Synthesis and Effect of Surface Modified Nano ZnO in Natural Rubber Vulcanization

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ABSTRACT: It is well known that surface of ZnO acts both as a reactant and a catalytic reaction template in rubber vulcanization by activating and bringing together reactants. The particles of accelerators, fatty acid, and sulfur diffuse through the polymer matrix and get adsorbed on the surface of ZnO, forming intermediate complexes. Hence dispersion of ZnO in the elastomer matrix is a determining parameter. Capping is one of the novel techniques for increasing ZnO-stearic acid/accelerator interaction, thereby enhancing their activities. During the sol–gel precipitation of nano ZnO, if a suitable capping agent is added, agglomeration of ZnO particles gets reduced, leading to the formation of nano particles. Since only very few studies are found reported on synthesis of accelerator-capped ZnO and its application in rubber vulcanization, attempts have been made in this study to synthesize our novel accelerator N-benzylimine aminothioformamide (BIAT)-capped-stearic acid-coated nano ZnO (ZOBS), and BIAT-capped ZnO (ZOB) to investigate their effects in natural rubber (NR) vulcanization. Efforts have also been made to synthesize stearic acid-coated nano zinc phosphate (ZPS) with an aim to find an alternative to conventional ZnO in vulcanization. Mechanical properties like tensile strength, tear resistance, abrasion resistance, and compression set were found out. Swelling values of the vulcanizates as a measure of crosslink densities were also determined. Optimum dosage of ZOBS and a combination of ZOB and ZPS were also derived and found that capped ZnO is superior in NR vulcanization to conventional ZnO in improving cure properties including scorch safety and mechanical properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3099–3107, 2012

Key words: natural rubber; capping; vulcanization; mechanical properties

INTRODUCTION

According to Nieuwenhuizen,[1] the surface of ZnO acts both as a reactant and catalytic reaction template by activating and bringing together reactants. The particles of accelerators, fatty acid, and sulfur diffuse through the polymer matrix and get adsorbed on the surface of ZnO forming intermediate complexes. Therefore, dispersion of ZnO in the polymer matrix is a determining factor in rubber vulcanization. Mark et al.[2] proved that addition of ZnO affects different stages of vulcanization process. It increases the rate of formation of crosslink precursors. Chapman and Porter[3] further investigated the role of ZnO activator in accelerated sulfur vulcanization of NR. In the presence of ZnO, sulfuration is mainly effected by substitution of allylic hydrogen atoms. Thus a network with a greater proportion of mono and disulfidic crosslinks is resulted.[4] The Zn^{+2} from ZnO react with accelerators to form zinc–accelerator complex. Therefore, to enhance the reactivity of ZnO, the availability of Zn^{+2} must be increased.[5]

The extra time and energy required by the accelerator and fatty acid particles to diffuse through the visco-elastic polymer matrix leading to the adsorption of these particles on to the surface of ZnO particles can be saved by capping[6–8] of ZnO during its sol–gel precipitation.[9–13] It is well known that due to large surface area/mass available for nano ZnO, it is more advantageous to use it in sulfur vulcanization of rubber. But agglomeration of particles during the synthesis of nano ZnO is a real problem. Capping is also a solution to the agglomeration problem. Thio compounds are effective capping agents due to the possibility of formation of strong bond between zinc and sulfur. Since only a very few studies are found reported on the synthesis of accelerator-capped ZnO, in this study efforts have been made to synthesize our novel accelerator[14] N-benzylimine aminothioformamide (BIAT)-capped-stearic acid-coated nano zinc oxide (ZOBS) and BIAT-capped zinc oxide (ZOB).

Investigations were done to show the effect of these capped compounds in affecting the cure and mechanical properties of NR gum vulcanizates. Also to find an alternative for conventional ZnO which in higher dosage is toxic to aquatic systems, attempts have been made to synthesize stearic-acid-coated nano zinc phosphate (ZPS) and to investigate the effect of combined system of ZOB and ZPS in NR vulcanization. The novel capped compounds were characterized by FTIR, scanning electron microscope (SEM), TEM and X-ray diffraction (XRD). The mechanical properties like tensile strength, tear resistance, abrasion resistance, and compression set of vulcanizates were evaluated to derive the optimum dosage of ZOBS alone and combination of ZOB and ZPS.

EXPERIMENTAL

Synthesis of BIAT-capped stearic acid-coated nano ZnO (ZOBS)

Materials used

Zinc acetate (GR), NaOH pellets, stearic acid, zinc oxide, sulfur (rubber grade), 2-propanol and dichloromethane, and ammonium hydrogen phosphate were supplied by Cimpson Scientific Syndicate, Kottayam. Natural rubber of grade ISNR-5 was supplied by Rubber Research Institute of India.

