UDC 678.046.3

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THE USE OF THE HEAT-TREATED RICE HUSKS AS ELASTOMERIC COMPOSITIONS FILLERS

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The characteristics of the products of rice husk (RH) after its thermal treatment are determined, these products being fine dispersed silicon- and carbon-containing powders with amorphous-crystalline structure. The comparative evaluation and experimental verification of possible application of wide range products produced during various conditions of the thermal treatment of crashed rice husk as fillers of elastomeric compositions based on carbon-chain diene rubber are performed. The introduction of 20 phr (parts per hundred rubber) of either the product of carbonized or silicon dioxide obtained by the thermal treatment of rice husk is shown to have a positive effect on both plastic and viscous properties of rubber mixtures based on butadiene-styrene rubber SKS-30 ARK, as well as on the relative extent of cross-linking, the formation of cross-links between rubber and filler during vulcanization and the kinetic parameters of sulphuric vulcanization. This positive effect is observed in this case as opposed to the known semi-enforcing compositions. The semi-enforcing effect of fillers obtained from RH is stated to provide the vulcanizates with high values of equilibrium shear modulus, temperature and heat resistivity as concerns the resilient strength properties relative to the effects of known fillers. The complex of the properties of elastomeric compositions is strongly affected by time-temperature regime of the production of RH.

Keywords: products, thermal treatment, rice husk, elastomeric compositions based on SKS-30 ARK, properties.

Introduction

Both the prices and costs instability of the production of carbon black, which is commonly used as rubber filler [1], as well as environmental issues stimulate intensive researches focused on the creation of fillers of new types that meet the current requirements for the ingredients of rubber production. Products derived from natural minerals or synthetic silica [2] may be promising among them, their widespread use being limited due to the deterioration of the technological properties of rubber mixtures or strength characteristics of vulcanizates.

Renewable raw materials of plant origin can be an accessible and cheap source for the production of rubber and ingredients [3–4]. Silicon-carbon powder materials [5–6] and silicon dioxide [7] obtained from the secondary raw materials of the multi-tonnage procedure of rice processing, i.e. rice husk, are shown to be used as semi-reinforcing fillers based on butadiene-methyl-styrene rubber sulfur vulcanization with positive influence on the formation of technological properties of rubber mixtures.

The present work is focused on the comparative evaluation and experimental verification of possible application of wide range of products produced during various conditions of thermal treatment of crashed rice husk as fillers of elastomeric compositions based on carbon-chain diene rubber.

Experimental

It is known that the mechanism of thermo-chemical transformations of rice husk (RH) containing about 20% silicon dioxide, 50% poly-saccharides and more than 20% lignin is multi-stage [8]. The process of carbonization of RH in an exhaust gases atmosphere in the wide temperature range [9] allows obtaining finely dispersed amorphous products containing silicon dioxide and carbon with a maximum specific surface at the temperature of 700–800^{0}C (Fig. 1). As the temperature increases, the undeveloped structure of the products from the RH is small-porous, which is connected, first of all, with the process of their decarbonization. The final stage of decarbonization is the production of nano-sized particles of silicon dioxide [10].

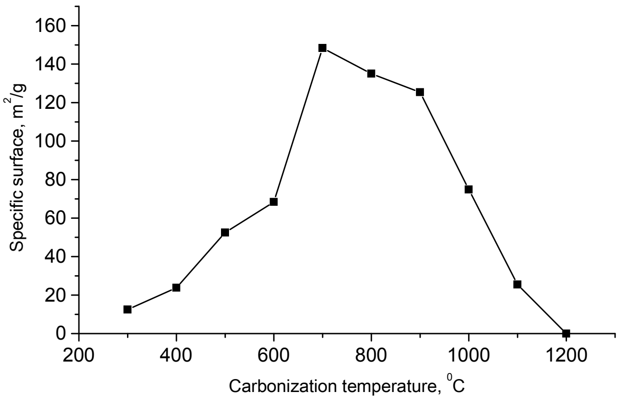


Fig. 1. Specific surface of obtained products vs. rice husk carbonization temperature

The obtained products of thermochemical transformations of rice husk in the temperature range of 500–830°C for 2–6 hours were highly dispersed powders of black (products SiO_2+C-2, SiO_2+C-3), black and gray (product SiO_2+C-4) or white (SiO_2–1 products) colors. These products are characterized by a SiO_2 content of 49.4 to 96.2% by weight, a mass fraction of moisture of 0.04 to 2.85% by weight, pH of aqueous suspension of 7.1 to 10.5, bulk density of 246.0 to 483.2 g/dm^3, the residue on the sieve 014 of 0 to 30% by weight and ash content of 55.19 to 99.52% by weight (Table 1). As compared with the well-known amorphous silica of the brand Ultrasil VN 2 GR (Degussa, Germany), the SiO_2–1 product obtained from rice husks was characterized by a higher proportion of silicon dioxide, a lack of moistu-re; it had 1.3 times higher bulk density (Table 1). The bulk density of the tested products SiO_2+C-2 and SiO_2+C-3 is at the level typical of semi-intensifying furnace tungsten carbons [2]; and the bulk density of the product SiO_2+C-4 was lesser than that of the industrial silicon (Table 1). Significant residue after sifting through a sieve with mesh 014 of the tested products of carbonized crushed rice husk is probably due to the presence of agglomerates. The value of ash content after calcination of prototype samples can be explained by the presence of organic and inorganic components in them.

This is confirmed by the results of the differential thermal analysis on the Derivatograph QOM 1500 of the IOM (Fig. 2).

As a result of exothermic processes of combustion of carbonaceous substances from heat-treated rice husk, a significant mass loss is observed at temperatures above 400°C as follows: 45.7% for SiO_2+C-2; 51.1% for SiO_2+C-3; and 38.1% for SiO_2+C-4. The loss of mass of the SiO_2–1 product in the studied temperature range was only 1.1%, this can be attributed to the removal of molecular water from silicon dioxide. In general, the experimental composite products based on crushed plant material are stated to be thermostable at technological processes temperatures of rubber production.

