تاثیر استئارات روی، روی خواص لاستیک طبیعی پخت شده در حضور یا عدم حضور پرکننده

صنایع لاستیک در هر جامعه کمک قابل توجهی به اقتصاد ملی می کند.هدف نهایی در صنایع لاستیک، افزایش ایمنی و کیفیت و خواص لاستیک ومحصولات لاستیکی است. لاستیک طبیعی یک ماده چند منظوره با خواص فیزیوشیمیایی منحصر به فرد است کهکاربردهای مختلفی در تایر، نوار نقاله ، شیلنگ و غیره دارد.

ZnO و استئاریک اسید نقش مهمی در فرآیند پخت لاستیک ایفا می کنند.پس انتظار می رود که استئارات روی نیز نقش مهمی در فرآیند پخت لاستیک داشته باشد. استئارات روی در بین سایر صابون های فلزی، قدرتمندترین عامل جداکننده از قالب و روان کننده است که در صنایع لاستیک و پلاستیک مورد استفاده قرار میگیرد. حضور فیلر نیز بسیار مهم است.

در این مقاله استئارات روی در حضور یا عدم حضور فیلر در پروسه تولید لاستیک طبیعی مورد استفاده قرار می گیرد. پخت لاستیک در دمای 142 درجه سانتیگراد اتفاق می افتد. نتایج نشان داد که جایگزین کردن استئارات روی به صورت جزئی یا کلی با ZnO و استئاریک اسید خواص فیزیوشیمیایی لاستیک طبیعی را بهبود می بخشد. به این ترتیب که استئارات روی به عنوان فعال کننده سولفور در فرآیند پخت لاستیک عمل می کند و باعث تسریع کراسلینک (شبکه ای) شدن گوگرد می شود.

Effect of synthesized zinc stearate on the properties of natural rubber vulcanizates in the absence and presence of some fillers

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ABSTRACT

Zinc stearate was synthesized by precipitation method through two steps; neutralization of stearic acid by sodium hydroxide then double decomposition using zinc sulphate to precipitate zinc stearate. Mass balances of the two steps were calculated and the physical properties of the prepared zinc stearate were measured and compared to standard. It was characterized and incorporated it into natural rubber in the absence and presence of some filler through mixing process of rubber. The vulcanization process was carried out at 142 °C. The rheological properties of natural rubber mixes were measured using oscillating disc rheometer. The plysico-mechanical properties of the vulcanizates were determined using tensile testing machine. It was found that, partial and complete replacement of synthesized zinc stearate instead of the conventional zinc oxide and stearic acid; enhanced the physico-mechanical properties of natural rubber. The measured reinforcing parameter value α_f can be arranged according to the type of filler as follows:

$$HAF > Hisil > CaCO_3 > Ca_3(PO_4)_2 > BaSO_4 > Talc$$

The highest value of α_f represents the strength of filler and consequently the reinforcing effect of carbon black (HAF) filler while the lowest value of α_f was observed for Talc which show moderate reinforcing effect of Talc. The scanning electron microscope study showed high surface homogeneity and good dispersion of zinc stearate through natural rubber chains in case of the vulcanize containing 9 phr zinc stearate without filler. The investigated natural rubber vulcanizates tolerated thermal oxidative aging at 90 °C for 7 days.

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1. Introduction

The rubber industries contribute significantly to the nation's economy. Enhancements to quality, safety, security and properties of rubber architectures and products based on recommended developed technology and the elemental additives applied [1–3]. Condensed studies are carried out on rubbers and their ingredients to develop academic interest and to improve industrial applications [4–6]. Natural rubber is one of versatile materials of unique chemical and physico-mechanical properties assessed to various applications as tires, conveyor belts, hoses, etc.

Stearic acid and ZnO play an important role in the mechanism of vulcanization process of rubber. They act as activators for the accelerator and sulfur element to promote construction of sulfur crosslinking to the unsaturated part of long rubber chains under the vulcanization conditions as temperature, pressure, time, etc.

[7]. So, it was expected that zinc stearate may have an important effect on the vulcanization process.

Zinc stearate is a typical example of metallic soaps which are usually described as alkaline earth and heavy metal salts of fatty acids. They are insoluble in water and polar solvents such as alcohol and ether. Zinc stearate is the most powerful mold release agent and lubricant among all metal soaps that can be used in plastics and rubber industry [8,9].

Fillers are necessary as reinforcing materials for rubber in order to gain specific properties through two different ways; vanderval force and chemical bonds [10]. Research work was done using the following Einstein's equation to determine the volume fraction or shear modulus of filler [11].

$$G = G_o(1 + 2.5\varphi + 14.1\varphi^2) \tag{1}$$

where G and G_o are shear modulus of filled and unfilled rubber, φ is filler volume fraction.

Medalia [12] introduced the concept of rubber occlusion and replaced filler volume fraction with the effective filler volume

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fraction (φ_{eff}) which accounts for rubber occluded inside the geometrical complex fillers.

The aim of the present work is to prepare zinc stearate and evaluate its effect on the properties of natural rubber vulcanizates in the absence and in presence of some investigated conventional fillers compared with the common compounds of ZnO and stearic acid used in rubber industry. Also, throw light on the morphological characteristics of the investigated vulcanizates.

