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Preparation of Nano Zinc Oxide, its Characterisation and Use in Styrene Butadiene Rubber

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Zinc oxide (ZnO) of nanometer particle size was prepared by precipitation and solid state pyrolytic method. TEM, XRD and the surface area studies showed that zinc oxide prepared in the laboratory has a particle size in the nanometer range and a high surface area. This nano zinc oxide was used as an activator in non-polar synthetic rubber compounds. The cure characteristics and mechanical properties were compared with that containing conventional zinc oxide. It is found that a low dosage of zinc oxide was enough to give equivalent curing and mechanical properties compared to the one containing a higher dosage of conventional zinc oxide.

Keywords: nano zinc oxide; styrene butadiene rubber; precipitation method; solid state pyrolytic method

Zinc oxide (ZnO) of nanometer particle size range has been a focus for its unique properties. It is widely used for solar energy conversion, non-linear optics, catalysis, varistors, pigments, gas sensors, cosmetics *etc*.[1–10]. Zinc oxide is added to rubber compounds as an activator to activate sulphur vulcanisation and thereby reduce the vulcanisation time. Besides its effects on the curing process, the zinc content in rubber products has come under increased scrutiny due to environmental concerns. The trend in the rubber industry is therefore to reduce or completely eliminate the zinc content, although to date no viable alternative for ZnO and zinc containing species for vulcanisation purposes has been found[11]. There is a general agreement that zinc cations from ZnO and/or zinc compounds react with organic accelerators to give active zinc–accelerator complexes, which is one of the main steps in the vulcanisation scheme[12]. It has been suggested in many different studies that these active complexes of Zn^{2+} ions with accelerators are more reactive than the free accelerators[13,14]. This active sulphurating agent reacts at the allylic sites of the rubber polymer unsaturations to form a rubber bound intermediate, which reacts with another rubber bound intermediate or with another polymer chain to generate a crosslink. The exact activator role of ZnO is highly dependent on the type of accelerator present in the initial vulcanisation system.

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Fatty acids as co–activators in rubber vulcanisation increase the crosslink yield[15]. It is assumed that stearic acid reacts with ZnO to form zinc stearate, which is an essential cure activator. Its function has been the subject of extensive research by Kruger and McGill[16]. Morrison and Porter reported that zinc stearate inhibits zinc promoted decomposition of mono sulphide cross links, though the mechanism is unclear[17].

The unsaturation in SBR is less than that in NR and the double bonds are chemically less active than the double bonds of the isoprenoid unit in NR. The compounding of SBR is done in a way more or less similar to that of NR and other unsaturated hydrocarbon rubbers[18]. All types of SBR require less sulphur than NR for curing. On the other hand, SBR requires more accelerators, because of lower unsaturation.

This study explains the use of nano ZnO samples prepared in the laboratory [ZnO from precipitation method ZnO(p), ZnO from solid state pyrolytic method ZnO(s)] in dry SBR and the mechanical properties of the vulcanisates are evaluated with the vulcanisates prepared from SBR and conventional ZnO (ZnO(c)).

EXPERIMENTAL

Materials

Zinc sulphate, ammonium bicarbonate, zinc acetate and sodium bicarbonate were supplied by S.D. Fine-chem. Ltd., Mumbai, India.

Method 1: Precipitation Method

1.5 mol/L zinc sulphate and 2.5 mol/L NH_4HCO_3 were prepared in distilled water and 100 mL $ZnSO_4$ solution was added to 126 mL NH_4HCO_3 solution while stirring and the reaction mixture was kept at 45ºC. The slurry of basic zinc carbonate (BZC) in the form of a white precipitate was obtained. It was then filtered, washed and dried. Finally the ZnO nanoparticle (ZnO(p)) was prepared by calcining the precipitate at 500ºC for 1 hour.

In this process, the reaction of Zn^{2+} ions and ammonium acid carbonate proceeds according to *Equation 1*.

$$5ZnSO_4 + 10NH_4HCO_3 \rightleftharpoons Zn_5(OH)_6(CO_3)_{2(S)} + 5\,(NH_4)_2SO_4 + 8CO_2\uparrow + 2H_2O \quad \ldots 1$$

The complex formed decomposes upon calcining to ZnO according to *Equation 2*.

$$Zn_5(OH)_6(CO_3)_2 \rightleftharpoons 5ZnO + 2CO_2\uparrow + 3H_2O\uparrow \quad \ldots 2$$

Method 2: Solid State Pyrolytic Reaction

2.2 g (10 mmoL) of $Zn(CH_3COO)_2\ 2H_2O$ and 2 g (23.8 mmoL) of $NaHCO_3$ were mixed at room temperature. The mixture was pyrolysed at 300ºC for 3 hours. The $Zn(CH_3COO)_2.\ 2H_2O$ was changed into ZnO nanoparticles, while the $NaHCO_3$ was changed into CH_3COONa and eventually washed away with deionised water. Consequently, white ZnO nanoparticles (ZnO(s)) were obtained through the thermal decomposition process.