Method

Distilled water (200 mL); 440 mL of 2-propanol; and 40 mL of dichloromethane were mixed together. This solution was heated to 50°C, and then divided into two equal portions A and B. In the solution A, 21.95 g of zinc acetate (0.1 mol) was dissolved and 8 g (0.2 mol) of sodium hydroxide was dissolved in solution B. 0.01 mol of BIAT (1.79 g) was dissolved in a hot mixture of 40 mL of dichloromethane and 10 mL of 2-propanol. Two grams of stearic acid was dissolved in this solution. The solution B was added in thin stream to A with continuous stirring (using magnetic stirrer). Then BIAT-stearic acid solution was added to the above solution with stirring, which was continued for 15 min. After settling the solution was decanted and centrifuged. The slurry was dried in vacuum oven at 60–65°C. The solid was powdered in a ball mill.

Synthesis of BIAT-capped nano ZnO (ZOB)

Method

Distilled water (200 mL) and 440 mL of 2-propanol were mixed together. Forty milliliters of dichloromethane were added to this mixture. This solution was heated to 50°C, then divided into two equal portions A and B. In the solution A, 21.95 g of zinc acetate

was dissolved and 8 g of sodium hydroxide was dissolved in B. 0.01 mol of BIAT (1.79 g) was dissolved in 50 mL of dichloromethane. The solution B was added in thin stream to A with continuous stirring (using magnetic stirrer). Then BIAT solution was added to the above solution with stirring. The stirring was continued for 15 min. After settling the solution was decanted and centrifuged. The slurry was dried in vacuum oven at 60–65°C. The solid was powdered in a ball mill.

Synthesis of stearic acid -coated nano zinc phosphate (ZPS)

Method

The solutions A and B were prepared as above and in the solution A, 21.95 g of zinc acetate was dissolved. 12.9 g of ammonium hydrogen phosphate was dissolved in the solution B. Five grams of stearic acid was dissolved in 50 mL of dichloromethane. The solution B was added in thin stream to A with continuous stirring (using magnetic stirrer). To this, stearic acid solution was added with stirring. The stirring was continued for 10–15 min and then the mixture was allowed to settle, centrifuged, and the slurry was dried as above. The solid was powdered in a ball mill.

NR formulations

Different NR mixes were prepared using NR of grade ISNR-5, as per the Table I. The mixes NZ_1 to NZ_R contain 100 g of NR, 1.32 g of N-cyclohexyl benzothiazyl sulfenamide (CBS), and 1.5 g of sulfur. In addition to this, NZ_1 to NZ_5 contain 3–7 g of ZOBS and NZ_6 to NZ_7 contain 3–5 g of ZPS and 3 g of ZOB. The reference mix NZ_R contains 5 g of ZnO, 2 g of stearic acid, and 1.3425 g of BIAT. ZOB and ZPS were not taken in the reference mix. The various mixes were prepared on a laboratory size two-roll mixing mill (15.3 cm × 30.5 cm, Indian Expeller) as per ASTM designation D3182-89, first by masticating NR for 10 min and then mixing other ingredients in the order as shown in Table I. Mixing was continued for a further 3 min and the batch was homogenized by passing it in single direction to ensure orientation of chains and to preserve mill direction before molding.

Evaluation of the cure properties

The optimum cure time (t_{90}) of the mixes (time to reach the 90% of the maximum torque) was determined on a Goettfert elastograph, model Vario (German) at 150°C. The cure properties were obtained directly and the values are given in the Table II. Elastographic scorch time (Ts_2) is the time required

TABLE I
NR Formulations Containing Stearic Acid-Coated-BIAT-Capped Zinc Oxide (ZOBS), Stearic Acid-Coated Zinc Phosphate (ZPS), and BIAT-Capped Zinc Oxide(ZOB)

Ingredients (phr[a])	Mixes								
	NZ_1	NZ_2	NZ_3	NZ_4	NZ_5	NZ_6	NZ_7	NZ_8	NZ_R
NR	100	100	100	100	100	100	100	100	100
ZnO	0	0	0	0	0	0	0	0	5
Stearic acid	0	0	0	0	0	0	0	0	2
BIAT	0	0	0	0	0	0	0	0	1.3425
CBS	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32
ZOBS	3	4	5	6	7	0	0	0	0
ZOB	0	0	0	0	0	3	3	3	0
ZPS	0	0	0	0	0	2	3	4	0
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

[a] Parts per hundred parts of rubber.

for two units to raise above the minimum torque (about 10% of vulcanization). The compounds were then vulcanized up to the optimum cure time in an electrically heated laboratory type hydraulic press (Indian Expeller) at 150°C at a pressure of 120 kg cm^{-2}.

Tensile properties and tear resistance

The tensile properties of the vulcanized samples were determined on a Universal Testing Machine, Instron Corp., series IX model 1034, using a cross-head speed of 500 mm/min. as per ASTM D412-87, using dumbbell specimen.

Hardness

Hardness (Shore A) was measured as per ASTM D2240-86 using a Zwick 3114 hardness tester on unstressed molded cylindrical samples (30 mm diameter × 6 mm thick). For each vulcanized sample three measurements were taken and the result was reported as the average.