2. Materials and experimental techniques

2.1. Materials

- *Sodium hydroxide* (NaOH) and *stearic acid* ($C_{17}H_{35}COOH$) were supplied by El Nasr Pharmaceutical Chemicals Company, Egypt
- *Zinc sulphate* ($ZnSO_4 \cdot H_2O$) was supplied from s.d. fiNE-CHEM LTd.
- *Natural rubber* (NR), of the type SMR-20, density 0.931, Mooney viscosity $M_L(1+4)$ at 100 °C = 60–90 poise and glass transition temperature $T_g = -75$ °C, kindly obtained from transport and Engineering, company (TRENCO), Alexandria.
- *Fillers*, six types of the following fillers were incorporated into NR:
  – Barium sulphate ($BaSO_4$), it is white in colour and it has a specific gravity 4.46, oil absorption 13 and particle size 20 nm produced from Sina for Manganese Company.
  – Talc, it is white in colour it has a specific gravity 2.79, oil absorption 35.4, mean particle diameter 63 µm and pH value 7.27, it was obtained from Misr Elhegaz Company – Egypt.
  – Hisil, hydrated silicon dioxide, white powder, specific gravity 1.95, pH value 6.2 ± 0.8 and mean particle size 22 nm, supplied from Bayer AG-germany.
  – Calcium carbonate, it is white in colour and it has a specific gravity 2.65, oil absorption 35, pH value 9.5, and produce from the Egyptian Jordan Company for Carbonate, particle size distribution top cut 20 µm.
  – Calcium phosphate, M.wt. 72, iron Fe^{+2} max. 0.05%, sulphate $(SO_4)^{-2}$ mol, 0.1% from ADWIC.
  – High abrasion furnace black (HAF) with specific gravity 1.78–1.82, pH value 8–9.3, particle size 29 nm and fine granules was supplied by Aldrich company, Germany .
- *Plasticizer*, Naphthenic processing oil, with specific gravity at 15 °C = 0.94–0.96, viscosity at 100 °C = 80–90 poise, it was deep green viscous oil supplied by Aldrich Company, Germany.
- *Accelerator*, N-Cyclohexyl-2-benzothiazole sulphenamide (CBS); pale grey. Non hygroscopic powder, has a melting point of 95–100 °C and density 1.27–1.31 g/cm³, it was supplied by Aldrich Company, Germany.

The other rubber ingredients listed in Table 4 were customarily used in rubber industries; the solvents and chemicals were of pure grade.

2.2. Experimental techniques

2.2.1. Preparation of zinc stearate

Zinc stearate was prepared by precipitation method in two steps; the first step was the preparation of sodium stearate from stearic acid and sodium hydroxide by neutralization reaction using equimolar amounts of both stearic acid and sodium hydroxide. Sodium hydroxide solution (5.63 g in 1 l dist. water) was heated using boiling water bath. Calculated quantity of stearic acid (45 g) was added slowly during a period 15 min with continuous stirring at 58 °C. Samples (5 ml) of the reaction mixture were withdrawn at 5 min intervals and the reaction was tested to its completion by determination of percentage fatty acid conversion.

The second step was the precipitation of zinc stearate using zinc sulphate. Stoichemtrically calculated amount of zinc sulphate dissolved in distilled water to give 5% aqueous solution was added slowly within 15 min at 85 °C to the resulting mixture from the first step (sodium stearate solution) with continuous stirring. After complete addition of zinc sulphate solution, stirring and heating were continued for two hours to insure complete reaction. Zinc stearate product was collected from the top of the reaction mixture and washed three times with hot water to remove water soluble salts. The product was then centrifuged and dried at 105 °C. The process flow diagram of zinc stearate preparation is shown in Fig. 1.

The produced zinc stearate was analyzed to its physical properties [13]; moisture%, ash%, free fatty acid%, melting point and its solubility in both water and organic solvents. X-ray diffraction was carried out in the central laboratories sector at National Center for Radiation Research and Technology, Cairo, Egypt using Philips X-ray diffraction equipment model PW 1730 with Ni Filter, Cu radiation ($\lambda = 1.542$Å) at 40 k volt, 30 MA and a scanning speed 0.13 deg/s. The scanning range is between 4–50°. The relative intensities (I/I_o) were obtained and compared with the standard data ICDD Card No. 579.

2.2.2. Mixing

Rubber ingredients were accurately weighed and mixed on a laboratory size two-roll mill (diameter 470 mm, with 300 mm at friction ratio 1:1.4, speed of slow roll, 16 rpm). The rubber was mixed with ingredients and careful control of temperature, nip gap and sequence of addition of ingredients [14].

2.2.3. Bound rubber

For determination of the bound rubber content, fillers/NR master batches (without curatives) were kept at room temperature for
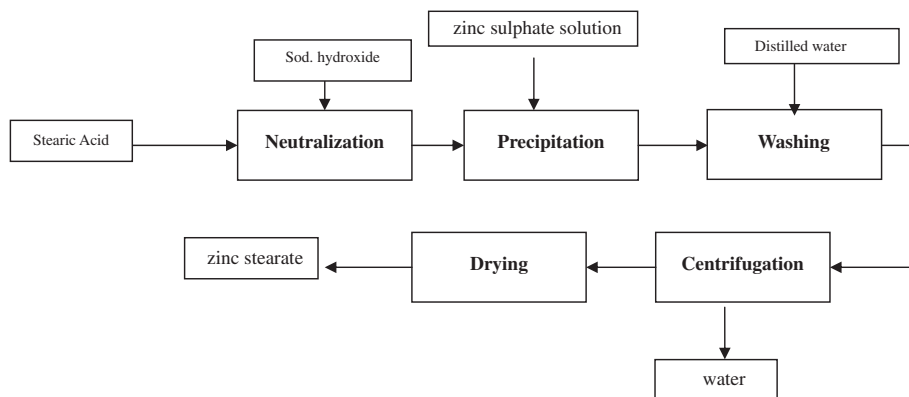

Fig. 1. Process flow diagram of zinc stearate preparation.

7 days for conditioning. After this period, the compound was cut into small pieces. About 0.5 g was precisely weighted and wrapped with filter paper. The wrap was immersed in 100 ml toluene at room temperature. The solvent was renewed on the fourth day and after 7 days, the samples were taken out from the solvent and dried to a constant weight in vacuum. The bound rubber percentage (BR%) was calculated by the following equation [15]

$$BR\% = \frac{w_d - F}{R} \times 100 \qquad (2)$$

where w_d was the weight of the dried gel, F was the weight of the filler in the gel (same as weight of the filler in the original sample), and R was the weight of the rubber in the original sample.

