

Nanofiller as Vulcanizing Aid for Styrene-Butadiene Elastomer

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Abstract: The use of ZnO and stearic acid is very well known in sulfenamide accelerated sulfur vulcanization of diene elastomers. Zn-ion coated nano filler has been developed and tested, in styrene-butadiene rubber (SBR) as sulfur vulcanizing activator cum reinforcing filler. In this study Zinc oxide has been replaced by the Zn-ion coated nano silica filler with an aim to study the dual role of this nanofiller in SBR. The presence of Zn-ion on the nano silica filler surface activates the sulfur vulcanization by involving Zn^{++} in to the sulfurating complex formed with thiazole from sulfenamide. The increase of Zn-ion, on the nanofiller, decrease the scorch safety of the elastomer compound but increase the tensile strength, state of cure and tear strength and attain maximum at its 10% level. The presence of stearic acid increases the rate of vulcanization. Replacement of stearic acid with mono-stearate, however, increases the vulcanization rate but decrease the ultimate state of cure. A mechanistic scheme involving dual function of this nanofiller has been suggested.

Keywords: vulcanization, styrene-butadiene rubber, nanofiller, silica, zinc ion.

Introduction

Presently the nanoscale materials have inspired the scientist and technologists, in the field of composites, by the fact that they often give rise to dramatically improved properties than their macro counterpart.^{1,2} Nanocomposites possess unique properties such as stiffness, strength and barrier action depending on their dispersion structure in the matrix.^{3,4} The nano particles are often used in a blending with polymers but this direct blending can not avoid the clustering tendency and the polymer matrix must have good process properties.⁵ Clay has been used enormously as filler for rubber and plastic in conventional microcomposites. Wang *et al.*,⁵ while preparing and characterizing the rubber-clay nanocomposites, suggested the latex method as most convenient in order to use clay as promising reinforcing agent. Although clay nanocomposites have been studied in Nylon-6⁶ and PET⁷ as matrix polymer, very little informations are available regarding the use of nano fillers in elastomer composites. Probably no information is available specially in the field where surface modification of the nanofiller can affect the composite properties by directly participating in the elastomer

vulcanization process.

Efforts have been made in this study, to elucidate the vulcanization mechanisms as affected by the Zn-ion of the Zn-ion coated nano silica filler in the composites based on the styrene-butadiene rubber (SBR) and *co*-related with the properties thus developed.

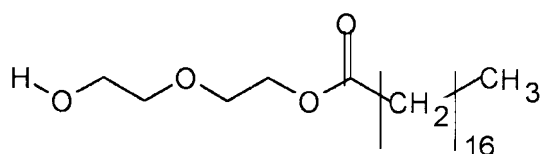
Experimental

Compounding formulations were shown in the Table I. SBR 1502 was mixed with nanofiller along with stearic acid, sulfur, *N*-cyclohexyl-2-benzothiazyl-sulfenamide (CBS) in a two roll open mixing mill at a fixed nip gap at around 35 °C. The nanofiller was Zn-ion coated silica having average particle size 15-20 nm, which has been developed following the chemical process in our laboratory. The particles are spherical in shape and amorphous in nature. IR spectroscopy of pure nano silica filler and Zn-ion coated nano silica filler revealed that there is no chemical lattice replacement of Si and Zn rather Zn-ion adsorbed at the surface. The peak at 466 cm^{-1} is observed in both the cases of nano silica filler with and without Zn-ion coated suggesting Si-O-Si bending vibration remains unaffected. However, the symmetric stretching vibration of Si-O-Si appeared⁸ at 799 cm^{-1} in the case of pure SiO₂ is shifted to 792 cm^{-1} in the case of Zn-ion

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coated nano silica filler. The peak at 1547 cm^{-1} in the case of nano silica filler is shifted to 1420 cm^{-1} in the case of Zn-ion coated nano silica filler. The IR spectra thus revealed that there is some microscopic interaction between the two-lattice structure.⁸⁻¹⁰ The effect of long chain fatty acid was studied by replacing the stearic acid with diethylene glycol monostearate (DEGS). The structure of the DEGS is given below.