Compression set

Compression set was determined as per ASTM D395-89 (method B) using the apparatus manufac-

TABLE II
Cure Properties of NR Mixes Containing ZOBS, ZPS, and ZOB

Mixes	t_{90} (min)	Ts_2 (min)	Minimum torque (dNm)	Maximum Torque (dNm)	Cure rate index (CRI)
NZ_1	7.1	3.5	0.13	4.67	27.78
NZ_2	6	3.3	0.14	5.76	37.03
NZ_3	5	3.0	0.16	6.10	50.00
NZ_4	4.8	3.1	0.16	6.90	58.82
NZ_5	4.5	2.9	0.17	6.95	62.50
NZ_6	6.5	4.6	0.20	6.23	52.63
NZ_7	6.0	5.1	0.22	6.75	111.11
NZ_8	5.5	4.0	0.30	7.01	66.67
NZ_R	9.4	1.0	0.22	6.11	12.00

tured by Prolific Engineers India Ltd. The molded samples (1.25 cm thick and 2.8 cm diameter) in duplicate compressed to constant deflection (25%) were kept for 22 h at 27°C. The samples were taken out and after keeping for 30 min, final thickness was measured. The compression set % was calculated as in Eq. (1)

$$\text{Compression set} \% = \frac{(t_0 - t_1) \times 100}{t_0 - t_s} \qquad (1)$$

where t_0 and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the space bar used.

For each molded sample, average of the duplicate measurements was reported as the final result.
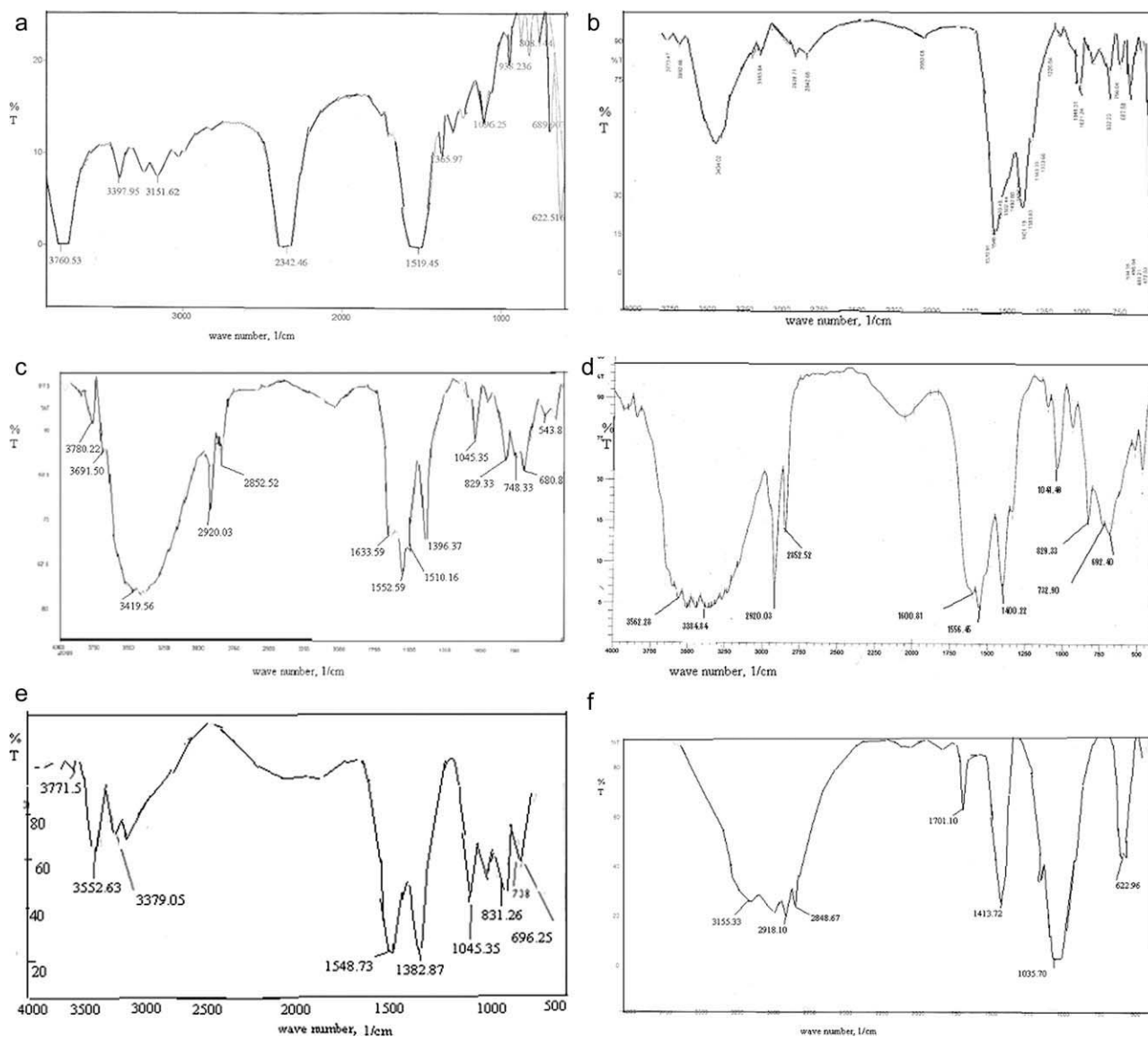
Abrasion loss