Vulcanization was carried out in a single daylight electrically heated auto controlled hydraulic press at (142 ± 1 °C) and pressure 4 MPa. The compounded rubber and vulcanizates were tested according to standard methods, named:

- Curing characteristics: An oscillating disc rheometer model 100 from Monsanto, USA was used for measuring the curie characteristics of rubber compounds according to [16].
- Physico-mechanical properties determined using Zwick tensile testing machine (model 1425) [17] testing machine at a cross-head speed of 500 mm/min.
- Shore A hardness was measured with a shore instrument, durometer according to ISO868. All tests were conducted at room temperature (25 °C ± 1). Average of five samples was taken for each measurement points [18].
- Fatigue properties were determined using a Monsanto Fatigue Failure testing machine, according to ASTM [19].
- Thermal oxidative aging according to ASTM [20].
- Strain energy determination; Strain energy values were obtained by plotting a stress–strain curves for vulcanized rubber samples and integrating the area under the curve up to the particular extension used. To calculate the strain energy, Simpson's rule is applied [21].

2.2.4. Scanning electron microscopy

Scanning electron microscope (SEM) images were taken by JEOL JSM-T20. Vulcanizate was broken in liquid nitrogen; cross section surface was covered with a very thin layer of gold to avoid electrostatic charging during examination.
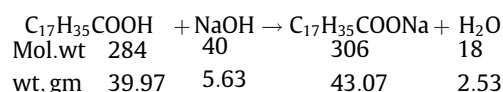
3. Results and discussions

3.1. Characterization of zinc stearate prepared

Zinc stearate was prepared through two steps, the results of the first step sodium stearate preparation were obtained by the determination of percentage stearic acid conversion. These results are shown in Table 1.

It was clear that, the neutralization reaction happened instantaneously at the temperature produced by combined heat of solution and neutralization. The reaction was completed after 15 min and the percentage acid conversion was found to be 96.9%. This conver-
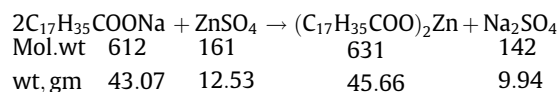
sion reached to 98.7% during the next 15 min. The equation of neutralization reaction can be represented as follows:

$$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COONa + H_2O$$

	$C_{17}H_{35}COOH$	NaOH	$C_{17}H_{35}COONa$	H_2O
Mol.wt	284	40	306	18
wt, gm	39.97	5.63	43.07	2.53

The mass balance of sodium stearate formation was calculated and represented in Fig. 2, based on stearic acid purity 90% and 98.7% acid conversion.

This reaction was an exothermic reaction whereas the temperature raised from 58 °C to 82 °C during the reaction course. The amount of heat liberated, $Q = 42$ kcal was calculated as $mC_p \Delta t$ where m = 1000 ml or g based on C_p, specific heat of water equals 1 Cal/gm °C and Δt is the difference between two temperatures 58 and 82°C; as discussed by Perry et al.[22]. The final solution contained 48.1 g solid containing 0.53 g unreacted stearic acid and the total reaction mixture was 1002.5 g (considering specific gravity of the reaction mixture was 1 g/ml) so the percentage sodium stearate in the solid content 43.07/48.1 was 89.54% and the total dry solid content in the mixture was 48.1 g/1050.63 g or 4.58%.

In the second step, double decomposition reaction occurred between sodium stearate and zinc sulphate at 85 °C. The reaction was completed within 15 min after addition and zinc stearate product was floated on the top of the reaction mixture. Stirring was continued for two hours to improve the separation and insure the completion of the reaction. The reaction equation is represented as follows:

$$2C_{17}H_{35}COONa + ZnSO_4 \rightarrow (C_{17}H_{35}COO)_2Zn + Na_2SO_4$$

	$2C_{17}H_{35}COONa$	$ZnSO_4$	$(C_{17}H_{35}COO)_2Zn$	Na_2SO_4
Mol.wt	612	161	631	142
wt, gm	43.07	12.53	45.66	9.94

The mass balance of zinc stearate formation was calculated and represented in Fig. 3. It was clear that the final solution contained 60.63 g solid and the total reaction mixture was about 1253.13 g. The percentage zinc stearate in the solid content was 75.3% and the total dry solid content in the mixture was 4.6%. Characteristics, namely moisture%, ash%, free fatty acid% (FFA%), melting point and solubility in different solvents of the prepared zinc stearate were determined and shown in Table 2.

3.1.1. X-ray analysis of the prepared zinc stearate

X-ray diffraction of the prepared zinc stearate is shown in Fig. 4. The values of both 2θ and relative intensity (I/I_o) of the prepared
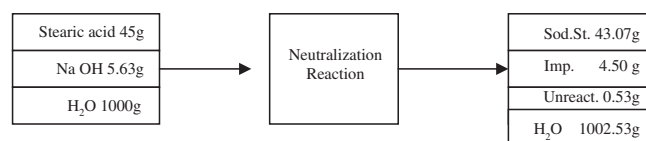
Table 1
Stearic acid conversion with time during the reaction.

Time (min)	Acid conversion (%)
5	70.2
10	85.1
15	96.9
30	98.7

Fig. 2. Mass balance of sodium stearate formation.
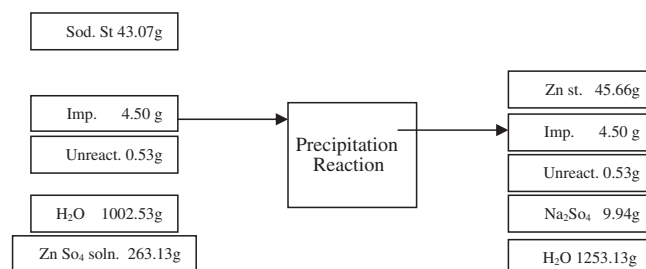
Fig. 3. Mass balance diagram of zinc stearate formation.