CHARACTERISATION OF ZnO

The morphology and particle size of ZnO were observed using a transmission electron microscope (TEM). TEM images were taken on a JEOL GEM 3010 Transmission Electron Microscope operating at 300 KV. X-ray powder diffraction (XRD) was used to characterise the ZnO powders. XRD patterns were collected using Bruker, D8 advance rotaflex diffraction meter using CuK α radiation and $\lambda = 1.5406$ Aº.

Surface area of the ZnO nanoparticles and commercial ZnO were measured using the BET method. Surface area analysis was done using a Micromeritics BJH surface analyser Tri-Star 3000. Measurements were carried out under nitrogen adsorption at liquid nitrogen temperature. Infra-red absorption spectra were collected using a ThermoAvtar 370 spectrometer.

RUBBER COMPOUNDING

Materials

Styrene butadiene rubber used was SBR 1502 grade, obtained from JSR Company, Japan. The Mooney viscosity (ML 1+4, 100ºC) was 52. Commercial ZnO was supplied by M/s meta Zinc, Bombay with specific gravity 5.5 g/cm^3. Stearic acid was supplied by Godrej Soap (Pvt) Ltd., Bombay with a melting point of 65ºC and acid number 200. High abrasion furnace black (N 330)[HAF] was supplied by M/s Philips Carbon Ltd., Kerala, India with DBP absorption 102 ± 5CC/100g and iodine number 82. Aromatic oil was supplied by Hindustan Organic Chemicals, Kerala, India with specific gravity 0.98 (g/cm^3). Antioxidant HS (1, 2 dihydro – 2, 2, 4-trimethyl Quinoline polymerised) was obtained from Bayer India Ltd., having specific gravity of 1.1 (g/cm^3). Cyclohexyl-2-benzthiazyl sulfenamide (CBS) used in this study was santacure CBS supplied by Polyolefins Industries Mumbai with specific gravity 1.27 (g/cm^3). Tetra methyl thiuram disulfide (TMTD) was supplied by Polyolefins Industries Ltd., Bombay with specific gravity 1.3 (g/cm^3). Sulphur was supplied by M/s Standard Chemicals Co. Pvt. Ltd. Madras with specific gravity 2.05 (g/cm^3).

Compounding

The rubber was compounded on a laboratory two-roll mill (16 × 33 cm) employing the formulation given in *Table 1*. The mixing was done according to *ASTM D 3184-89 (2001)*. The mixing was carried out at a friction ratio of 1:1.2. After the completion of mixing, homogenisation of the compound was carried out by passing six times through a tight nip gap and finally sheeted out.

TABLE 1. BASE FORMULATION FOR SBR COMPOUNDS

Ingredient p.h.r.	S-1	S-2	S-3	S-4	S-5	S-6
SBR 1502	100	100	100	100	100	100
ZnO(c)	4.5	–	–	2	–	–
ZnO(p)	–	2	–	–	1	–
ZnO(s)	–	–	2	–	–	1
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
HS	1.0	1.0	1.0	1.0	1.0	1.0
HAF	40	40	40	40	40	40
Aromatic oil	7.0	7.0	7.0	7.0	7.0	7.0
CBS	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.2	0.2	0.2	0.2	0.2	0.2
S	2.0	2.0	2.0	2.0	2.0	2.0

Cure characteristics of the mixes were determined at 150ºC using a Rubber Process Analyser RPA 2000 Alpha Technologies, USA as per *ASTM D2084-01*. Vulcanisation up to optimum cure time was then carried out in an electrically heated hydraulic press kept at 150ºC. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 hours.

PROPERTY MEASUREMENTS

The vulcanisates were tested for mechanical properties according to relevant ASTM standards. The tensile properties were measured using Shimadzu model AG1 Universal Testing machine according to *ASTM D 412*. Samples were punched out from the moulded sheet using a dumb-bell shaped die. The cross head speed was maintained at 500 mm/min. The tear strength was determined according to *ASTM D-624* using angular specimens punched out from the moulded sheet. The test speed was 500 mm/minute. The hardness of the sample (Shore A) was determined using Zwick 3114 hardness tester according to *ASTM D-2240*. Compression set (25%) was determined according to *ASTM D 395-86* (Method B). The compression set was calculated using the following *Equation 3*.