Abrasion loss was measured using DIN abrader (DIN 53516). Molded sample having a diameter of 6 ± 0.2 mm and a thickness of 6 mm was inserted into the sample holder so that 2 mm of the sample remained exposed and allowed to move across the surface of an abrasive sheet mounted on a revolving drum. Weight of the test specimen was noted before and after the test. The difference in weight was converted into volume loss by dividing the weight loss by the density of the specimen. Three molded samples of each mix were used for the determination of abrasion loss and the final result was expressed as the average of these results.

Crosslink density

Circular samples of approximately 1 cm diameter and 0.2 cm thickness were punched out from the central portions of the vulcanizate and allowed to swell in toluene for 24 h. The swollen samples were taken out and weighed again after removing the solvent from the surface of the samples using blotting

Figure 1 (a) FTIR spectrum of BIAT. (b) FTIR spectrum of ZOB. (c) FTIR spectrum of ZOBS. (d) FTIR spectrum of ZOS. (e) FTIR spectrum of ZnO. (f) FTIR spectrum of ZPS.

paper. The solvent was removed in vacuum and the weight of the de-swollen samples was again noted to calculate the crosslink density of each sample using Flory–Rhener equation [Eq. (2)][15]

$$\frac{1}{2M_c} = \frac{-[\ln(1 - V_r) + \chi V_r^2 + V_r]}{V_s(V_r)^{1/3}\rho_r} \qquad (2)$$

where V_s is the molar volume of the solvent (toluene $V_s = 106.2$ cm^3 mol^{-1}), ρ_r is the density of test specimen (0.921 g/cm^3, χ is the interaction parameter for NR-solvent (χ for NR-toluene = 0.42),[16] V_r is the volume fraction of rubber in the swollen network which was calculated by the method reported by Ellis and Welding[17] and using Eq. (3) and M_c is the number average molecular weight of the rubber chains between crosslinks.

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_s\rho_s^{-1}} \qquad (3)$$

where T is the weight of the test specimen, D is the weight of de-swollen test specimen, F is the weight fraction of the insoluble components, A_s is the weight of absorbed solvent corrected for the swelling increment, ρ_r is the density of test specimen, ρ_s is the density solvent, toluene (0.886 g/cm^3).

RESULTS AND DISCUSSIONS

Characterization of nano Zobs, ZOB and ZPS

When BIAT was used during the sol–gel precipitation[9] of ZnO with solvents of different polarity, capping[10] of the nano ZnO occurred as evident from
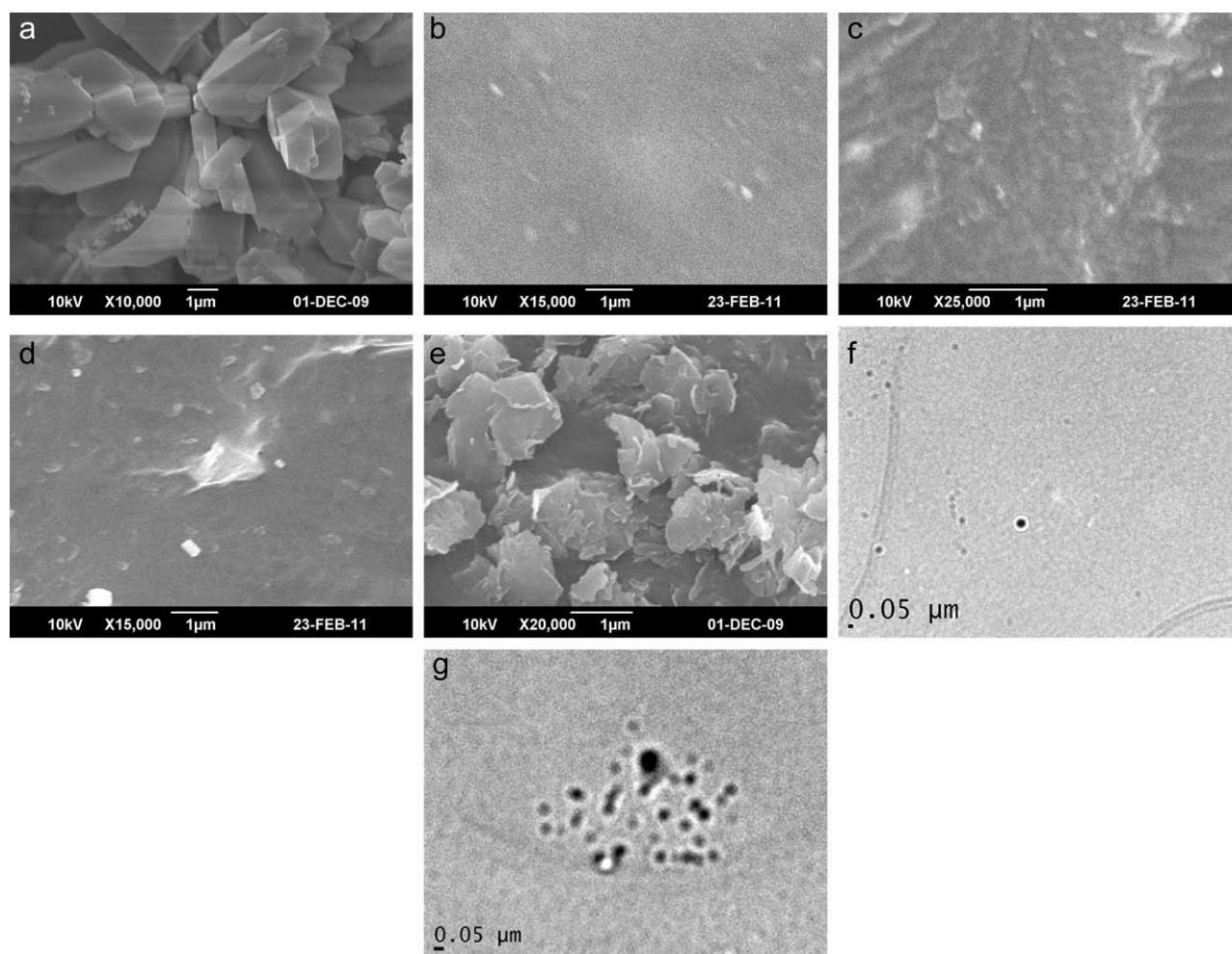
Figure 2 (a) SEM image of ZPS. (b) SEM image of NZ_5. (c) SEM image of NZ_7. (d) SEM image of NZ_R. (e) SEM image of ZOBS. (f) TEM image of ZOBS. (g) TEM image of ZPS.