The mixed compound was sheeted out from the mixing mill and vulcanized by compression molding at 150°C up to the optimum extent (t_{90}) under a pressure of 20 MPa. The physical property was measured on this vulcanized sheet. Cure characteristics of the compounds were measured with a help of Monsanto Rheometer 100. Degree of reinforcement was studied from the rheometric torque as earlier.¹¹ Percent volume swell was studied by immersing the sample in the toluene up to equilibrium.

Results and Discussion

The rheometric plots of compounds were shown in Figure 1 as variation of torque against time. The minimum viscosity of the compound increases with increase in Zn-ion content in the nanofiller. The initial rate of vulcanization however, is maximum at 5% Zn-ion and goes on decreasing with the increasing Zn-ion content, although the optimum cure time (t_{90}) goes on decreasing with the increase in Zn-ion content of the nanofiller (Table II). Scorch time (t_2) decreases with the increase in Zn-ion content. The rate of cure is higher in the compound when stearic acid is being replaced by DEGS

Table I. Compounding Formulations

Ingredients	A	B	C	D	E	F	G
SBR	100	100	100	100	100	100	100
Filler-5	30	-	-	-	-	-	-
Filler-10	-	30	-	30	30	-	-
Filler-15	-	-	30	-	-	-	-
Filler-0	-	-	-	-	-	-	30
ZnO	-	-	-	-	-	-	2.0
Stearic acid	2.5	2.5	2.5	-	-	2.5	2.5
DEGS	-	-	-	-	2.5	-	-
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0

0, 5, 10, 15, in "Filler" stands for percentage of Zn-ion on silica.

(mix E) accompanied by low state of cure and lowest optimum cure time. Presence of stearic acid increases the scorch time but decreases the optimum cure time (mixes B and D). In presence of stearic acid nanofiller increases the scorch safety and the optimum cure time (mixes B and F). However, the presence of ZnO (added separately) in conjunction with silica filler having no Zn-ion (mix G) enhanced the cure rate with higher state of cure and lower cure time.

Figure 2 reveals that the ultimate extent of cure ($T_{max} - T_{min}$) attains highest value at 10% level of Zn-ion in the nanofiller. This is in line with the modulus value (upper portion of Figure 2). The degree of reinforcement followed the similar trend i.e. increased with the Zn-ion content attains a maximum value at its 10% level and then drastically decreased. Presence of stearic acid increases the state of cure. Modulus and tensile strength are also followed the same trend (mixes B and D). Replacement of stearic acid by DEGS reduced the state of cure and simultaneously reduced the tensile strength, modulus

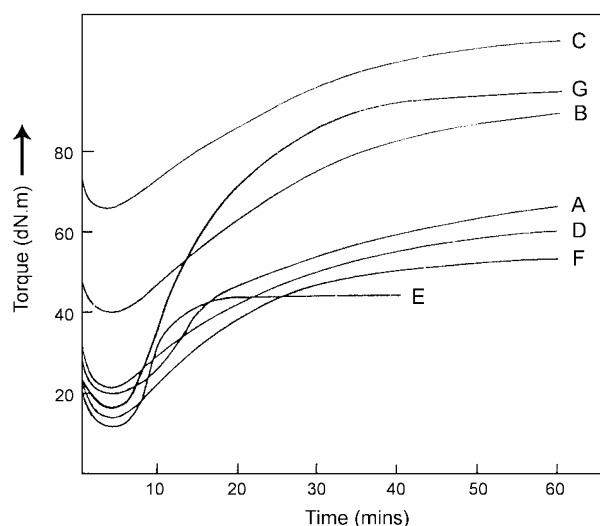


Figure 1. Rheometric torque against the time for the compounding.