Photographs obtained with the use of the Levenhok microscope (DSM-50 camera) show the SiO_2–1 fine particle size of 20 to 100 мm, they are less susceptible to agglomeration than SiO_2+C products (Fig. 3). The composition products SiO_2+C-2, SiO_2+C-3, and SiO_2+C-4 are observed to be powders with particles of black and white with an amorphous crystalline structure. Thermal treatment of RH at 500°C for 6 hours (product SiO_2+C-4) allows obtaining powdered material with geometric forms of undefeated cellular fragments of the original plant material.

IR-spectral analysis of rice husk carbonization products showed [11] that the spectral bands of SiO_2

Table 1

Physico-chemical characteristics of thermal processing products of rice husk

Characteristic	Experimental products				Industrial silicon dioxide Ultrasil VN 2 GR
	SiO_2–1	SiO_2+C-2	SiO_2+C-3	SiO_2+C-4	
	Obtaining conditions (T, °C)/(τ, h)				
	830/6	830/3	750/2	500/6	
SiO_2, wt.%	96.2	53.1	49.4	56.9	91.0
Humidity, wt.%	0.04	1.64	1.78	2.85	4.20
Water suspension pH	7.1	9.8	9.6	10.5	6.8
Residue on the sieve 014, wt.%	0	24.7	30.2	26.2	0
Packed density, g/dm^3	355.4	483.2	456.6	246.0	275.4
Ash, wt.%	99.52	55.19	55.69	62.31	5–7*

Note: * – loss of ignition index for industrial silicon dioxide (wt. %) is given according to ref [2].

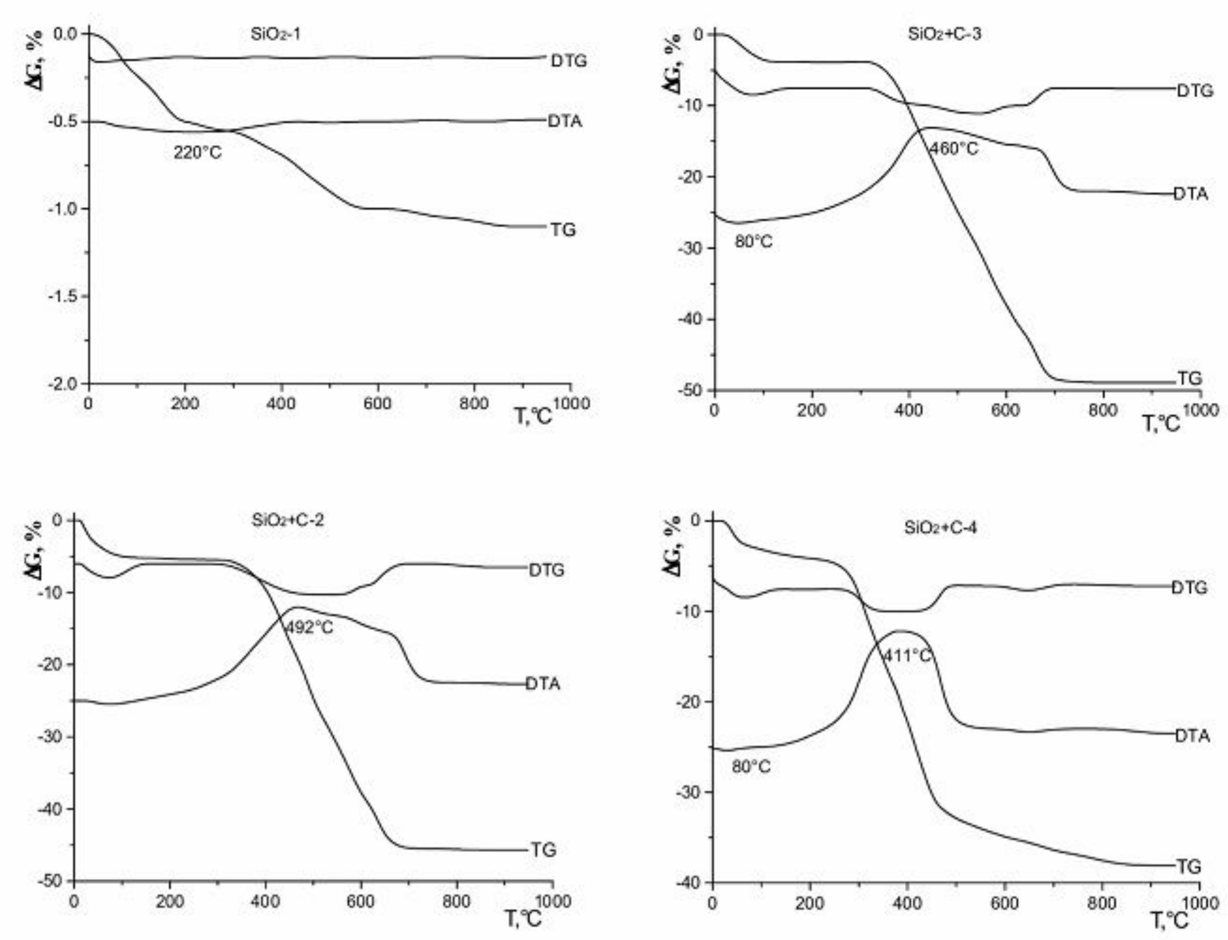
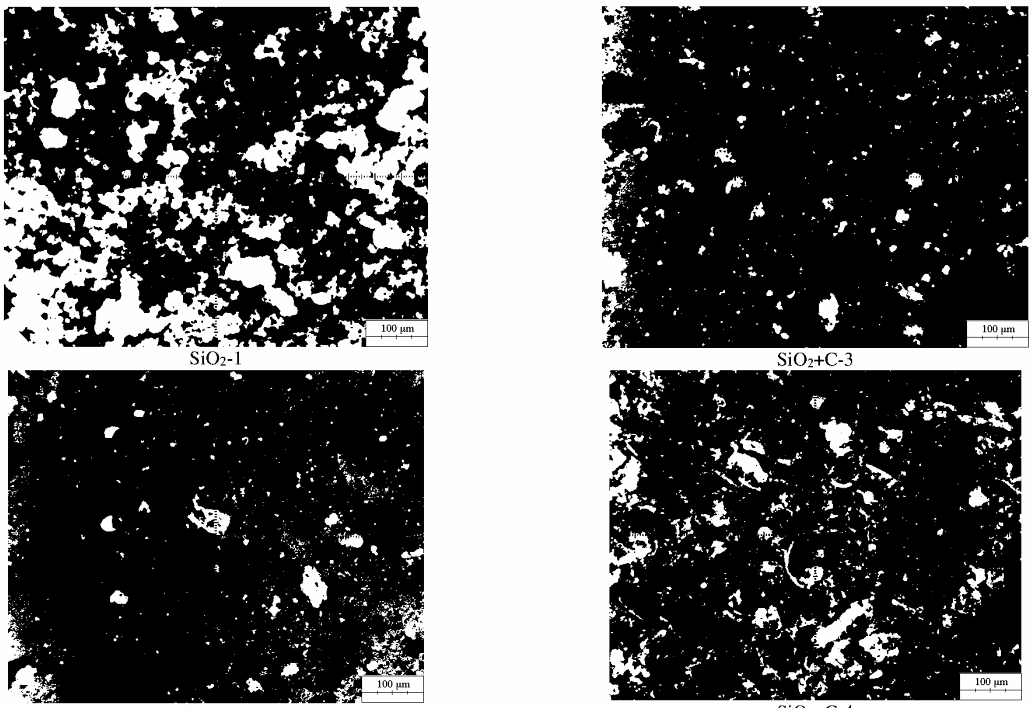