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100 \quad \ldots 3$$

Where t_o and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the spacer bar used. The abrasion resistances of the samples were studied with a DIN Abrader (DIN 53516). Moulded samples of 6 ± 0.2 mm diameter and 12 mm thickness were prepared as per *ASTM D 3183* and abrasion loss was measured as per *ASTM D 5963–04*. Abrasion loss was calculated using *Equation 4*.

$$\text{Abrasion loss} = (\text{loss of wt.} / \text{sp.gr.}) \quad \ldots 4$$

Ageing tests were carried out for 24, 48 and 96 hours in accordance with *ASTM 573-88* using an air oven at 100ºC. Tensile properties and tear resistance of the samples were determined for specified periods.

RESULTS AND DISCUSSION

ZnO Characterisation

Figure 1 and *Figure 2* show TEM images of ZnO prepared by precipitation method (ZnO(p)) and solid state pyrolytic method (ZnO(s)). It can be seen that ZnO prepared by the precipitation method has an average particle size of 20 nm and that prepared by the pyrolytic technique has an average particle size of 30 nm. *Figure 3* shows the XRD patterns of ZnO samples. Crystallite size of the ZnO samples was calculated using Scherrer's Equation. The crystallite size for ZnO prepared from methods 1 and 2 ranges from 15–30 nm and the crystallite size for commercial ZnO ranges from 45 to 60 nm. *Figure 4* shows the IR spectrum of ZnO samples. The peak around 450 cm^{-1} shows a distinct stretching mode of zinc oxide. *Table 2* shows surface area for commercial ZnO and ZnO nano particles prepared from methods 1 and 2 respectively. The surface area is found to be about 8 times higher for ZnO(p) and about 3 times higher for ZnO(s) compared to ZnO(c).

Cure Characteristics

Torque values of filled compounds are shown in *Table 3*. Compounds with 4.5 p.h.r. ZnO(c) showed better torque values compared to compounds with 2 p.h.r. ZnO(c). The torque values of filled compounds with 2 p.h.r. ZnO(p) and 2 p.h.r. ZnO(s) are comparable with that

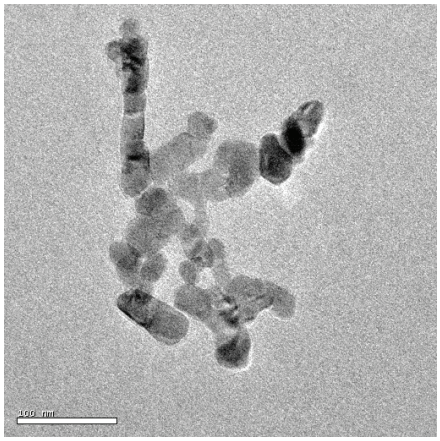

Figure 1. TEM image of ZnO nanoparticles from the precipitation method.

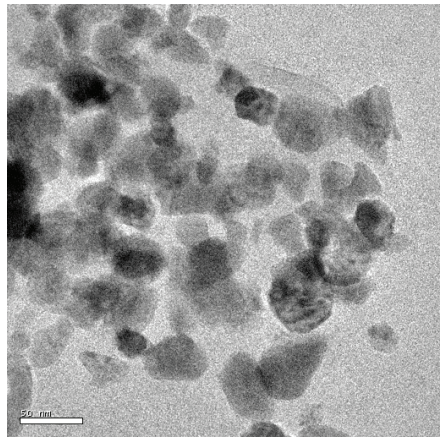

Figure 2. TEM image of ZnO nanoparticles from the solid-state pyrolytic method.

of filled compounds with 4.5 p.h.r. of ZnO(c). However, the torque values of filled compounds with 2 p.h.r. of ZnO(p) and ZnO(s) are better than that with 1 p.h.r. of ZnO(p) and ZnO(s). Therefore, compounds with 2 p.h.r. ZnO(p) and ZnO(s) showed higher cross linking in the rubber matrix compared to compounds with 1 p.h.r. of ZnO(p) and ZnO(s). Upon evaluating the torque values, 2 p.h.r. ZnO(p) and ZnO(s) are selected as the optimum dosage of filled compounds that can give better reinforcement.

Cure times of filled SBR compounds with ZnO(p), ZnO(s) and ZnO(c) are given in *Table 4*. Cure graphs of styrene butadiene compounds are shown in *Figure 5*. Compared to the cure characteristics of filled compounds of 2 p.h.r. ZnO(c), the cure properties of compounds with 4.5 p.h.r. ZnO(c) are superior. Similarly, compounds with 2 p.h.r. ZnO(p) and 2 p.h.r. ZnO(s) are superior compared to compounds with 1 p.h.r. ZnO(p) and 1 p.h.r. ZnO(s). The compounds with low dosage (2 p.h.r.) of ZnO(p) and ZnO(s) showed similar cure characteristics as that with a higher dosage (4.5 p.h.r.) of conventional ZnO(c).