the IR spectral values (Fig. 1). The BIAT molecules were adsorbed on to ZnO and established interactions between the sulfur of BIAT and Zn^{+2} ions. This is evident from the reduction in IR frequency of the C=S from 808 cm^{-1} [pure BIAT, Fig. 1(a)] to 756 cm^{-1} [Fig. 1(b)] in the case of capped BIAT (ZOB). The BIAT cap interferes and prevents the normal growth of ZnO and thus limits the particle size of ZnO. It is true that the hydrophilicity and lipophobicity of ZnO could cause the agglomeration of ZnO particles. The microscopic interaction between ZnO and BIAT lattices prevents agglomeration of nano ZnO particles. The BIAT capping on ZnO is depicted in the Figure 4. Similarly stearic acid was adsorbed on the surface of ZnO along with BIAT to form ZOBS. FTIR of ZOB [Fig. 1(b)] shows peaks at 3434 cm^{-1} due to NH stretching, 687 cm^{-1} due to phenyl CH bending vibrations. These peaks are seen in the FTIR of pure BIAT [Fig. 1(a)] with slight shifts, confirming the BIAT caps on ZnO. In ZOBS [Fig. 1(c)], the peak at 748 cm^{-1} is due to C=S, 3419 cm^{-1} due to NH stretching, and 680 cm^{-1} due to phenyl CH

bending vibrations (of BIAT). Additionally the peaks at 1633.59 is due to C=O stretching vibrations and 2920.03 and 2852.52 are due to C—H stretching vibrations of the stearic acid coating on ZOBS. These peaks are also found in the spectrum of stearic acid-coated zinc oxide (ZOS) with slight shift as given in Figure 1(d). The stearic acid coating is further confirmed by the fact that these peaks are absent in the FTIR of nano ZnO [Fig. 1(f)].

Stearic acid used during the sol–gel precipitation of zinc phosphate nano particles also could reduce the agglomeration of the particles, as evident from the SEM of ZPS [Fig. 2(a)]. The peaks [Fig. 1(f)] at 1701.10 cm^{-1} is due to C=O stretching and 2918.10 and 2848.67 are due to CH stretching vibrations of stearic acid coating on nano zinc phosphate (ZPS).

From the XRD curve [Fig. 3(a)], the particle dimension D of ZOB was calculated using Scherer equation [Eq. (4)][18]