Fig. 2. DTA curves of rice husk after thermal treatment



SiO2-1 SiO2+C-3 SiO2+C-2 SiO2+C-4

Fig. 3. Microphotograph of rice husk thermal processing products

and carbon-containing compounds are dominant. When the heat treatment of RH is carried out at a temperature above 700^{0}C, the absorption bands of carbonaceous compounds are observed to disappear.

The investigations of silicon dioxide SiO_2–1, composite carbon and silicon containing products SiO_2+C-2, SiO_2+C-3, SiO_2+C-4 obtained from plant raw materials as fillers were performed in model elastomeric compositions based on non-stereoregular butadiene styrene rubber SKS-30 ARC (TU 38.40355–99) composition (mass per 100 phr (parts per hundred rubber) of rubber): rubber 100.0; sulfur-milled 1.7; N-tert-butyl (2-benzthiazolyl) sulfenamide 1.0; zinc oxide 3.0; stearic acid 1.0 and filler 20.0. The study of the effect of rice husk heat treatment products on the properties of rubber mixtures and rubber has been carried out in comparison with the weight-bearing content of known fillers: the amorphous silicon enhancer brand Ultrasil VN 2 GR, semi-enhancing mineral filler kaolin and the furnace semi-reinforcing technical carbon brand N 550. A filler was absent in the control elastomeric composition. The production of rubber mixtures was carried out on laboratory rolls, based on 400 g of rubber base according to the generally accepted regimes. The determination of the properties of rubber mixtures and rubber in the optimum of vulcanization (at 155^{0}C) was performed in accordance with the current standards [12] and the techniques given in refs. [1,5–7].

Results and discussion

The feature of rubber compounds based on SKS-30 ARK, containing in their composition 20 parts of rice husk heat treatment products by weight, is stated to be increased by 5–20% ductility at 70^{0}C relative to the level of this parameter of the uncompleted rubber compound (Table 2).

Then, the level of the plasticity index is reduced by 6–15% when the equal weight dosage of known fillers was introduced into the composition of the rubber mixtures under study. When the temperature and duration of heat treatment decreased, the positive influence of experimental products as fillers on this parameter of elastomeric compositions increased.

Taken into account the correlation of the plastoelastic properties of rubber compounds with the initial ($M_{initial}$) and minimum (M_L) torque parameters from rheometry data at vulcanization temperatures (Table 2), we calculated the thermoplasticity ($M_{initial}/M_L$) and the gain ($M_{L\ filled}/M_{L\ unfilled}$) by the parameter M_L of the unfilled ($M_{L\ unfilled}$) and filled ($M_{L\ filled}$) rubber mixtures. It is shown that the more positive effect of the heat treatment products of the RS relative to the known fillers on thermoplasticity at temperatures of 155^{0}C and 165^{0}C is preserved. The established positive influence of the products from PC as fillers of elastomeric compositions probably results from their weaker interaction with the SKS-30 ARC rubber matrix and correlated with this smaller gain factor relative to the action of Ultrasil VN 2 GR silica and technical carbon N 550. For instance, the gain in the parameter M_L of the experimental product SiO_2–1 is 1.2–1.3 times lower than that of rubber compounds filled with Ultrasil VN 2 GR (Table 2) and is at the level of the known aluminosilicate filler of kaolin.