Tensile Properties

Tensile properties of SBR filled vulcanisates are shown in *Figure 6*. The tensile properties of vulcanisates with 4.5 p.h.r. ZnO(c) is superior compared to the tensile properties of vulcanisates with 2 p.h.r. ZnO(c). Similarly, the tensile properties of vulcanisates with 2 p.h.r. ZnO(p) and 2 p.h.r. ZnO(s) are superior compared to the tensile properties of vulcanisates with 1 p.h.r. ZnO(p) and 1 p.h.r. ZnO(s). *Figure 6* shows that the tensile strength, tensile modulus and tear strength values for vulcanisates with 2 p.h.r. ZnO(p) and 2 p.h.r. ZnO(s) are comparable to vulcanisates with 4.5 p.h.r. ZnO(c). Elongation at break is found to be less for vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s). As the reinforcing capacity increases, generally the EB % decreases. The accelerating effect is mainly influenced by the size of the particles. The results suggest that smaller particle size and larger surface area of ZnO(p) and ZnO(s) give a better accelerating effect compared to conventional zinc oxide.

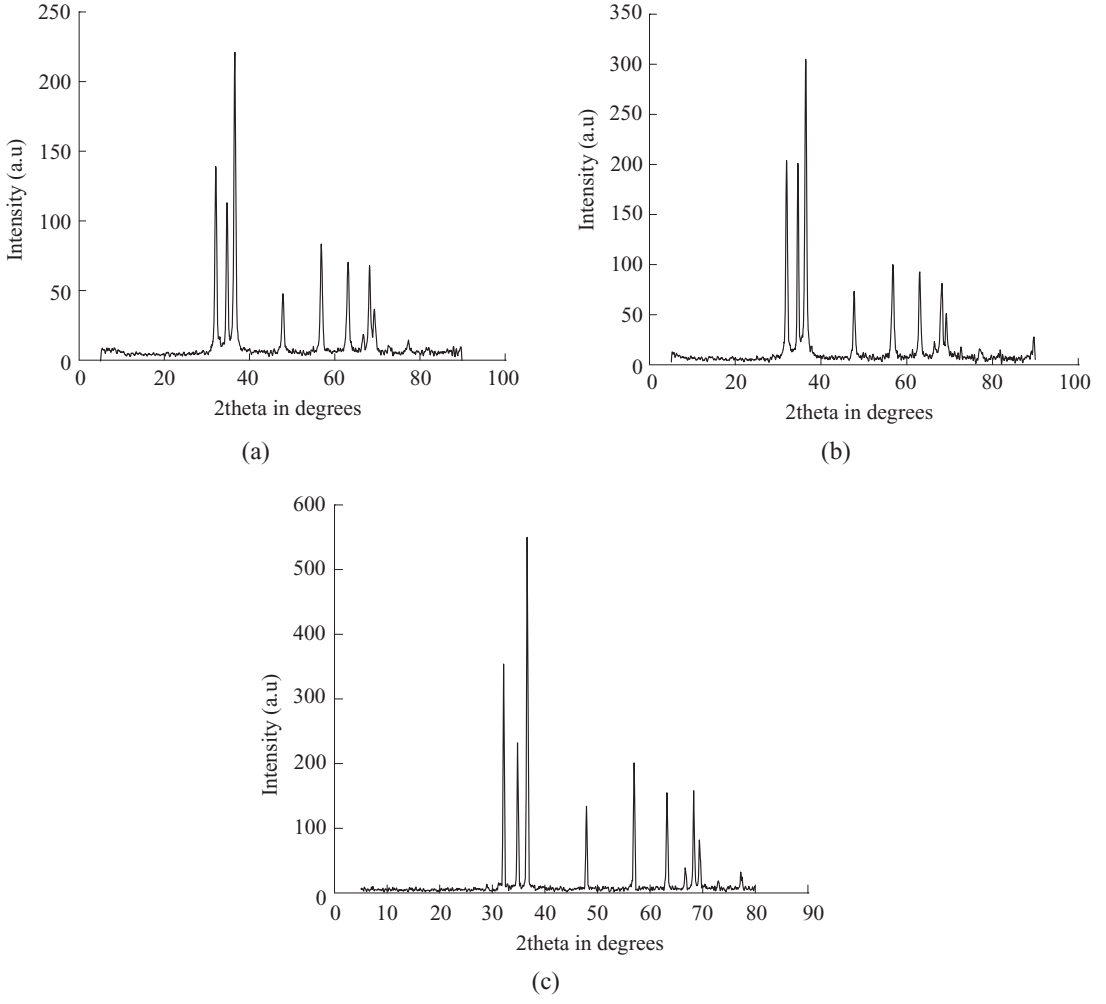

Figure 3. XRD patterns of ZnO prepared by (a) method 1 (b) method 2 (c) commercial ZnO.