Table 2
Measured characteristics of the prepared zinc stearate.

Appearance	Soft, white powder
Moisture, %	0.2
Ash, %	14.2
FFA, %	0.87
Melting point, ºC	125
Solubility	
In water	Insoluble
In alcohol, ether	Insoluble
In benzene	Slightly soluble

Table 3
Values of 2θ and relative intensity (I/I_o) of both prepared and standard zinc stearate.

Prepared zinc stearate		Standard ICDD card	
2θ	(I/I_o)	2θ	(I/I_o)
6.289	100	6.4	100
8.499	11.73	8.414	13
10.709	25	10.599	27
19.208	43	19.58	100
22.438	66	22.665	67

zinc stearate and standard ICDD Card No. 579 are shown in Table 3. Comparing these values, it is clear that all lines are present. The peak at 2θ = 19.58 shows different intensity in the prepared sample than that at ICDD card. This may be due to preferable orientation of zinc stearate.

3.2. Effect of zinc stearate on the properties of investigated natural rubber vulcanizates

Table 4 represents the investigated formulations as well as the results of rheometric characteristics of rubber mixes and the physico-mechanical properties of the vulcanizates. It was found that, good rheometric characteristics for the control formulation no. A; containing conventional common compounds as ZnO and stearic acid; the maximum torque was high and low cure rate index were obtained. If the amount of ZnO and stearic acid decreased and replaced by definite concentration of the synthesized zinc stearate (formulations no. B and C) an increase in minimum torque, optimum cure time and scorch time were recorded.

In case of incorporation of different concentration of the prepared zinc stearate to the investigated formulations instead of zinc oxide and stearic acid (formula no. D, E, F, G), the results showed notable decrease in maximum torque. The scorch time and cure rate index were generally increased compared with the control formula no. A. These observations can be attributed to the plasticity effect of zinc stearate which did not prevent the formation of ionic crosslinks; as reported by Frohlich et al. [1]. With respect to the obtained physico-mechanical properties Table 4, it was observed that, generally the modulus at 100% and 200% strain, tensile strength, strain at rupture, young's modulus, equilibrium swelling and fatigue life were increased, while the strain energy decreased.

On using zinc oxide and stearic acid in the presence of zinc stearate (formula B & C) the rheological and mechanical properties also generally improved. The values of improved properties depend on the concentration of zinc stearate, thus these values were more high than the control one (formula A). Fig. 5 represents the relation between young's modulus of the investigated natural rubber vulcanizate and concentration of zinc stearate. It was found that, this property increased with increasing the concentration of zinc stea-
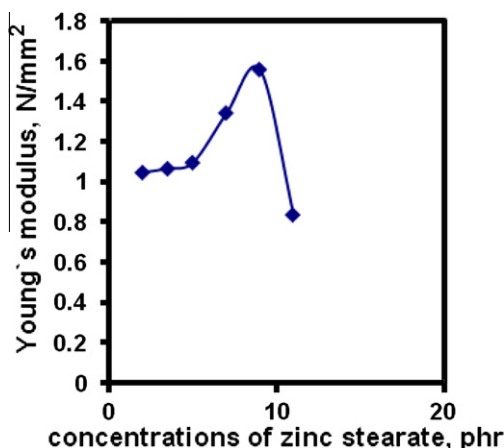

Fig. 5. The relation between Young's modulus of NR loaded with zinc stearate alone and zinc oxide/stearic acid.

rate up to 9 phr, after that it decreased. The optimum concentration of zinc stearate which gave the highest value of young's modulus was 7 and 9 phr, respectively. Sharp decrease in the value of young's modulus was obtained at 11 phr of zinc stearate.

From the above results, it can be concluded that, generally partial and complete replacement of zinc stearate instead of the common materials; ZnO and stearic acid; enhanced the physico-mechanical properties of natural rubber.

3.3. Effect of zinc stearate on the properties of natural rubber vulcanizates in absence and presence of some different types of filler

In this section different types of filler were used with natural rubber such as barium sulphate, Talc, Hisil, calcium carbonate, calcium phosphate and carbon black in the presence of 9 phr zinc stearate. The investigated formulations, bound rubber content and the rheometric characteristics are illustrated in Table 5.

The bound rubber was formed through physical adsorption of rubber molecules on the filler aggregates; as described by Schuater [2]; during mixing process. The rubber molecules can penetrate the
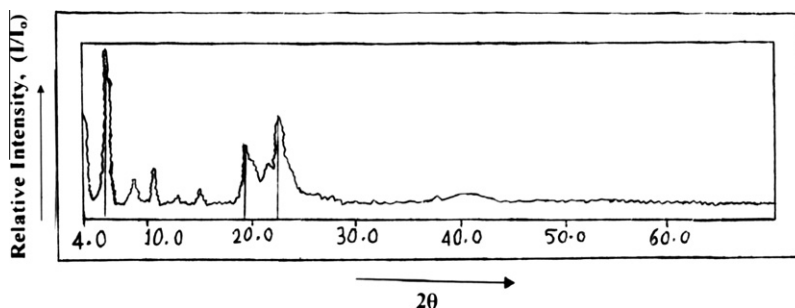

Fig. 4. X-ray diffraction of the prepared zinc stearate.

interior of an aggregate and leading to a physical entrapment of the free rubber molecules. The bound rubber control was calculated as percent as illustrated in Table 5. The highest value was found in case of NR/carbon black mixes, while in the investigated white fillers the values were less, this may be due to the high reactivity of the surface of carbon black (HAF) particles which led to an increase of rubber–carbon black bonding. The percent of bound rubber in the investigated fillers can be arranged as the following order

$$Carbon\ black\ (HAF) > Hisil > CaCO_3 > Ca_3(PO_4)_2 \simeq BaSO_4 > Talc$$

The rheometric characteristics show that, the maximum change in curometer torque during vulcanization increased. The ratio between the increase in torque of loaded natural rubber compound and that of gum was depending on the type of filler. The reinforcing parameter; according to Arroyo et al. [3]; (α_f) deduced from rheological properties was used to characterize the reinforcement of fillers, according the following equation

$$\frac{D_{max} - D_{min}}{D_{max}^o - D_{min}^o} - 1 = \alpha_f \frac{m_f}{m_p} \qquad (3)$$

where $D_{max} - D_{min}$ is the maximum change in torque during vulcanization for filled rubber $D_{max}^o - D_{min}^o$ is the maximum change in torque during vulcanization for rubber gum, and m_p is the mass of natural rubber in the compound and m_f: is the mass of filler in the compound.