20 phr fine powders obtained by the heat treatment of rice husks, carbonated RH and silicon dioxide, unlike known semi-reinforcing fillers, positively influences the plastic properties of rubber compounds based on SKS-30 ARK. The decrease in the carbonation temperature of the RS to 500^{0}C

Table 2

Technological properties of rubber mixtures based on SKS-30 ARK with 20 phr of filler

Characteristics	Filler type							
	without filler	Ultrasil VN 2 GR	Kaolin	Technical carbon N 550	SiO_2–1	SiO_2+C-2	SiO_2+C-3	SiO_2+C-4
T=70^{0}C								
Karrer plasticity	0.52	0.44	0.49	0.48	0.55	0.56	0.63	0.59
T=155^{0}C								
$M_{initial}$, dN·m	5.0	7.5	5.5	6.3	6.0	6.8	6.2	7.0
M_L, dN·m	3.9	5.6	4.4	5.0	4.3	4.5	4.4	4.7
$M_{initial}/M_L$	1.28	1.33	1.25	1.26	1.40	1.51	1.41	1.49
$M_{L\ filled}/M_{L\ unfilled}$	–	1.43	1.13	1.28	1.10	1.15	1.13	1.21
T=165^{0}C								
$M_{initial}$, dN·m	5.0	6.4	5.2	6.3	5.0	6.0	6.8	6.8
M_L, dN·m	3.4	4.4	3.5	4.4	3.7	3.6	4.2	4.3
$M_{initial}/M_L$	1.47	1.45	1.49	1.43	1.35	1.67	1.62	1.58
$M_{L\ filled}/M_{L\ unfilled}$	–	1.29	1.03	1.29	1.09	0.94	1.24	1.26

allows obtaining a product with the maximum effects on the plasticity of rubber compounds and their gain (according to rheometry data). The product SiO_2–1 obtained at 800°C and used as a filler is 1.2–1.3 times inferior to industrial silicon dioxide of the brand Ultrasil VN 2 GR by the reinforcement coefficient of rubber compounds from SKS-30 ARK.

Similar to the effect of thermally expanded graphite on the decrease in the viscosity of nonpolar carbon-chain rubbers, as was established by the authors, the above described changes in the technological properties of compositions from SKS-30 ARK in the presence of products from RH can be explained by decreasing the intermolecular interaction forces between macromolecules of rubber and facilitating the orientation of the elastomer macromolecules under shear and static loads.

Kinetic curves of the vulcanization of rubber compounds based on SKS-30 ARK according to rheometry data show a significant effect of 20 phr known fillers and experimental products from plant raw materials (Fig. 4,a, 4,b, respectively) on the nature of the vulcanization process, the level of the torque index at the stages of the induction period, the formation of vulcanization bonds and the vulcanization plateau, the kinetics of the process and the degree of sulfur vulcanization. Unlike the action of carbon black of grade N 550, known mineral fillers tend to slow down the process of vulcanization with respect to the unfilled rubber compound (Fig. 4,a). Rubber mixtures with carbonization products of RS (SiO_2+C) have kinetics of vulcanization similar to that of the rubber mixture containing technical carbon N 550. According to the slope of the kinetic curve at the stage of vulcanization cross-linking, the kinetic curve of the elastomeric composition with silica from rice husk is characterized by higher vulcanization rate with respect to the unfilled rubber mixture and also significantly exceeds the rubber mixture with an even weight content of silica of Ultrasil VN 2 GR brand (Fig. 4).

According to the vibration-metric data, the relative degree of cross-linking of $M_{HF}-M_L$ of elastomeric compositions with products from RH depends essentially on the conditions of preparation and composition (Table 3).

The introduction of 20 phr products of the heat treatment of plant raw materials into an elastomeric composition increases the level of this parameter by 1.1–1.3 times and an maximum is achieved for the products of the rice husk (SiO_2+C-2) carbonized at 830°C and silicon dioxide (SiO_2–1). The reduction of the carbonation temperature of the RH to 500°C (SiO_2+C-4) allows obtaining the product with minimal increase in the $M_{HF}-M_L$ parameter of the elastomeric composition in its presence and similar to the aluminosilicate filler kaolin as concerns the effect on the index of the relative degree of cross-linking. All carbonation products of the SiO_2+C type ceded their influence on the parameter $M_{HF}-M_L$ rubbers of the known semi-active filler of technical carbon N 550.

In terms of the difference between the maximum equilibrium (M_{HF}) and the minimum (M_L) torque of filled and unfilled rubbers $(M_{HF}\text{-}M_L)_{filled} - (M_{HF}-M_L)_{unfilled}$ (Table 3), the rubber-filler interaction effect was separated from the cross-linking effect only due to the vulcanization system. It was established that all products obtained by heat treatment of RH (except SiO_2+C-4) actively participated in the formation of rubber-filler crosslinks and surpassed the known mineral fillers in activity, but they were inferior to those of technical carbon N 550. The general dependence of the

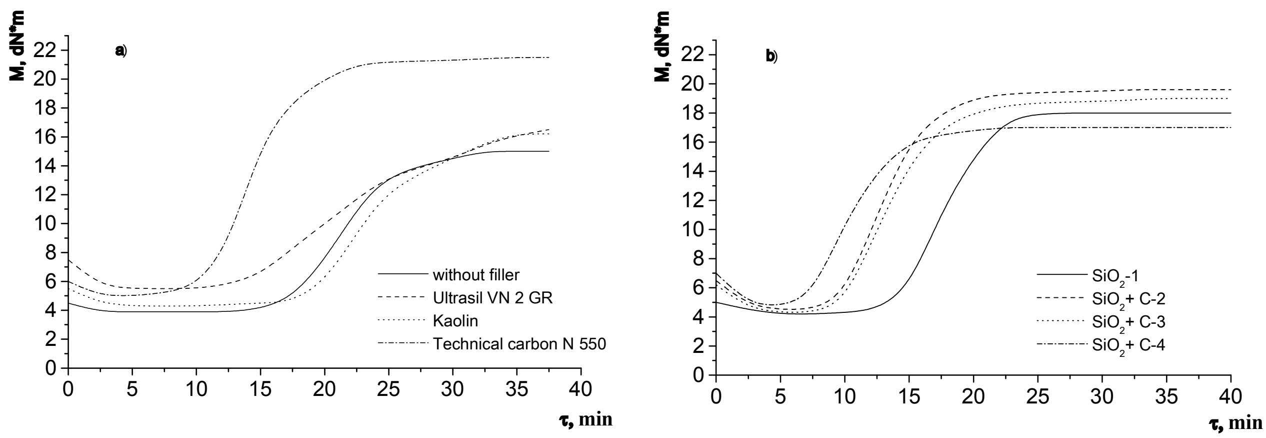


Fig. 4. Sulfur vulcanization kinetic curves of rubber mixtures based on SKS-30 ARK at 155°C at 20 phr of fillers: (a) traditional; (b) experimental