Other Mechanical Properties

Mechanical properties like hardness, compression set, abrasion loss, heat build-up and flex resistance of filled vulcanisates are given in the *Table 5*. The mechanical properties for filled vulcanisates with 4.5 p.h.r. ZnO(c) are superior compared to vulcanisates with 2 p.h.r. ZnO(c). Vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s) showed better abrasion resistance, compression set and flex resistance compared to vulcanisates with 4.5 p.h.r. ZnO(c). This may be due to smaller particle sizes of ZnO(p) and ZnO(s). Hardness values are comparable with the conventional ZnO vulcanisates. Heat build-up values are low for vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s) vulcanisates. Crosslink densities of filled vulcanisates of SBR are given in *Table 6*. Swelling of the vulcanised samples

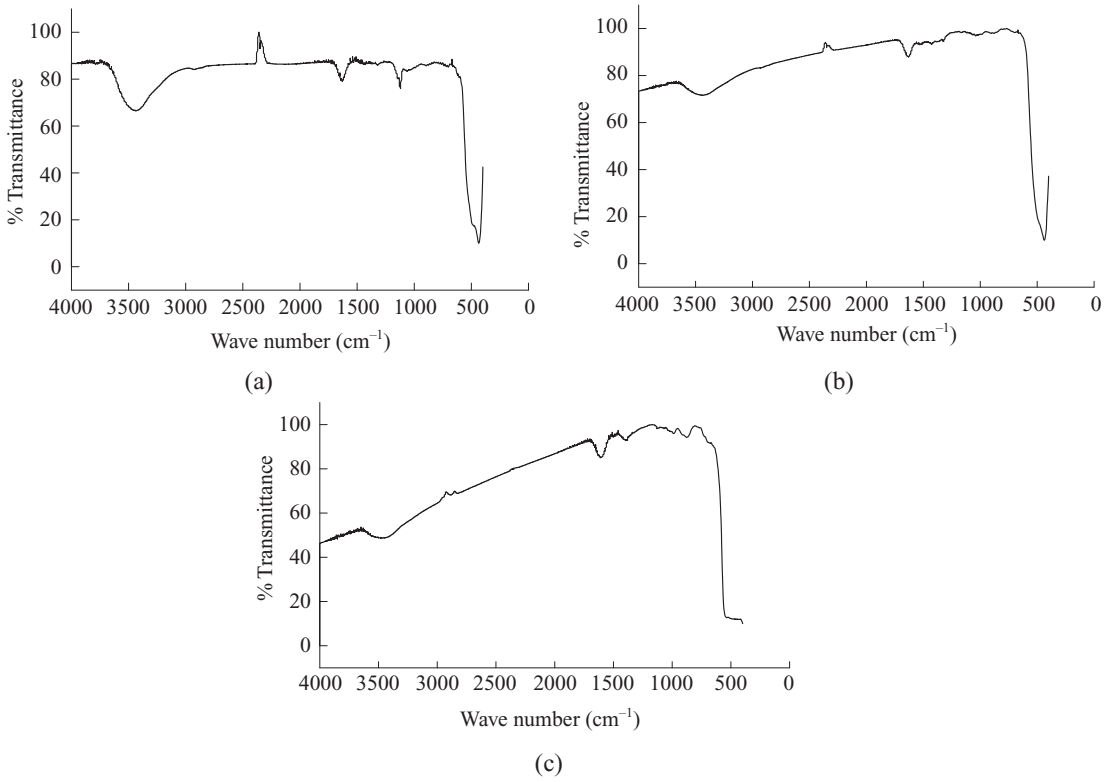

Figure 4. FTIR spectrum of ZnO sample prepared by (a) method 1 (b) method 2 (c) commercial ZnO.

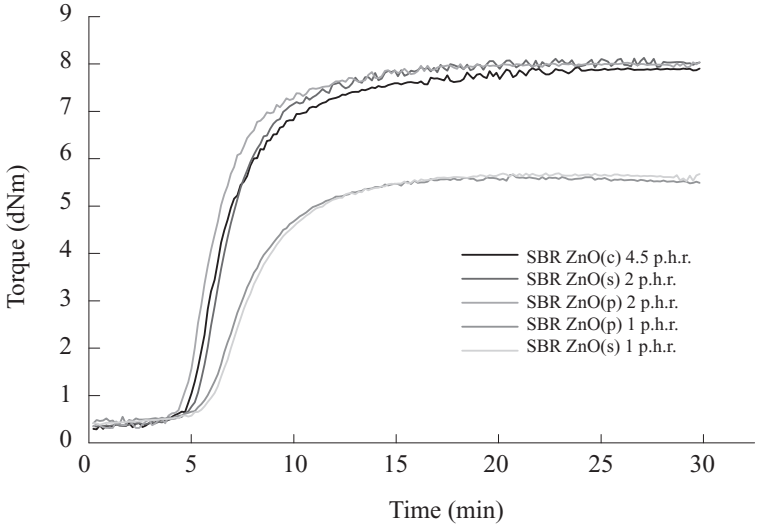

Figure 5. Cure graph of styrene butadiene compounds.

