁻¹ depending on the content of kapron fibre. Thereby doubling of the fibre amount from 0.3 to 0.7 wt % with the length of 2 and 5 mm resulted in increase of value k from 1.38– 1.66 to 2.14 – 2.25 h⁻¹. Such increase of swelling velocity in chloroform with the growth of the kapron fibre amount apparently is explained by greater interphase interaction of rubber matrix with filler because of smaller differences between $r_{rubber} = 17.4$ and $r_{kapron} = 27.8$ (mJ)^{0.5} · (m^{-1.5}), for which $b = (r_{rubber} - r_{kapron})^2 = 108$ (mJ) · (m⁻³), owing to the high contribution of hydrogen bonds in the presence of chloroform [9].

On the contrary, for toluene which does not form hydrogen bonds, decrease of swelling velocity constant k is observed with the increase of kapron fibres amount, conditioned by the barrier properties of the boundary layers having high polarity.

4. Conclusions

1. The new technological direction for the successful solution of the environmental problem of fibres waste products recycling consisting in preliminary mixture of fibre with acidifying agent before latex supply at the final stage of its coagulation has been offered.

2. Scientific bases of the offered approach allowing obtaining of rubbers filled with fibres at the stage of rubber emulsion production have been developed.

3. The expediency of the offered approach is experimentally proven:

- the offered approach allows to achieve uniform distribution of fibre in a rubber volume with positive effect on individual properties of the obtained vulcanizates;

- the optimum length of cotton, viscose and kapron fibres is 2–5 mm while their optimum contents in rubber is within the range of 0.3–0.7 wt %;

- introduction of cotton fibre does not worsen vulcanizates properties and introduction of viscose and kapron fibres allows to increase such parameters of vulcanizates as thermal aging resistance, multifold tensile resistance and tear resistance without deterioration of other operational characteristics;

- influence of kapron fibre additives on the properties of SKS-30 ARK rubber and rubber mixes differs from that of cotton and viscose fibre additives due to distinctions in their nature;

- distinction in interphase interaction between the surfaces of viscose and kapron fibres and vulcanizates matrix of butadiene-styrene rubber, affected swelling velocity of vulcanizate in solvents of different nature.

4. Deviations of rheological, vulcanization properties and physico-mechanical parameters of vulcanizates in the presence of viscose and kapron fibre additives have been explained.

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ВОЛОКНИСТІ МАТЕРІАЛИ – ЯК ТЕХНОЛОГІЧНІ ДОДАТКИ У ВИРОБНИЦТВІ БУТАДІЄН-СТИРОЛЬНОГО КАУЧУКУ І ГУМ

Анотація. Показано перспективність утилізації відходів волокнистих матеріалів (бавовняного, віскозного і капронового) для одержання еластичних композиційних матеріалів внаслідок створення композиції волокно–латекс з наступною коагуляцією і вулканізацією наповненої суміші. Визначено оптимальний вміст волокна і його довжину.

Ключові слова: композиція, каучук, латекс, волокно, вулканізація.