Table II. Physical Properties and Processing Parameters of the Compounding

Physical Properties	A	B	C	D	E	F	G
Hardness (Shore A)	72	85	82	70	56	48	68
Tensile Strength(MPa)	2.7	4.2	4.0	1.8	2.2	1.5	4.9
Modulus (200%)(MPa)	2.4	2.9	-	1.7	1.2	1.0	3.1
Tear Strength(N/m $\times 10^3$)	18.6	19.6	11.7	9.8	12.7	7.8	21.1
Elongation at Break (%)	320	220	170	210	450	250	470
Volume Swell(%)	215	140	107	205	420	465	240
t_2 (min)	8.0	5.5	3.5	3.0	5.5	4.5	5.1
t_{90} (min)	46	43	40	46	10.5	40.5	30.2

and tear strength. It is observed from the Table II that the tensile strength, tear strength and modulus attained maximum value at 10% level of Zn-ion in the nanofiller. Elongation at break however, decreased with a increase in Zn-ion. Presence of stearic acid (mixes B and D) increases all the properties. Replacement of stearic acid with DEGS (mixes B and D), however, decreases all the physical properties except the elongation at break, which is increased. In order to study the effect of ZnO, the silica filler without Zn-ion has been used in the compounding (mix G) in the presence of ZnO, which has been added separately. As usual the presence of ZnO enhanced the state of cure thereby modulus, tensile and tear strength.

Percent volume swell is decreased with increasing the Zn-ion content in the nano filler. Presence of stearic acid decreased percent volume swell. The presence of DEGS in place of stearic acid increases the solvent swelling similar to the gum-stock (mixes E and F). Comparatively higher swelling in the case of mix G may be due to more number of polysulfidic linkages.

The wide spread use of ZnO parallels the acceptance of thiazole and its derivatives as accelerators. ZnO is required for the property development in conjunction with thiazole accelerators and develop tight cures with diphenyl guanidine accelerators. Adams *et al.*¹² emphasized the importance of rubber soluble Zn in the form of Zn-ion is the precursor for the sulfurating complex for the sulfur vulcanization of butadiene containing rubbers. This solubilization is the main function of long chain fatty acid, like stearic acid. Apart from the function of activator Zn-ion affects the conversion of polysulfide cross-links to di - and mono- sulfide crosslink as

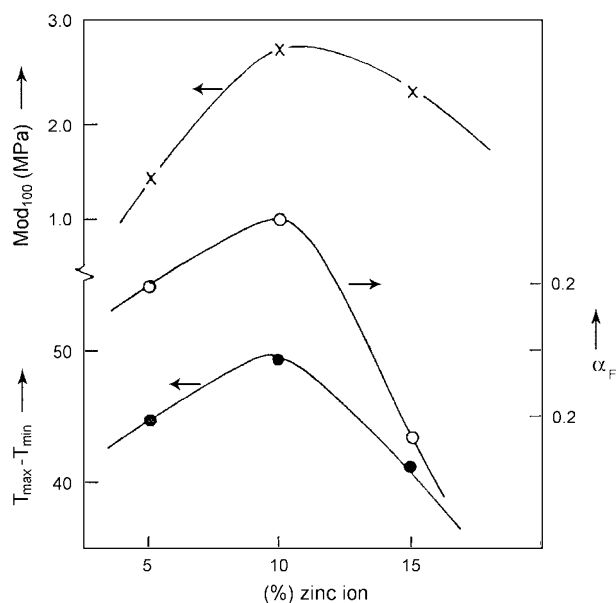


Figure 2. Variation of $T_{max} - T_{min}$, degree of reinforcement and modulus (100%) against the Zn-ion content in the nanofiller.