The measured reinforcing parameter value (α_f) can be arranged according to the type of filler as follows:

$$Carbon\ black\ (HAF) > Hisil > CaCO_3 > Ca_3(PO_4)_2$$
$$> Barium\ sulphate > Talc$$

The highest value of α_f represents the strength of filler and consequently reinforcing effect of carbon black. The increase in maximum torque (ΔM) was ascribed to the crosslinking of rubber phase. ΔM was high in case of carbon black among the investigated white fillers used. The cure rate index and curing time depend on the type of filler.

In case of using Talc, the value of reinforcing parameter (α_f) was low while the cure rate index was high, these results were confirmed with that obtained by Mathew et al. [23]. From the above

Table 4
Rheometric characteristic and physico-mechanical properties of NR vulcanizates with and without zinc streate.

Ingredient, phr	Formula no.						
	A	B	C	D	E	F	G
Zinc oxide	5	2.5	1	–	–	–	–
Stearic acid	2	1	0.5	–	–	–	–
Zinc streate	–	2	3.5	5	7	9	11
Rheometric characteristic at 140 °C							
Minimum torque, dN m	3	4	4	3.75	3.5	3.25	2.75
Maximum torque, dN m	56.5	55	51	35	36.5	38	35
Optimum cure time, min	16.25	20.25	19.25	14.25	14.75	17.75	21.5
Scorch time, min	5	8	7.5	7	7.25	9.75	10.5
Cure rate index, min^{-1}	8.88	8.16	8.51	13.79	13.33	12.75	9.09
Physico-mechanical properties of the samples at optimum cure time							
Modulus at 100%, MPa	1.12	1.19	1.38	1.17	1.4	1.615	0.886
Modulus at 200%, MPa	1.76	2.1	2.31	1.51	1.81	2.1	1.31
Tensile strength, MPa	12.84	23.5	25.47	18.1	22.17	27.96	20.58
Strain at rupture, %	684	863	954	915	1169	1155	1139
Young's modulus, N/mm^2	1.02	1.07	1.18	1.12	1.37	1.59	0.86
Equilibrium swelling, %	356	353	364	387	422	358	424'
Fatigue life, K cycle	63.5	123.3	123.6	148.5	149.5	159	149.8
Hardness, shore A	41	47	45	45	46	41	43
Strain energy, MJ/m^3	4.21	5.45	6.4	3.23	3.29	3.91	3.4

Base recipe in phr: 100 NR; 0.6 CBS; 1 PBN; 2.5 sulfur.

Table 5
Formulation and rheometric characteristic of NR vulcanized loaded with different type of fillers.

Ingredient, phr	Formula no.						
	F	S1	S2	S3	S4	S5	S6
Barium sulphate	–	40	–	–	–	–	–
Talc	–	–	40	–	–	–	–
Hisil	–	–	–	40	–	–	–
Calcium carbonate	–	–	–	–	40	–	–
Calcium Phosphate	–	–	–	–	–	40	–
Carbon black	–	–	–	–	–	–	40
Bound rubber, %	–	40.2	38.6	43.7	43	40.5	49.3
Rheometric characteristic at 140 °C							
Minimum torque, dN M	3.25	5	4.5	5.5	3.25	3.5	3
Maximum torque, dN M	38	45	40	49.5	46.5	45.5	52
ΔM, dN m	34.75	40	35.5	44	43.25	42	49
Scorch time, min	9.75	5.4	5.8	6.5	6.06	6.75	4.06
Optimum cure time, min	17.75	10.75	11.25	13	11.75	14.57	10
Cure rate index, min^{-1}	12.75	18.69	18.34	15.38	17.57	12.5	16.83
α_f	–	0.375	0.0539	0.665	0.6115	0.52	1.025
Volume fraction of fillers (φ_f)	–	0.0756	0.1187	0.1572	0.1187	0.136	0.24

Base recipe in phr: 100 NR; 9 zinc stearate; 0.6 CBS; 1 PBN; 2.5 sulfur, φ_f is given by $\varphi_f = V_{filler}/(V_{filler} + V_{rubber})$ where V is the volume.

results it is clear that zinc stearate can be used as activator for sulfur vulcanization process of rubber instead of ZnO and stearic acid which are commonly used in rubber industry.

3.4. Effect of synthesized zinc stearate on the mechanical properties of natural rubber vulcanizates in the absence and presence of some investigated fillers

The stress–strain plots resulted from tensile experiment data are displayed in Fig. 6. It was clear that, high tensile strength was observed at 1100% elongation for natural rubber valucanizate without filler. In the presence of fillers the tensile strength increased depending on the type of the filler according to the following order