TABLE 2. SURFACE AREA VALUES FOR VARIOUS ZnO

Sl. No.	Samples	Surface area (m^2/g)
1	Commercial zinc oxide	4.35
2	Zinc oxide from method 1	33.67
3	Zinc oxide from method 2	12.13

TABLE 3. CURE CHARACTERISTICS OF SBR COMPOUNDS

Property	S-1	S-2	S-3	S-4	S-5	S-6
Min torque (dNm)	0.23	0.33	0.29	0.27	0.34	0.37
Max torque (dNm)	7.93	8.13	8.06	5.72	5.66	5.70
Δ torque (dNm)	7.70	7.79	7.76	5.45	5.31	5.32

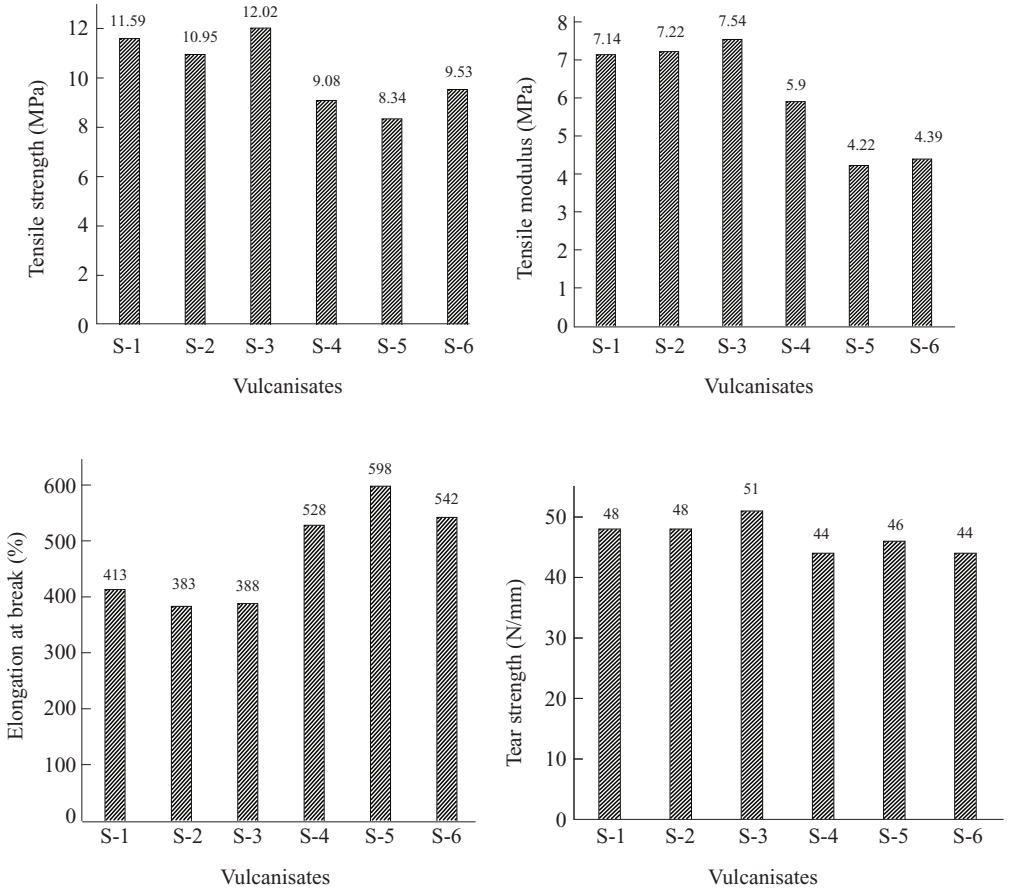

Figure 6. Tensile properties of filled vulcanisates of SBR.

TABLE 4. CURE TIME VALUES OF SBR COMPOUNDS

Property	S-1	S-2	S-3	S-4	S-5	S-6
Scorch time (t_{s2}), min	5.64	5.92	5.29	5.10	4.52	4.22
Optimum cure time (t_{90}), min	11.13	11.27	10.39	12.38	12.12	11.74
Cure rate index ($100/t_{90}$-t_{s2})	18.21	18.69	19.60	13.73	13.15	13.29

TABLE 5. MECHANICAL PROPERTIES OF SBR FILLED COMPOSITES

Composite	Hardness (Shore A)	Compression set (%)	Abrasion loss (cc/hr)	Heat build up (ΔT)ºC	Flex resistance (k cycle)
S-1	69	22.8	2.64	12.9	28.2
S-2	69	21.7	2.55	11.5	38.39
S-3	69	20.4	2.60	8.8	40.29
S-4	65	24	3.08	13.2	26.3

TABLE 6. CROSSLINK DENSITY OF FILLED SBR VULCANISATES

Composite	Crosslink density × 10^{-5} moles /g
S-1	7.16
S-2	7.28
S-3	7.36

was done in toluene and crosslink densities were calculated using Flory-Rehner Equation[19]. It can be seen that the vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s) showed better crosslink densities compared to vulcanisates with 4.5 p.h.r. conventional Zinc oxide.