observed by Studebaker *et al.*¹³ It was also reported that the increased of stearic acid substantially increases the ZnS but at the same time decreases the combined sulfur.¹⁴ Bateman *et al.*¹⁵ suggested that the reaction of sulfur with the elastomers proceed through ionic mechanism in presence of ZnO. Krebs¹⁶ also suggested the involvement of Zn-ion in the formation of sulfurating complex in the presence of amines. Scheele¹⁷ also suggested the formation of an intermediate sulfurating complex involving Zn-ion, accelerator and the sulfur. It was also reported by the author¹⁸ that mechanism of CBS accelerated sulfuration in no way differ from thiazole acceleration, except that the amine moiety, formed from CBS, play a vital role as binary accelerator system as discussed in previous publications.¹⁹ In the presence of zinc oxide and stearic acid the sulfuration was initiated by radical but proceeds through polar mechanism. In the present study the nanofiller itself containing Zn-ion on its surface facilitating its free access to form the rubber soluble sulfurating complex^{18,20} as shown in Figure 4. Presence of stearic acid again facilitates the solubilization process by salt formation then enhancing the rate of cure and reducing the optimum cure time. The effect of DEGS was more dominating for reducing the optimum cure time but drastically reduced the state of cure suggesting lack of efficiency to take part in the sulfurating complex forming mechanism. It is evident from the structure of the DEGS that it has the polarity equivalent to stearic acid (as studied by chromatography) but is free from any acid group and thus it is unable to dissolve Zn-ion from the surface of nanofiller. Based on the results a model has been put forward for the dual role of the Zn-ion coated nanofiller for the development of vulcanizate properties^{21,22} (Figures 3-5). In Figure 4, NH_2R_1 is the amine moiety of the CBS. From the structure (Figure 3) it appears that the Zn-ion is chemically adsorbed on the surface of silica through

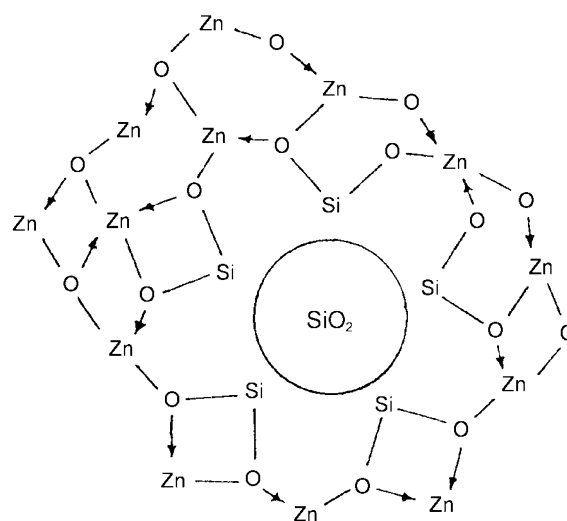


Figure 3. Tentative model structure of Zn and oxygen network over silica.

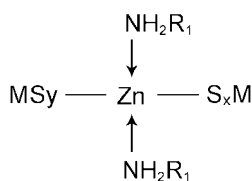


Figure 4. Structure of sulfurating complex.

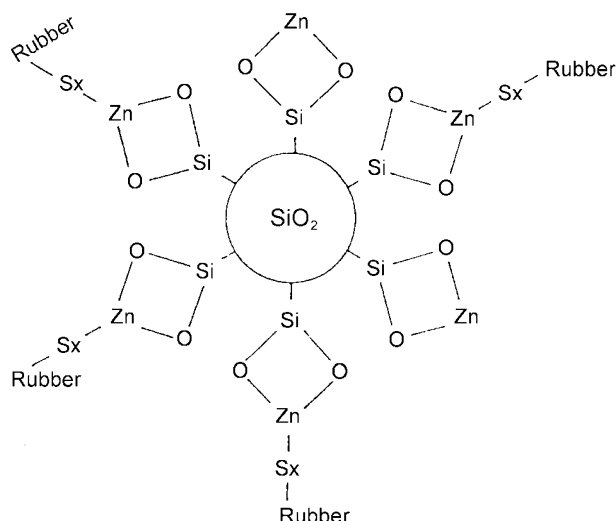


Figure 5. Structure of silica bound styrene-butadiene rubber.

-OH group with more labile Zn-ion at the outer layer. These free Zn-ion take part in sulfurating complex formation process (Figure 4), at the same time form a composite structure bound silica with elastomeric chain as in Figure 5. A tentative cage type model structure has been suggested (Figure 3) which is similar to network of ZnO crystal structure involving both covalent and co-ordinate bonds. As the silica filler retains in the vulcanizate structure as elastomer bound filler and thus enhanced the properties. However it needs more experimentation to draw the conclusion on the structures.

Conclusions

Zn-ion coated nano silica fillers are having a dual role in

sulfenamide accelerated sulfur vulcanization of butadiene containing elastomers. It can produce bound silica filler containing elastomeric chains with enhanced technical properties.

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