$$D = \frac{0.9\lambda}{\beta \cos \theta} \qquad (4)$$
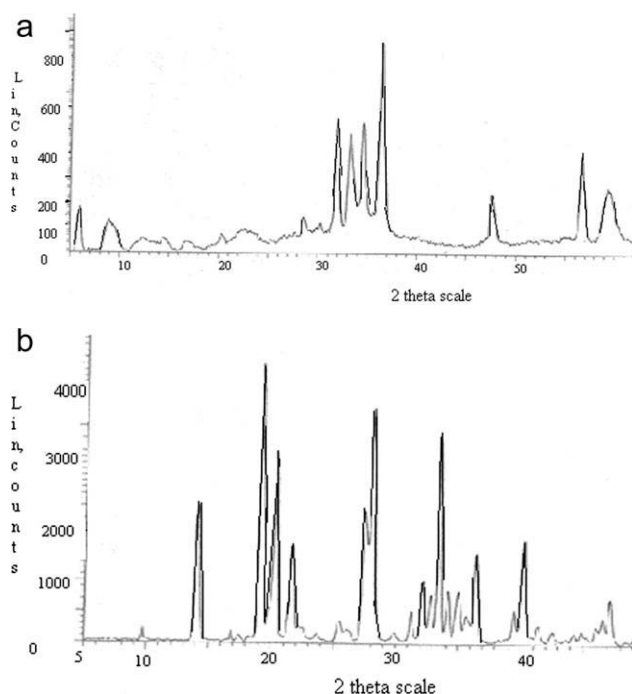
Figure 3 (a) XRD spectrum of ZOB. (b) XRD spectrum of ZPS.

λ is the wavelength of X-ray, β is given as FWHM (in radians), and θ is the angle. In this X-ray analysis $\lambda = 1.5406$ Å, FWHM $= 0.595°$.

The dimension D was calculated for 2θ values 47.584, 34.481, and 28.510° and found equal to 14.6, 13.9, and 15.2 nm respectively. The D values correspond to nano particles. This was further verified using TEM image at 50,000 resolution [Fig. 2(f)] and found that the particles were below 50 nm. In a similar procedure, particle dimensions of ZPS were calculated from the curve [Fig. 3(b)]. The D values for 2θ values 36.389, 27.394, and 25.442° were calculated and found equal to 22.9, 22.5, and 22.4 nm, respectively. These values correspond to nano particles. This was also further verified using TEM image at 35,000 resolution [Fig. 2(g)] and found that the particles were below 50 nm.

Since for 5 g of ZnO, 2 g of stearic acid is usually used in the vulcanization, for 17 g of zinc phosphate product in our synthesis, 5 g of stearic acid was used for coating, so as to keep the amount of stearic acid content in the vulcanizate almost the same. Stearic acid which has polar carboxylic group and nonpolar hydrocarbon part could reduce surface energy of zinc phosphate particles causing reduction in particle–particle interactions. As a result of this reduction in particle–particle interaction, agglomeration of the mineral particle is reduced.[8,12,13]

The SEM and TEM images of ZPS [Fig. 2(a,g)] show that the particles are nano and suitable for rubber matrix interaction. The SEM and TEM images of ZOBS [Fig. 2(e,f)] show that their particles are

also nano and hence they are suitable for better and uniform dispersion in rubber matrix.

Since the concentration of ZPS and ZOBS in the aqueous dispersion made for TEM analysis was much low, the number of particles [seen as black spheres in Fig. 2(g) and slightly elongated black spheres in Fig. 2(f)] are less compared to that in SEM images [Fig. 2(a,b)]. The SEM images were taken by coating the grid with the powder directly and aggregate formation could be possible. It is well known that the primary particles can aggregate in different shapes like spheroids, ellipsoids, linear, or branched.[19] Aggregate formation could be the reason for the rod-like appearance in the SEM image of ZPS [Fig. 2(a)] and flaky structures in the SEM image of ZOBS [Fig. 2(e)].

Cure properties of mixes

Cure time (t_{90}) decreased with increase in concentration of ZOBS and the mix NZ_5 containing 7 phr of ZOBS exhibited minimum (t_{90}) (Table II). All mixes exhibited lower (t_{90}) values than the reference mix (NZ_R) containing uncapped ZnO. This was due to the enhancement in ZnO-BIAT-stearic acid interactions on the surface of ZnO, thereby activating them.[1] The extra time and energy required for the diffusion of BIAT and stearic acid particles was saved by capping ZnO with BIAT and stearic acid.[8] Thus, the capping technique increased the activities of BIAT and stearic acid particles on the catalytic surface of ZnO and made easy path for the formation of zinc–accelerator complex. The surface of ZnO was saturated with BIAT and stearic acid particles at 7 phr concentration. The T_{s2} values (scorch safety) of the mixes showed considerable enhancement when compared with the reference mix (NZ_R). This could be due to the delayed release of BIAT to interact with CBS for further synergic action between BIAT and CBS. The release of BIAT was delayed due to the previously established comparatively stronger interaction between the sulfur of BIAT and Zn^{+2} of ZnO as shown in Figure 4. The improved dispersion of the capped ZnO in the rubber matrix could cause an additional improvement in the cure properties.
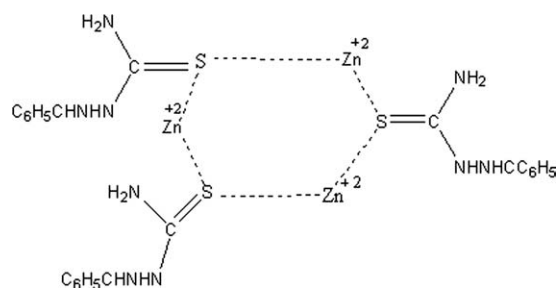
Figure 4 BIAT capping on ZnO.