Table 3

Reometrical characteristics of elastomeric compositions based on SKS-30 ARK with 20 phr of fillers

Characteristic	Filler type							
	without filler	Ultrasil VN 2 GR	Kaolin	Technical carbon N 550	SiO_2–1	SiO_2+C-2	SiO_2+C-3	SiO_2+C-4
$T=155^0C$								
M_{HF}–M_L, dN·m	11.5	12.0	12.6	16.5	14.8	15.1	14.4	12.4
$(M_{HF}–M_L)_{filled}–(M_{HF}–M_L)_{unfilled}$, dN·m	–	0.5	1.1	5.0	3.3	3.6	2.9	0.9
t_s, min	17.6	15.1	19.3	10.5	14.4	10.0	10.3	7.8
t_{C90}, min	26.1	33.5	30.4	19.4	23.3	17.8	18.4	15.4
Vc, dN·m/min	0.98	0.47	0.84	1.44	1.27	1.48	2.02	1.20
k, min^{-1}	0.19	0.09	0.15	0.22	0.21	0.26	0.22	0.21
$T=165^0C$								
M_{HF} – M_L, dN·m	10.9	11.5	12.1	16.0	14.3	14.2	13.4	11.8
$(M_{HF}–M_L)_{filled}–(M_{HF}–M_L)_{unfilled}$, dN·m	–	0.6	1.2	5.1	3.4	3.3	2.5	0.9
t_s, min	7.7	7.2	9.5	6.0	7.5	5.1	6.6	4.6
t_{C90}, min	12.6	16.8	15.4	11.8	12.6	9.0	11.3	8.2
Vc, dN·m/min	1.59	0.87	1.52	2.14	2.13	2.76	2.14	2.40

influence of the type of products from RH on the formation of additional cross-linking correlates with their effect on the M_{HF}–M_L parameter (Table 3).

Thus, the experimental products obtained from RH positively affect the formation of the viscous properties of rubber compounds from SKS-30 ARK during the induction period, they tend to form an additional 8–35% cross-linking of the rubber filler at the stage of vulcanization. According to the degree of influence on this parameter, the experimental silicon dioxide SiO_2–1 is much times superior to the action of industrial silica of Ultrasil VN 2 GR grade. The experimental products in the studied temperature range of carbonation of RH containing silica are inferior to the carbon black of grade N 550 (especially the product SiO_2+C-4, obtained at 500⁰C, Table 3).

The effect of experimental products obtained from RH and known fillers on the kinetic parameters of sulfur vulcanization of elastomeric compositions based on SKS-30 ARK at 155⁰C and 165°C was estimated. The time of the onset of vulcanization t_s, optimal curing time t_{C90}, cure rate, taking into account the increase in torque at the stage of formation of vulcanization cross-links $V_c=Mt_{c90}-Mt_s/t_{c90}-t_s$, the conditional rate constant of vulcanization k were determined (Table 3). It was found that 20 phr of SiO_2–1, in contrast to Ultrasil VN 2 GR, does not adversely affect the time of reaching the vulcanization optimum, providing an increase in the rate and conventional rate constant of vulcanization relative to the elastomeric compositions with commercial silica and the relatively uncompleted rubber compound. Carbon-silicon-containing products SiO_2+C-2 and SiO_2+C-3 of high-temperature carbonation of RH, like technical carbon N 550, cause a shortening of the duration of the induction period of vulcanization (t_s) of elastomeric compositions and the time for achieving the vulcanization optimum, an increase in the rate and relative rate constant of vulcanization relatively unfilled composition. The introduction of 20 phr of the product SiO_2+C-4 (the production temperature was 500⁰C) is accompanied by a maximum (twofold) decrease in the duration of t_s and t_{c90}, but at low values V_c and k for compositions with products SiO_2+C (Table 3).

The values of the effective activation energy of the vulcanization process E calculated from the values of the conditional constant k at 155⁰C and 165⁰C are shown in Fig. 5. Experimental products obtained from RH or known fillers are characterized by the 1.2–1.7 times increase in the value of activation energy.

Among the products of carbonization of rice husks, the minimum effective activation energy is characterized by a rubber mixture of the product SiO_2+C-3 (production temperature was 750⁰C) and the maximum effective activation energy is observed for the product SiO_2+C-4 (production temperature was 500⁰C). As concerns the compositions with commercial carbon black of grade N 550, rubber compounds of with the products of the SiO_2+C type reveal higher values of the effective activation energy. Rubber mixtures with the experimental SiO_2–1 silica exhibit the values of the parameter E, which is equal to that of the rubber mixtures with kaolin, but it is