Carbon black > Hisil > Talc > $Ca_3(PO_4)_2$ > $BaSO_4$ > $CaCO_3$

In case of using carbon black or calcium carbonate, the elongation at break decreased considerably. It may be presumed that, zinc stearate promote calcium carbonate or carbon black to disperse uniformly with a sufficient degree of exfoliation and interchelia-tion and consequently the rubber matrix become strongly reinforced than using other fillers.
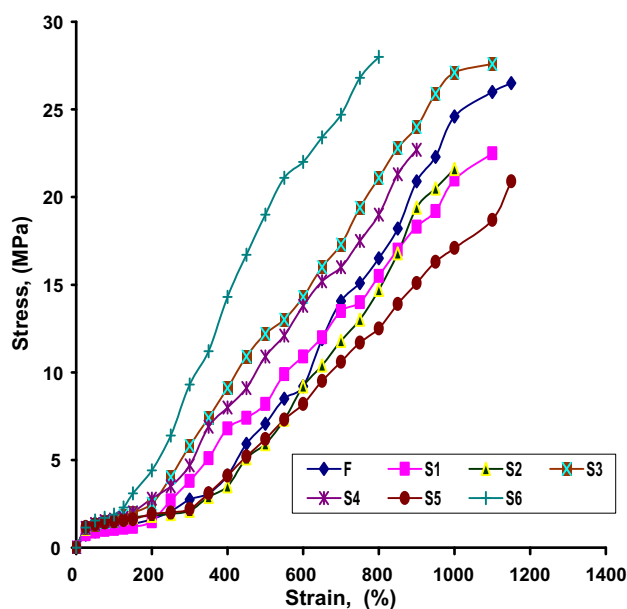

Fig. 6. Stress strain curves of NR loaded with different type of fillers.

Table 6 shows the physico-mechanical properties of natural rubber vuclanizates loaded with different types of filler in the presence of zinc stearate. It is shown that, an improvement and increase in the modulus at 100% and 200% strain of natural rubber while releasing in the other properties depending on the nature, particle size, surface area, particle shape and the type of filler used.

The increase in modulus was due to the measuring before any significant rubber deformation without taking into consideration the interaction between the filler and natural rubber matrix; according to Murray [6]. The increase in tensile strength in case of using calcium carbonate or carbon black can be referred to the platy nature of these fillers and to the good filler–rubber interaction, which create fewer micro voids between the filler and rubber matrix.

The reinforcing index (RI) seen in Table 6 is an empirical parameter representing reinforcing effect and calculated from the mechanical properties according to the following equation:

$$RI = (N/N_o)(\text{silica content}\%/100) \qquad (4)$$

where N and N_o are nominal values obtained by tested specimens in the absence and presence of filler. The obtained data was confirmed with some published results [6,12,24]. Also it is observed that the hardness and young's modulus generally increased or remain at the same value in the presence of filler while the fatigue life decreased. This was expected because as fillers were incorporated in the natural rubber matrix the plasticity of the rubber chain was reduced resulting in rigidity; as reported by Medalia [12].

The elastic modulus was affected by several factors depending on the surface reactivity such as particle size and shape, structure and dispersion of the filler in rubber chains; as discussed by Mathew et al. [23]. The relation between hysteresis and strength is illustrated through the simple empirical low as follows.

$$U_b \simeq B(H_b\Sigma_b)^{1/2} \qquad (5)$$

where U_b is the energy input per unit volume to break the tested sample (area under the stress strain curve), H_b is the energy dissipated in the deformation prior to break (area of the hysteresis loop), Σ_b is the strain at break and B is a constant.

The hysteresis depends on the type of investigated fillers as shown in Figs. 7a–7c the hysteresis of unfilled natural rubber vulcanizate can be arranged according to the following order; formula no. A (ZnO/stearic acid) < formula no. B (ZnO/stearic acid–zinc stearate) < formula no. F (zinc stearate alone). In the presence of fillers the hysteresis follows the order: Formula no. S_6 (carbon black/znic stearate) > formula no. S_3 (Hisil/znic stearate) > formula no. S_4 (calcium carbonate/zinc stearate) > formula no. S_1 (barium sulphate/zinc stearate) > formula no. S_5 (calcium phosphate/zinc stearate > formula no. S_2 (Talc/zinc stearate). It can be concluded

Table 6
Physico-mechanical of NR vulcanized loaded with different type of fillers.

| Ingredient, phr	Formula no.						
	F	S1	S2	S3	S4	S5	S6
Modulus at 100%, MPa	1.615	2.1	1.742	2.61	1.905	2.547	1.98
RI	–	4.98	4.133	6.192	4.519	6.042	4.697
Modulus at 200%, MPa	2.1	2.6	2.177	3.02	2.815	2.96	3.17
RI	–	4.744	3.972	5.51	5.136	5.4	5.784
Tensile strength, MPa	27.96	23.46	21.52	28.69	23.65	22.14	28.91
RI	–	3.214	2.949	3.93	3.24	3.034	3.961
Strain at rupture, %	1155	1117	1202	1111	922	1032	846
Young's modulus, N/mm^2	1.59	2.03	1.54	1.53	1.55	1.69	1.62
Fatigue life. K cycle	159	101	96.2	94	89	99	100
Hardness, shore A	41	45	56	63.5	63	56	65
Strain energy, MJ/m^3	1.17	1.38	1.615	1.12	1.19	1.4	0.886
Hysteresis loss, MJ/m^3	1.76	2.1	2.31	1.51	1.81	2.1	1.31
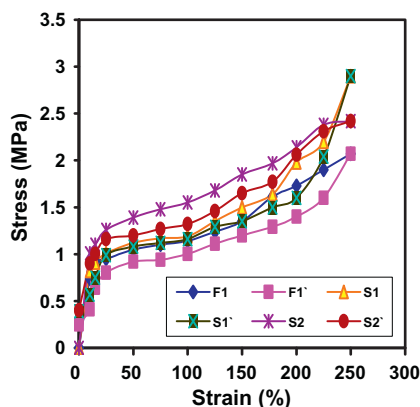
Fig. 7a. Hysteresis loops for NR loaded with barium sulphate and Talc.
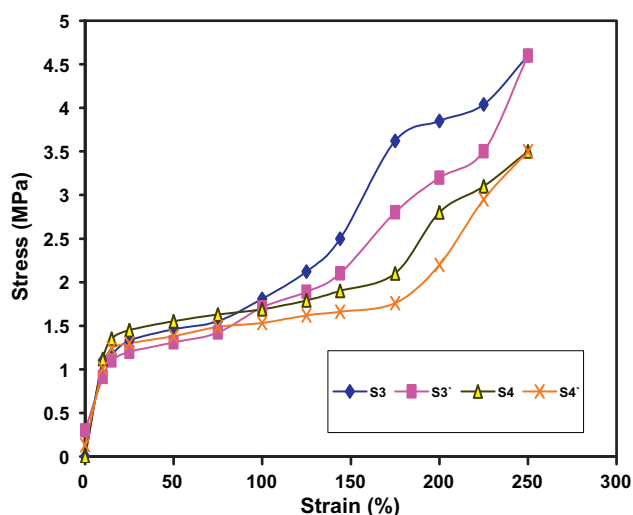