The increased dispersion of surface modified ZnO was due to reduction in agglomeration of nano ZnO as evident from the SEM images of ZOB and the vulcanizates [Fig. 2(b–d)]. The SEM images of NZ_5 and NZ_7 [Fig. 2(b,c)] show only very few agglomerates, which are micro particles of CBS. Since other ingredients were nano modified, they were better dispersed in the rubber matrix of these vulcanizates (NZ_1–NZ_8). But due to the presence of micro particles of the conventional rubber ingredients and micro BIAT, dispersion is not uniform in the reference mix NZ_R, as evident from the SEM image [Fig. 2(d)].

The BIAT-capped zinc oxide (ZOB) along with stearic acid coated zinc phosphate (ZPS) were also effective in reducing the cure time (NZ_6–NZ_8). On increasing the dosage of ZPS, there was decrease in the cure time. As in the case of ZOBS, activity of the reactant particles was increased by the capping process. The long nano particles of ZPS, as evident from the SEM and TEM images [Fig. 2(a,g)], increased the interaction with rubber chains. The combined action of ZOB and ZPS could improve cure properties compared with the reference mix. This was probably also due to improved dispersion of nano particles as clear from the SEM image of the vulcanizate [Fig. 2(c)]. Scorch safety and cure rate index (CRI) were maximum for the mix NZ_7. Most of the mixes had higher delta torque values indicating better cure state.

Physicomechanical properties

Tensile properties

Tensile strength increased with increase in dosage of ZOBS up to 7 phr in the mix NZ_5 (Table III). This was due to increase in the number of sulfidic crosslinks by the enhanced synergic action between BIAT caps on zinc oxide surface and the CBS particles diffusing on to ZnO. Enhancement in the synergism could probably occur because of (i) the increased dispersion of stearic acid and BIAT in the rubber matrix by the capping process, (ii) reduction of agglomeration of nano ZnO due to the presence of BIAT and stearic acid caps, and (iii) elimination of extra time and energy required for diffusion of stearic acid and BIAT particles on to the surface of ZnO. The synergic action between BIAT caps on zinc oxide surface and the CBS particles diffusing on to ZnO could increase the crosslink density as the concentration of BIAT, stearic acid, and zinc ion increased in ZOBS (which is maximum in 7 g of ZOBS). This has imparted maximum tensile strength to NZ_5.

As the dosage of ZOBS was increased, elongation at break percent showed a decreasing trend from

TABLE III
Tensile Properties of NR Mixes Containing ZOBS, ZPS, and ZOB

Mixes	Tensile strength (MPa)	100% modulus (MPa)	200% modulus (MPa)	300% modulus (MPa)	Elongation at break %
NZ_1	12.92	0.73	1.21	1.87	573
NZ_2	14.32	0.76	1.27	1.90	570
NZ_3	16.13	0.79	1.32	2.07	565
NZ_4	18.28	0.81	1.40	2.63	558
NZ_5	20.98	0.95	1.94	4.26	476
NZ_6	18.20	0.83	1.49	2.92	532
NZ_7	20.47	0.94	1.97	4.85	424
NZ_8	19.05	0.89	1.91	4.52	443
NZ_R	18.66	0.92	1.89	4.16	420

NZ_1 to NZ_5 and consequently modulus showed an increasing trend. The mix NZ_5 which contained optimum concentration of ZOBS exhibited higher modulus than the reference mix NZ_R. Since 21.95 g of zinc acetate, 1.79 g of BIAT, and 2 g of stearic acid produced 14 g of ZOBS, 7 g of ZOBS could contain maximum 0.895 g of BIAT, 1 g of stearic acid, and 5.105 g of ZnO. Therefore, other mixes containing lower dosage of ZOBS could not exhibit better tensile properties than the reference due to the insufficiency in the concentration of BIAT, stearic acid, and zinc ions in ZOBS. The higher concentration of ZOBS in NZ_5 could increase the number of mono and disulfidic linkages and the higher energy of mono and disulfidic bonds compared with polysulfidic linkages could increase the stiffness. Though the mix NZ_5 contains only 7 g of ZOBS which is less than the general dosage of 1.3425 g (7.5 mmol) of BIAT, 5 g of ZnO, and 2 g of stearic acid making a total dosage of 8.3425 g for 100 g rubber, better tensile properties were exhibited by the NZ_5 vulcanizate due to the much improved dispersion of BIAT, stearic acid, and zinc ion particles in the rubber matrix by the capping mechanism as evident from the SEM image [Fig. 2(b)]. The improved dispersion could increase the crosslink density.