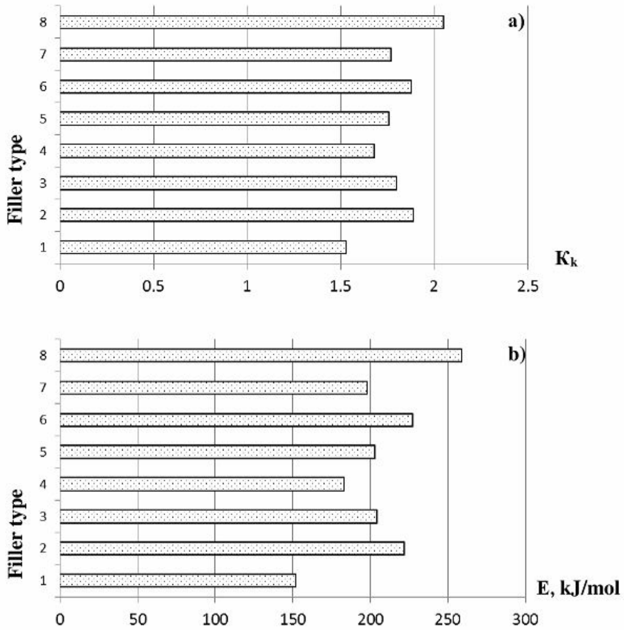


Fig. 5. Temperature vulcanization factor by convenient rate constant of vulcanization K_k (a) and effective activation energy E (b) for elastomeric composition based on SKS-30 ARK with 20 phr of fillers: 1 – without filler; 2 – Ultrasil VN 2 GR; 3 – kaolin; 4 – technical carbon N 550; 5 – SiO_2–1; 6 – SiO_2+C–2; 7 – SiO_2+C–3; 8 – SiO_2+C–4

1.1 times lower than this parameter of rubber compounds with Ultrasil VN 2 GR.

Hence, the value of the effective activation energy E as a generalizing indicator corrected with the change in the temperature by coefficient K_k (Fig. 5) shows a negative effect of mineral fillers and experimental composite fillers with an inorganic component on this parameter. The heat treated product of the RH (SiO_2+C-3) minimally affects the value of the E-parameter of the sulfur vulcanization process of the SKS-30 ARC; the SiO_2–1 silicon dioxide exceeds the known industrial Ultrasil VN 2 GR.

Thus, according to rheometry data of elastomeric compositions based on SKS-30 ARK, the effects of 20 phr products of the heat treatment of rice husks on the degree of crosslinking and kinetic parameter were found to depend on the conditions of their preparation and composition and, on the whole, it being accompanied by an increase in the relative degree of crosslinking, i.e. the formation of additional cross-linking of filler rubber at the stage of vulcanization, an increase in the level of kinetic parameters and effective activation energy of the sulfur vulcanization process. Among the products of carbonization of rice husk, the elastomeric compositions containing the product SiO_2+C-2 (production temperature 830^{0}C) have the best complex of rheometric parameters. The minimal effect on the degree of cross-linking of SKS-30 ARK and the formation of cross-linking rubber fillers, but the maximum activation of sulfur vulcanization during the induction period and the formation of vulcanization cross-links was observed for the product SiO_2+C-4 (the production temperature was 500^{0}C). Silicon dioxide from RH SiO_2–1 influences the kinetic parameters of elastomeric compositions better than the known Ultrasil VN 2 GR; the products of carbonation of RH are inferior to technical carbon N 550.

According to the procedure given in ref. [13], the mechanical characteristics of vulcanizates were calculated as a conditionally equilibrium shear modulus from the vibration rheometry data at 155^{0}C (G_{p155}) and 165^{0}C (G_{p165}) and recalculated to the temperature of 25^{0}C (G_{p25}). As follows from the data presented in Table 4, the addition of 20 phr to the composition of the unfilled elastomeric composition fillers results in an increase in the level of the parameter G_p and, accordingly, the resistance of the filled rubbers to the development of the shear strain increases. Technical carbon N 550 gives the rubber on the basis of SKS-30 ARK with a maximum value of the parameter G_p relative to rubbers with the same weight content of known mineral fillers. Carbonaceous products SiO_2+C obtained from RH were stated to be 1.1–1.4 times inferior to the effect of rubber carbon black on this parameter. The efficiency of the influence of the products obtained on the level of the equilibrium-equilibrium shear modulus decreased with a decrease in the carbonation temperature of the RH. The vulcanizates with an experimental silica with SiO_2–1 product have a 23% higher G_p value and, correspondingly, higher stiffness

Table 4

Shear equilibrium modulus for rubbers based on SCS-30 ARK with 20 phr of fillers

Characteristic	Filler type							
	without filler	Ultrasil VN 2 GR	Kaolin	Technical carbon N 550	SiO_2–1	SiO_2+C-2	SiO_2+C-3	SiO_2+C-4
Gp_{155}	1.02	1.08	1.13	1.49	1.33	1.36	1.29	1.11
Gp_{165}	0.97	1.03	1.08	1.44	1.28	1.27	1.20	1.05
Gp_{25}	0.71	0.75	0.78	1.04	0.92	0.94	0.90	0.77

Table 5

Physical-mechanical properties of rubbers based on SKS-30 ARK with 20 phr of fillers

Characteristic	Filler type							
	without filler	Ultrasil VN 2 GR	Kaolin	Technical carbon N 550	SiO_2-1	SiO_2+C-2	SiO_2+C-3	SiO_2+C-4
Normal test conditions								
f_{100}, MPa	0.4	0.6	0.7	0.9	0.7	0.6	0.8	0.6
f_{300}, MPa	0.8	1.0	1.1	2.7	0.9	1.0	1.2	1.0
f_p, MPa	2.2	13.6	5.4	23.0	2.4	2.8	2.7	3.3
ε, %	540	900	810	810	640	630	610	830
B, kH/m	10	25	11	36	10	12	12	13
H, ShA	40	45	45	49	44	45	45	42
S, %	51	46	50	47	50	50	50	50
at 100^0C								
f_p, MPa	2.3	11.9	3.7	3.8	2.6	2.2	2.3	2.2
ε, %	160	510	200	320	150	160	150	260
B, kH/m	6	9	6	9	8	6	5	6
H, ShA	39	43	44	48	43	44	44	41
S, %	58	50	56	54	56	56	54	52
After heat ageing at 100^0C for 72 h								
f_{100}, MPa	0.4	1.2	1.0	2.0	–	1.3	1.1	0.8
f_p, MPa	1.6	13.2	3.6	11.0	3.1	2.3	2.4	2.9
B, kH/m	8	29	14	25	9	12	11	12
H, ShA	48	54	53	68	54	55	55	51
S, %	46	42	46	40	44	44	44	44

than those with Ultrasil VN 2 GR (Table 4).