Fig. 7b. Hysteresis loops for NR loaded with Hisil and calcium carbonate.
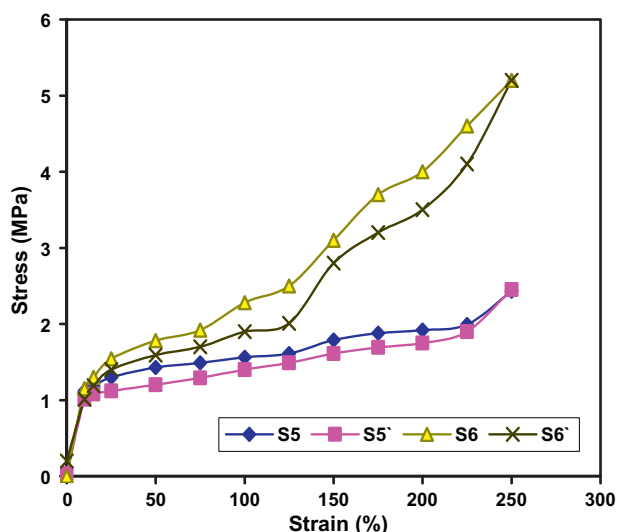

Fig. 7c. Hysteresis loops for NR loaded with calcium phosphate and carbon black.

that znic stearate in absence and presence of filler can be used as an activator and reinforcing agent for natural rubber to improve their properties; according to Furtado, Dehui and Perez [25–27].

3.5. Swelling behaviour of the interacted zinc stearate / natural rubber vulcanizates

The swelling behaviour of the investigated rubber vulcanizates was studied according to the following equation:

$$Q_f/Q_g = ae^{-z} + b \qquad (6)$$

where Q is defined as grams solvent per grams of natural rubber and calculated from the following equation:

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100/\text{formula weight}} \qquad (7)$$

The subscripts f and g refer to filled and unfilled natural rubber vulcanizates respectively, z is the ratio of filler to rubber in the vulcanizates, while a and b are constants, also

$$\frac{Q_f}{Q_g} = \frac{V_{ro}[1 - V_{rf}]}{V_{rf}[1 - V_{ro}]} \simeq \frac{V_{ro}}{V_{rf}} \qquad (8)$$

So

$$V_{ro}/V_{rf} = ae^{-z} + b \qquad (9)$$

where V_{ro} is the volume fraction of the pure rubber and V_{rf} is the volume fraction of the filled rubber in the swollen gel.

The effect of interaction between rubber and filler can be determined by the value $1/Q$; according to Rattanasom et al. [28]. Higher value of (Q_f/Q_g) leads to lower interaction between the filler and the rubber matrix. The value of (Q_f/Q_g) and $(1/Q)$ were calculated and listed in Table 7. The data show that the lowest value of (Q_f/Q_g) and the greatest value of $(1/Q)$ were found in case of using carbon black or Hisil, i.e., stronger rubber filler interaction and hence sufficient adhesion between filler and rubber phase. The above results were confirmed with the cross linking density determined from the equilibrium swelling according to Flory–Rehner relation [29].

$$1/(2M_C) = (-1/2\rho V_o)((\ln(1 - V_R) + V_R + \mu V_R^2)/(V_R^{1/3} - 1/2V_R)) \qquad (10)$$

where M_C is the molar mass between crosslinks, ρ is the density of rubber, V_o is the molar volume of the solvent (toluene) = 106.3 cm³/mol, V_R is the volume fraction of swollen rubber that can be obtained from the mass, densities of rubber samples and solvent while μ is the interaction parameter between rubber and toluene which is 0.393 for natural rubber.

The degree of crosslinking υ is given by

$$\upsilon = 1/2M_C \qquad (11)$$

Table 7 shows that the values of υ were increased in case of using carbon black and Hisil (formula no. S_3, S_6). The increase of cross linking density due to the presence of additional physical and chemical crosslinks, as it was observed from the swelling and values of M_C data.

3.6. Scanning electron microscope study

The scanning electron microscope study was represented in Fig. 8. Fig. 8a shows the morphology of natural rubber vulcanizates containing zinc stearate without filler, it is clear that zinc stearate was homogeneously dispersed in natural rubber chains. Fig. 8b demonstrated noticeable particle agglomeration of barium sulphate in the compounded natural rubber.

Fig. 8c–g shows the dispersion of the other fillers in the compounded natural rubber, the homogeneity and dispersion can be arranged according to the type of filer in the following order:
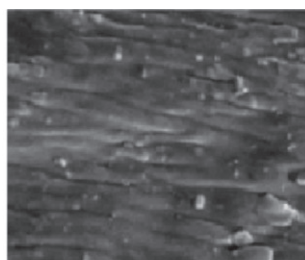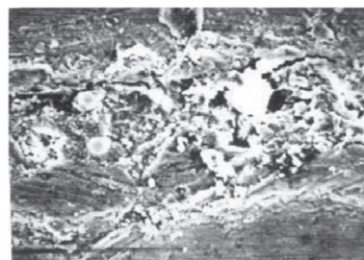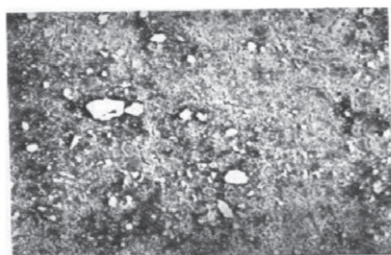
Hisil > carbon black > calcium phosphate > Talc > calcium carbonate > barium sulphate. The surface homogeneity of the filled rubber depends on the type and nature of the applied filler.