Similarly as the dosage of ZPS was increased from 2 to 4 phr (NZ_6–NZ_8), tensile strength was improved. The mixes NZ_7 and NZ_8 exhibited higher tensile strength and modulus than the reference mix NZ_R. Since 21.95 g of zinc acetate and 1.79 g of BIAT produced 12 g of ZOB, and 21.95 g of zinc acetate, 12.9 g of ammonium hydrogen phosphate, and 5 g of stearic acid produced 10 g of ZPS, NZ_7 which contains 3 g of ZOB and 3 g of ZPS could contain maximum 0.4475 of BIAT, 2.5525 g of ZnO (from 3 g of ZOB), 1.5 g of stearic acid, and 1.5 g of zinc phosphate (from 3 g of ZPS). This amount is less than the general dosage of 1.3425 g of BIAT, 5 g of ZnO, and 2 g of stearic acid making a total dosage of 8.3425 g for 100 g rubber. But the capping process

TABLE IV
Other Mechanical Properties of NR Mix Containing ZOBS, ZPS, and ZOB

Mixes	Tear resistance (N/mm)	Hardness (Shore A)	Compression set %	Abrasion loss (cm^3)	Crosslink density $\times 10^{-4}$ (g mol cm^{-3})
NZ$_1$	32.35	31	4.67	0.328	1.25
NZ$_2$	33.58	32	4.60	0.299	1.31
NZ$_3$	33.67	32	4.39	0.261	1.35
NZ$_4$	33.91	32	4.53	0.264	1.38
NZ$_5$	34.80	32	4.11	0.221	1.45
NZ$_6$	32.15	32	4.27	0.309	1.39
NZ$_7$	34.95	32	4.22	0.209	1.47
NZ$_8$	34.11	32	4.29	0.215	1.32
NZ$_R$	30.97	32	4.60	0.342	1.31

could improve the dispersion of BIAT, stearic acid, zinc oxide and ZPS, as clear from SEM images [Fig. 2(b,c)]. The mix NZ$_6$ could not exhibit better tensile properties than the reference due to the insufficiency in the concentration of BIAT, stearic acid, and zinc ions from both 3 g of ZOB and 2 g of ZPS. But the optimum concentration of ingredients in NZ$_7$ could increase the crosslink density of the vulcanizate. The remarkable increase in modulus of NZ$_7$ and NZ$_8$ could be due to the increased crosslink density caused by the ZPS particles.

Tear resistance

All test mixes exhibited higher tear resistance values than the reference mix NZ$_R$ and among the mixes, NZ$_5$ and NZ$_7$ exhibited maximum tear resistance values (Table IV). This was due to more sulfidic crosslinks in them compared with the reference vulcanizate probably due to the action of better dispersed capped nano zinc oxide as ZOBS, ZOB, and ZPS. Maximum and uniform dispersion might have occurred in the test mixes. The optimum dispersion could be in NZ$_5$ and NZ$_7$, since optimum concentrations of the capped nano compounds were required as that in NZ$_5$ and NZ$_7$.

Hardness and compression set

All test mixes had comparable hardness and compression set. Due to higher stiffness (lower elasticity), the mix NZ$_7$ showed a little higher compression set.

Abrasion loss

The mixes NZ$_5$, NZ$_7$, and NZ$_8$ exhibited maximum abrasion resistance (minimum abrasion loss). This could be due to their increased crosslink density achieved by capping process. The additional reinforcing action of ZPS particles could also increase abrasion resistance of NZ$_7$ and NZ$_8$. The ZPS particles could further increase the crosslink density of the vulcanizate.

Crosslink density

The mixes NZ$_5$, NZ$_7$, and NZ$_8$ had maximum crosslink density values (Table IV) due to the better dispersion of surface modified zinc oxide which caused better cure of the mixes. The crosslink density values were in agreement with the mechanical properties studied.

CONCLUSIONS

Zinc oxide surface can be modified using accelerators like BIAT and fatty acids like stearic acid. Capping reduces agglomeration of nano particles of ZnO during its sol–gel precipitation. Other nano zinc compounds like zinc phosphate can be also prepared by sol–gel precipitation and its agglomeration can be reduced by stearic acid coating. This capping technique is an effective method to improve cure and physicomechanical properties of NR. By capping ZnO with BIAT and stearic acid, it becomes possible to save the extra time and energy required for these particles to diffuse on to the surface of ZnO through the visco-elastic rubber matrix. This caused a further enhancement in acceleration of vulcanization and improvement in physicomechanical properties of the resulting vulcanizates. The mix containing optimum concentration of BIAT-capped-stearic acid-coated zinc oxide (ZOBS) has superior cure and physicomechanical properties compared to other homologues and the reference mix containing uncapped ZnO. The mix which contains 3 phr of BIAT-capped zinc oxide (ZOB) and 3 phr of ZPS and thatcontains 3 phr of ZOB and 4 phr of ZPS also have improved cure and physicomechanical properties. The increased crosslink density caused by the ZPS particles could increase the stiffness of the vulcanizates containing ZPS. The capping technique could improve scorch safety of the rubber compounds by the delayed release of BIAT from the capped ZnO into the rubber matrix for interaction with CBS.

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