Thermal Ageing

Ageing resistance of the vulcanisates with 2 p.h.r. ZnO(p), 2 p.h.r. ZnO(s) and 4.5 p.h.r. ZnO(c) are assessed by measuring the tensile properties after ageing to 96 hours and are shown in the *Figure 7(a-d)*. *Figure 7(a)* shows the variation in tensile strength of the vulcanisates with time of ageing at 100ºC. The vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s) show fairly good resistance to ageing at 100ºC compared to those containing 4.5 p.h.r. conventional ZnO. *Figure 7(b)* shows the modulus of the vulcanisates with time of ageing. The increase in modulus after ageing may be due to the increase in crosslink density. During thermal ageing, crosslink formation or crosslink breakage can take place or an existing crosslink may break and a stable linkage can be formed. All these changes greatly influence the performance of the vulcanisates. Tensile modulus of vulcanisates with 2 p.h.r. ZnO(p) and 2 p.h.r. ZnO(s) are superior compared to vulcanisates with 4.5 p.h.r. ZnO(c). *Figure 7(c)* shows the change in elongation at break of the vulcanisates with time of ageing. Vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s) showed better retention in elongation at break after ageing.

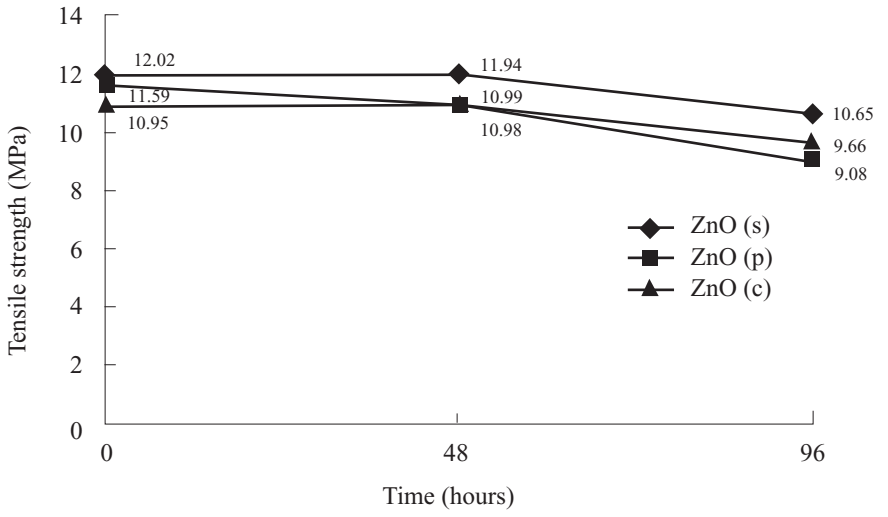

Figure 7(a). Variation in tensile strength of SBR vulcanisates with time of ageing at 100ºC.

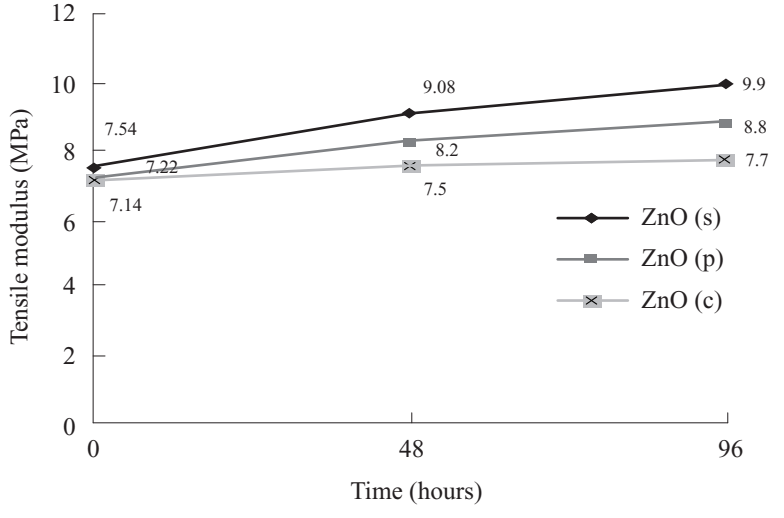

Figure 7(b). Variation in tensile modulus of SBR vulcanisates with time of ageing at 100ºC.