Analysis of the physical-mechanical properties of rubbers obtained by the optimum vulcanization at 155^0C under normal test conditions, at 100^0C and after thermal aging revealed a semi-reinforcing effect on the level of properties of unfilled rubbers and rubbers with known fillers for the products of the heat treatment of rice husk (Table 5).

According to the data on nominal stress at 100% and 300% elongation, hardness, elasticity under normal conditions, the rubber with the experimental products obtained from RH are characterized by the parameters which are inherent in the rubber with the known semi-reinforcing mineral fillers, but they are inferior to the rubber with half-strengthened technical carbon N 550. Among the rubbers with carbon-containing experimental products SiO_2+C, the vulcanizates filled with SiO_2+C-4 product (the temperature of production was 500^0C) exhibited the best physical-mechanical properties. Rubber based on non-crystallizing rubber SKS-30 ARK provide an increased level of elasto-strength properties under different test conditions in comparison with unfilled rubber; the experimental products obtained from RH used as fillers are inferior to the of known fillers, carbon black N 550, Ultrasil VN 2 GR and kaolin,

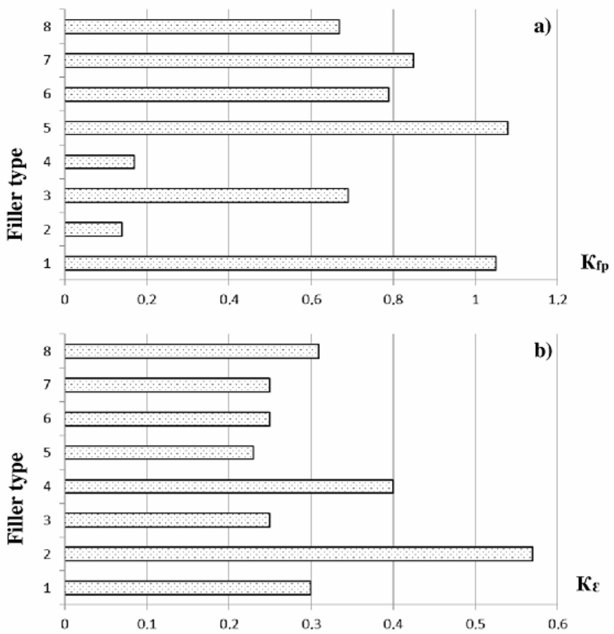


Fig. 6. Influence of 20 phr fillers on the coefficient of temperature stability at 100°C and the conditional durability K_{fp} (a) and the specific elongation at gap $K_ε$ of the elastomeric compositions based on SKS–30 ARK (b): 1 – without filer; 2 – Ultrasil VN 2 GR; 3 – kaolin; 5 – SiO_2–1; 6 – SiO_2+C–2; 7 – SiO_2+C–3; 8 – SiO_2+C–4; 4 – technical carbon N 550

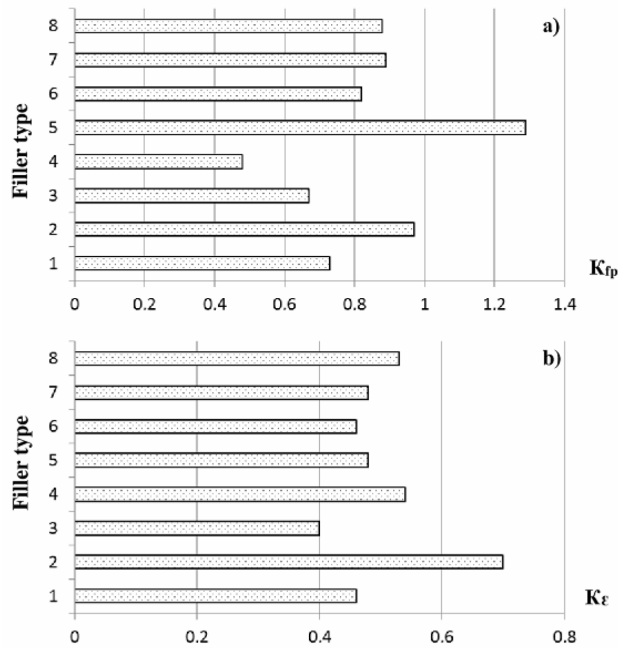


Fig. 7. Influence of 20 phr fillers on the coefficient of heat resistances after thermal influence at 100°C for 72 hours and the conditional durability K_{fp} (a) and the specific elongation at gap K_{ε} of the elastomeric compositions based on SKS–30 ARK (b): 1 – without filer; 2 – Ultrasil VN 2 GR; 3 – kaolin; 5 – SiO_2–1; 6 – SiO_2+C–2; 7 – SiO_2+C–3; 8 – SiO_2+C–4; 4 – technical carbon N 550

concerning their reinforcing action. The differences in the reinforcing effects of the products obtained from RH and known fillers can be probably explained by their various chemical nature and lower dispersion (Table 1).

According to the determined temperature coefficient (Fig. 6) and the heat resistance (Fig. 7), the relative strength of rubbers with the experimental SiO_2–1 silicon dioxide appeared to exceed those of Ultrasil VN 2 GR.

Carbon-based products based on SiO_2+C-type of RH as fillers were stated to provide rubber based on SKS-30 ARK with higher temperature and heat resistances according to the elastic-strength properties with respect to rubbers filled with kaolin. Thus, according to the results of the analysis of mechanical and physical-mechanical properties of rubbers based on non-crystallizing amorphous rubber grade SKS-30 ARC with 20 phr of different fillers, the products of the heat treatment of renewable plant raw materials (i.e. rice husk) showed a semi-reinforcing effect.