Table 7
Swelling characteristics for NR vulcanized loaded with different of fillers.

Ingredient, phr	Formula no.						
	F	S1	S2	S3	S4	S5	S6
$1/Q$	0.0028	0.00374	0.00332	0.0042	0.0039	0.0036	0.00458
Q_f/Q_g	–	0.745	0.8407	0.6675	0.7151	0.7737	0.6089
Mol.wt. between crosslinking (M_C), g/mol	5112	2973	3829	2518	2851	3289	2135
Crosslinking density, $\upsilon \times 10^{-4}$ mol/cm^3	0.978	1.68	1.306	1.99	1.75	1.52	2.34
Soluble fraction, %	5.99	5.19	5.312	5.02	5.17	5.21	5.083

NR blanck

Talc

Barium sulphate

Calcium phosphate
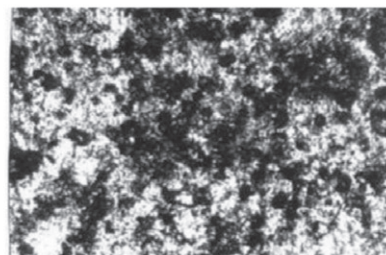
Carbon black
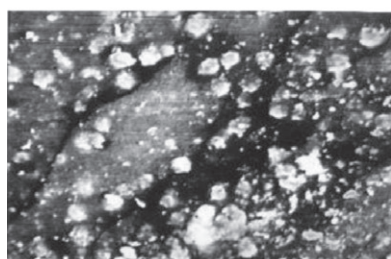
Calcium carbonate
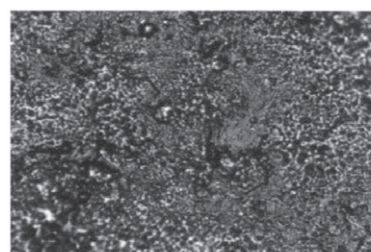
Hisil

Fig. 8. Scanning electron microscope of NR Vulcanizates loaded with different type of filler (magnification $X = 1000$).

3.7. Effect of thermal oxidative aging on the mechanical properties

The investigated rubber vulcanizates were subjected to thermal oxidative aging at 90 °C for different time periods, the mechanical properties were tested before and after aging and represented in Fig. 9a–c.

The retained values of tensile strength, stress at 100% strain and strain at break for natural rubber loaded zinc stearate and Hisil
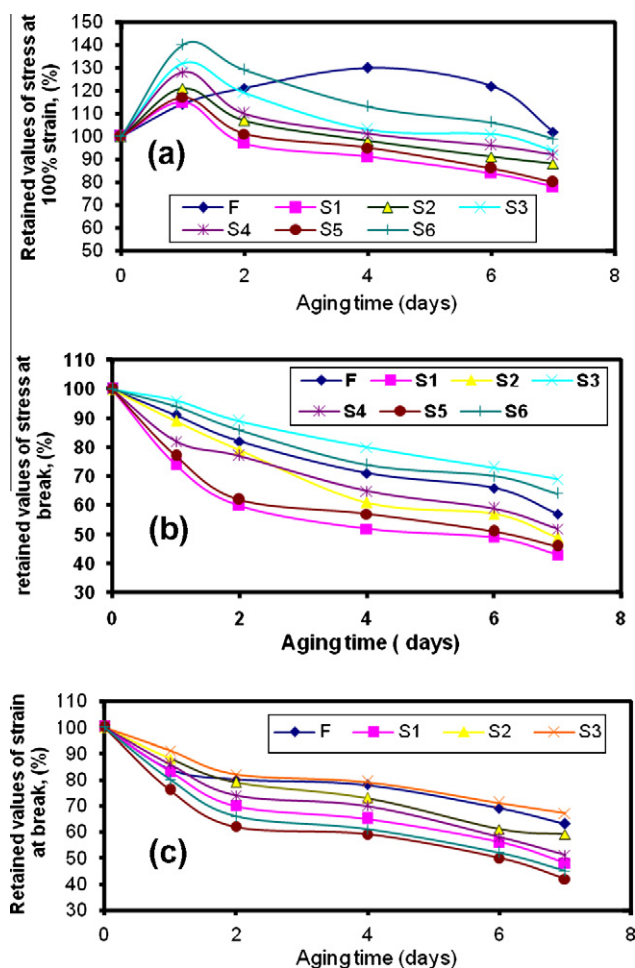
Fig. 9. The relation between aging time and retained values of different types of fillers in presence of zinc stearate, (a) retained values of stress at 100% strain, (b) retained values of tensile strength, (c) retained values of strain at break.

(formula no. S_3) were high among all other fillers used. On the other side, lowest value of strain at break was obtained for the formula containing calcium carbonate (formula no. S_4). At temperature near the melting point of zinc stearate (128 °C), solvation or exchange reaction may occur causing plasticization of compounded rubber. Therefore the investigated formulation tolerates thermal oxidative aging at 90 °C for seven days. From the above results it can be concluded that zinc stearate can be used instead of ZnO and stearic acid in natural rubber formulations in absence and presence of fillers.

4. Conclusions

It can be concluded that: enhanced physico-mechanical properties of natural rubber were obtained partial and complete replace-

ment of zinc stearate instead of the common materials; ZnO and stearic acid. So, zinc stearate can be used as activator for sulfur vulcanization process of rubber instead of ZnO and stearic acid which are commonly used in rubber industry; in absence and presence of fillers.

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