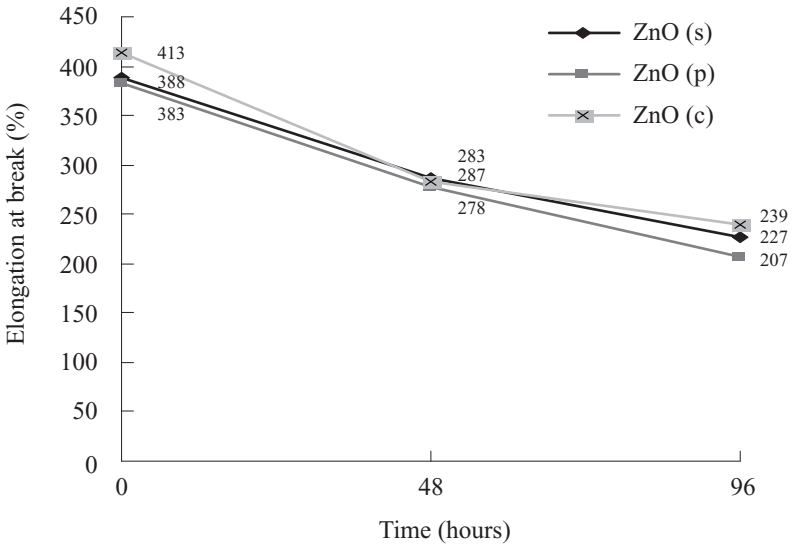

Figure 7(c). Variation in elongation at break of SBR vulcanisates with time of ageing at 100ºC.

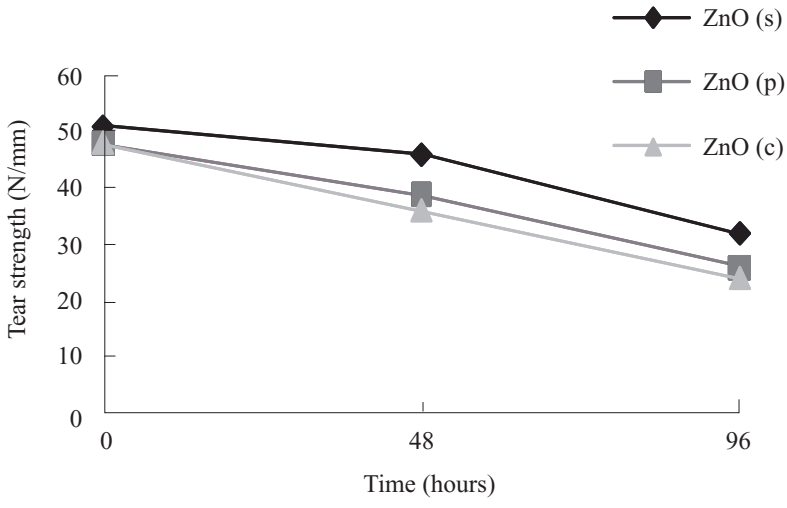

Figure 7(d). Variation in tear strength of SBR vulcanisates with time of ageing at 100ºC.

This again shows that vulcanisates with ZnO(p) and ZnO(s) can improve the ageing resistance of SBR vulcanisates. *Figure 7(d)* shows the tear strength of the vulcanisates with time of ageing at 100ºC. Retention in tear strength of the vulcanisates with 2 p.h.r. ZnO(p) and ZnO(s) after ageing is superior to vulcanisates with 4.5 p.h.r. conventional ZnO. The above results indicate that low dosage of ZnO(p), ZnO(s) can improve the tensile properties of vulcanisates compared to higher dosage of ZnO(c) vulcanisates.

CONCLUSIONS

Filled composites with 4.5 p.h.r. conventional ZnO (S-1) have better cure characteristics, tensile properties and other technological properties compared to composites with 2 p.h.r. ZnO(c) (S-4). Filled composites with 2 p.h.r. ZnO(p) and ZnO(s) (S-2 and S-3) showed better cure characteristics and tensile properties compared to composites with 1 p.h.r. ZnO(p) and 1phr ZnO(s) (S-5 and S-6). Compounds with low dosage (2 p.h.r.) of ZnO(p) and ZnO(s) showed similar cure characteristics as that with high dosage (4.5 p.h.r.) of conventional ZnO(c). Tensile properties of composites with optimum dosage of ZnO(p) and ZnO(s) are comparable to vulcanisates with 4.5 p.h.r. ZnO(c). Compression set, abrasion loss and heat build-up values are low for vulcanisates with optimum dosage of ZnO(p) and ZnO(s). Retention in tensile properties of the vulcanisates with low dosage of ZnO(p) and ZnO(s) after thermal ageing is superior compared to vulcanisates with 4.5 p.h.r. conventional ZnO. Crosslink densities of composites with optimum dosage of ZnO(p) and ZnO(s) are slightly higher than vulcanisates with 4.5 p.h.r. conventional zinc oxide.

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