The reinforcing effect of products obtained from RH used as fillers is determined by the temperature conditions of their preparation, chemical nature, dispersion and their influence on the degree and nature of vulcanization crosslinks. The introduction of experimental silica SiO_2–1 provides the vulcanizates with higher values of equilibrium shear modulus, thermal and heat resistance of rubbers according to the stress-related properties as compared to the industrial silica of the brand Ultrasil VN 2 GR. The product of the heat treatment of the rubber at 500°C (SiO_2+C-4) is characterized by a minimal effect on the formation of rubber-filler cross-links, the relative degree of cross-linking and the conditional-equilibrium shear modulus of rubber. As a filler, it ensures the optimum elastic-strength properties of vulcanizates.

Conclusions

Based on the results of experimental study of the products of the thermal treatment of rice husk, we stated that fine-grained silicon carbon-containing powders of amorphous crystal structure obtained from RH at temperatures of 500–830^{0}C are thermostable at the processing temperatures of rubber compounds and when using for carbureted diene rubbers.

The introduction of 20 phr of carbonization products of the RH and silicon dioxide, in contrast to the known semi-reinforcing fillers, leads to a positive effect on the plastic properties of rubber compounds based on SKS–30 ARK. A decrease in the carbonation temperature of the RH to 500^{0}C allows obtaining a product with a maximum positive effect on the plasticity of rubber compounds. The products obtained from RH at the vulcanization stage are shown to prone to the formation of additional cross-linking rubber filler. Silicon dioxide SiO_2–1 is much times superior to the action of industrial silica as compared with the brand Ultrasil VN 2 GR in terms of the degree of influence on this parameter.

The effects of the heat treatment of products on the degree of cross-linking and the kinetic parameters of sulfur vulcanization of SKS–30 ARK depend on the conditions of their preparation and the composition. The heat treatment is accompanied by an increase in the relative degree of cross-linking, the level of kinetic parameters and the effective activation energy of the vulcanization process. Among the products of carbonation of RH, the elastomeric compositions containing SiO_2+C-2 (the production temperature of 830^{0}C) are characterized by the best complex of rheometric parameters. The kinetic parameters of elastomeric compositions are superior to Ultrasil VN 2 GR; they are affected by experimental silicon dioxide obtained from RH SiO_2–1; the products of carbonization of RH are inferior to those of N 550.

The thermal processing of products of rubbers based on SKS-30 ARK ensures a semi-reinforcing effect. The introduction of SiO_2–1 silicon dioxide, in comparison with the industrial filler Ultrasil VN 2 GR, provides the vulcanizates with a higher equilibrium shear modulus, thermal and heat resistance of rubbers. The rubbers containing SiO_2+C-4 filler (the production temperature of 500^0C) showed better stress-strain characteristics.

Environmentally friendly products of the heat processing of rice husk as renewable plant raw materials can be considered as promising semi-reinforcing fillers of rubber compounds based on carboprene dienes for various purposes.

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Received 27.10.2017

ВИКОРИСТАННЯ ТЕРМООБРОБЛЕНОГО РИСОВОГО ЛУШПИННЯ В ЯКОСТІ НАПОВНЮВАЧІВ ЕЛАСТОМЕРНИХ КОМПОЗИЦІЙ

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Визначено характеристики продуктів термооброблення рисового лушпиння (РШ), що є тонкодисперсними силіцій-, вуглецьвмісними термостабільними порошками аморфно-кристалічної структури. Здійснено порівняльне оцінювання ефективності та експериментальну перевірку можливості використання низки продуктів, отриманих при різних умовах термооброблення подрібненого рисового лушпиння, в якості наповнювачів еластомерних композицій на основі карболанцюгових дієнових каучуків. Показано, що введення 20 мас.ч. продуктів карбонізації або діоксиду силіцію з РШ, на відміну від відомих напівпосилюючих наповнювачів, позитивно впливає на пластичні і в'язкісні властивості гумових сумішей на основі бутадієнстирольного каучуку марки СКС-30 АРК, на відносний ступінь зшивання і утворення зшивань каучук-наповнювач на стадії вулканізації, на рівень кінетичних параметрів сірчаної вулканізації. Встановлено, що як наповнювачі продукти з РШ в гумах мають напівпосилюючу дію, забезпечуючи вулканізатам високий рівень умовно-рівноважного модуля зсуву, температуро- і теплостійкість за пружно-міцнісними властивостями відносно впливу відомих наповнювачів. На комплекс властивостей еластомерних композицій впливає температурно-часовий режим одержання РШ.

Ключові слова: продукти, термооброблення, рисове лушпиння, наповнювачі, еластомерні композиції з СКС-30 АРК, властивості.

THE USE OF THE HEAT-TREATED RICE HUSKS AS ELASTOMERIC COMPOSITIONS FILLERS

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The characteristics of the products of rice husk (RH) after its thermal treatment are determined, these products being fine dispersed silicon- and carbon-containing powders with amorphous-crystalline structure. The comparative evaluation and experimental verification *of possible application of wide range products produced during various conditions of the thermal treatment of crashed rice husk as fillers of elastomeric compositions based on carbon-chain diene rubber are performed. The introduction of 20 phr (parts per hundred rubber) of either the product of carbonized or silicon dioxide obtained by the thermal treatment of rice husk is shown to have a positive effect on both plastic and viscous properties of rubber mixtures based on butadiene-styrene rubber SKS-30 ARK, as well as on the relative extent of cross-linking, the formation of cross-links between rubber and filler during vulcanization and the kinetic parameters of sulphuric vulcanization. This positive effect is observed in this case as opposed to the known semi-enforcing compositions. The semi-enforcing effect of fillers obtained from RH is stated to provide the vulcanizates with high values of equilibrium shear modulus, temperature and heat resistivity as concerns the resilient strength properties relative to the effects of known fillers. The complex of the properties of elastomeric compositions is strongly affected by time-temperature regime of the production of RH.*

Keywords: products; thermal treatment; rice husk; elastomeric compositions based on SKS-30 ARK; properties.

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